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FINAL
REMEDIAL INVESTIGATION WORK PLAN

South Shore Area
Former Mare Island Naval Shipyard
Vallejo, California
July 2015

Base Realignment and Closure
Program Management Office West
1455 Frazee Road, Suite 900
San Diego, California 92108

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Prepared under:

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DEPARTMENT OF THE NAVY
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ABBREVIATIONS AND ACRONYMS

^{226}Ra	radium 226
2,3,7,8-TCDD	2,3,7,8-tetrachlorodibenzo-p-Dioxin
4,4'-DDE	4,4'- dichlorodiphenyldichloroethylene
4,4'-DDT	4,4'- dichlorodiphenyltrichloroethane
µCi	microCuries
µg/L	microgram per liter
°C	degree Celsius
°F	degree Fahrenheit
ABM	abrasive blast material
AOC	area of concern
APP	Accident Prevention Plan
AST	aboveground storage tank
ASTM	American Society for Testing and Materials
BAF	bioaccumulation factor
BDL	below detection limit observation
BERA	Baseline Ecological Risk Assessment
bgs	below ground surface
BHHRA	Baseline Human Health Risk Assessment
BRAC	Base Realignment and Closure Program
BTEX	benzene, toluene, ethylbenzene, and xylenes
Cal/EPA	California Environmental Protection Agency
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CLP	Contract Laboratory Program
cm	centimeter
cm^2/s	square centimeters per second
CO	Navy Contracting Officer
COPC	Compound of Potential Concern
CSM	Conceptual Site Model
CSO	Caretaker Site Office
DADI	daily average daily intake
DGM	digital geophysical mapping
DMM	discarded military munitions
DO	dissolved oxygen
DOD	Department of Defense
DON	United States Department of the Navy
DPT	direct-push technology
DQO	Data Quality Objective
DRMO	Defense Reutilization and Marketing Office

ABBREVIATIONS AND ACRONYMS
(CONTINUED)

DTSC	Department of Toxic Substances Control
EDD	electronic data deliverable
EDF	electronic data file
EECA	Engineering Evaluation/Cost Analysis
EM	Engineering Manual
EODMU9	Explosive Ordnance Disposal Mobile Unit Nine
EPA	United States Environmental Protection Agency
EPP	Environmental Protection Plan
ERA	Ecological Risk Assessment
EWI	Environmental Work Instruction
FS	Feasibility Study
FSS	Final Status Survey
GIS	Geographic Information System
GPS	Global Positioning System
HE	high explosives
HI	hazard index
HHRA	Human Health Risk Assessment
HQ	hazard quotient
HSA	hollow-stem auger
IDW	investigation-derived waste
IR	Installation Restoration
IRIS	Integrated Risk Information System
IRP	Installation Restoration Program
IRAP	Interim Remedial Action Plan
J&E	Johnson and Ettinger
kg	kilograms
LADI	lifetime average daily intake
lbs	pounds
m	meter
m/s	meters per second
m^2	square meters
m^3/kg	cubic meters per kilogram
MARSSIM	Multi-Agency Radiation Survey and Site Investigation Manual
MC	munitions constituents
MCL	Maximum Contaminant Level
MD	munitions debris
MDAS	material documented as safe
MDEH	material documented as an explosive hazard

ABBREVIATIONS AND ACRONYMS
(CONTINUED)

MEC	munitions and explosives of concern
mg/day	milligrams per day
mg/kg	milligrams per kilogram
$(mg/m^2)/s$	milligrams per square meter per second
mg/m^3	milligrams per cubic meter
MINS	Mare Island Naval Shipyard
mm	millimeter
mph	miles per hour
MPPEH	munitions potentially presenting an explosive hazard
MR	Munitions Response
MRP	Munitions Response Program
MSL	mean sea level
NAD	North American Datum
NAVD	North American Vertical Datum
NAVFAC SW	Naval Facilities Engineering Command Southwest
NEDD	Navy Electronic Data Deliverable
NOREAS	NOREAS, Inc.
NTCRA	Non-Time Critical Removal Action
NTU	nephelometric turbidity units
OCP	organochlorine pesticide
OEHHA	Office of Health Hazard Assessment
ORNL	Oak Ridge National Labs
ORP	oxidation/reduction potential
PA	Preliminary Assessment
PAH	polycyclic aromatic hydrocarbon
PA/SI	Preliminary Assessment/Site Inspection
PCB	polychlorinated biphenyl
PEF	pathway exposure factor
PG	Professional Geologist
PM	Contracted Support Project Manager
PMA	Production Manufacturing Area
PMO	Program Management Office
PPRTV	Provisional Peer Reviewed Toxicity Values
PRG	Preliminary Remediation Goal
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
RACR	Remedial Action Closure Report

ABBREVIATIONS AND ACRONYMS
(CONTINUED)

RAGS	Risk Assessment Guidance for Superfund
RCRA	Resource Conservation and Recovery Act
RFA	RCRA Facility Assessment
RfD	reference dose
RI	Remedial Investigation
RL	reporting limit
RMMP	Radiological Materials Management Plan
ROICC	Resident Officer in Charge of Construction
RPM	Remedial Project Manager
RPP	Radiological Protection Plan
RSL	Regional Screening Level
SAP	Sampling and Analysis Plan
SF	square feet
SMHM	Salt Marsh Harvest Mouse
SSA	South Shore Area
SSHP	Site Safety and Health Plan
SUXOS	Site UXO Supervisor
SVOC	semivolatile organic compound
SWMU	Solid Waste Management Unit
SWRCB	State Water Resources Control Board
TCD	Toxicity Criteria Database
TDS	total dissolved solids
TEQ	toxic equivalency
TNT	trinitrotoluene
TPH	total petroleum hydrocarbons
TPH-g	TPH as gasoline
TPH-d	TPH as diesel
TPH-mo	TPH as motor oil
TRV	toxicity reference value
TSCA	Toxic Substances Control Act
UCL	upper-confidence limit
USCS	Unified Soil Classification System
USDA- SCS	United States Department of Agriculture Soil Conservation Service
USEPA	United States Environmental Protection Agency
UST	underground storage tank
UXO	unexploded ordnance
VI	vapor intrusion
VOC	volatile organic compound

1.0 INTRODUCTION

This Remedial Investigation (RI) Work Plan describes the proposed approach to conducting an RI at the South Shore Area (SSA) of the Former Mare Island Naval Shipyard (MINS), Vallejo, California. This RI Work Plan has been prepared for the Department of the Navy (DON), Base Realignment and Closure (BRAC) Program Management Office (PMO) West under Contract No. N62473-12-C-4812 by NOREAS, Inc. (NOREAS). The RI Work Plan is subject to requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the National Oil and Hazardous Substances Pollution Contingency Plan.

As the lead agency for implementation of the Installation Restoration Program (IRP) at the former MINS, the DON will work in cooperation with the United States Environmental Protection Agency (USEPA), California Environmental Protection Agency (Cal/EPA) Department of Toxic Substances Control (DTSC), and Cal/EPA Regional Water Quality Control Board (Water Board) San Francisco Bay Region to implement the RI activities described in this work plan. The DON, DTSC and Water Board are signatories to the July 2002 Federal Facilities Site Remediation Agreement that governs remediation activities at the former MINS.

The former MINS occupies an area of approximately 3.5 square miles located on a peninsula in Solano County, California, northeast of San Francisco. It is bound by San Pablo Bay on the west, Carquinez Strait on the south, and Mare Island Strait (Napa River) to the east (Figure 1-1). MINS was established by the DON in 1854 and operated continuously until it was closed under the BRAC Program in 1996. The primary mission of the former MINS was to build, maintain, and repair Navy ships and submarines, though it also served as a munitions storage and production facility from approximately 1857 until 1975.

The SSA consists of approximately 38 acres of uplands, wetlands, and tidal mudflat areas located on the southern end of the former MINS. The location of the SSA within Mare Island is illustrated on Figure 1-2. The SSA served a critical role with respect to munitions storage and assembly from 1857 until 1975. The SSA was also historically used for storage of general shipyard items.

A wide variety of buried munitions have been identified and removed from the subsurface soils at portions of the SSA. Since 1990, seven separate emergency response actions have been conducted, along with an intrusive investigation to identify unexploded ordnance (UXO). During the UXO intrusive investigation, 158,450 live ordnance items (including 1,582 items containing HE), 767,373 inert ordnance items (munitions-related debris), 688,419 pounds of scrap metal, and 567 cubic yards of lead and zinc contaminated soil were removed from the SSA (Weston, 2003). All of the munitions and explosives of concern (MEC) items were ultimately classified as discarded military munitions (DMM).

DMM are military munitions that have been abandoned without proper disposal and do not meet the criteria for classification as UXO. Additional details regarding the munitions classifications and terminology are provided in Section 2.3.

1.1 PURPOSE AND OBJECTIVES

The primary objective of the RI is to characterize the nature and extent of potential CERCLA, Resource Conservation and Recovery Act (RCRA), petroleum, munitions potentially presenting an explosive hazard (MPPEH), munitions constituents (energetics and metals), and radiological impacts to soil and groundwater at the SSA. Data from the RI will be used to prepare a feasibility study (FS) that will evaluate remedial actions/approaches to mitigate potential threats or risks to human health and the environment and will ultimately support site closure efforts. As such, this RI is intended to address all environmental programs applicable to the SSA, including the Installation Restoration (IR)/CERCLA, Munitions Response (MR), RCRA, and petroleum programs. The Toxic Substances Control Act (TSCA) program is conducted separately; however, the results of the program activities at the SSA to date will be summarized as part of this RI.

This RI Work Plan describes the procedures and methods that will be used to investigate and report on munitions-related and chemical contaminants that may be present in the soil and groundwater at the SSA due to past activities at MINS. A separate Work Plan for Radiological Screening and Survey Activities (RAD WP) has been prepared to describe the methods and procedures used to conduct a radiological survey to obtain the unrestricted release of a very limited area where a discrete radiological item was found during previous removal actions at the SSA. The RAD WP was prepared under separate cover; however, the results of the investigation for munitions, chemical contaminants and the radiological survey will be summarized within a single, comprehensive RI Report.

The objective for this RI Work Plan is to describe the procedures, methods, and approach used to investigate the nature and extent of potential contaminants at the SSA to ensure that data of sufficient quality and quantity are collected to evaluate current site conditions, conduct baseline human health and ecological risk assessments, and evaluate the potential need for further action to protect human health and the environment. The RI Work Plan and related documents will define the project objectives, decision making criteria, Data Quality Objectives (DQOs), and associated data needs necessary to meet the RI goals and objectives.

Due to efforts conducted under the Munitions Non-Time Critical Removal Action (NTCRA) conducted between 2012 and 2013 at the SSA, only minimal additional efforts to characterize and/or delineate MPPEH in one area (grid AF011) are expected during the course of this RI. If MPPEH are encountered in other areas during the implementation of the RI field activities, additional MPPEH management will be addressed under a separate contract option at the direction of the Navy Contracting Officer. The impacts along the shoreline between the SSA and

IR05 revealed during the MEC NTCRA visual survey will not be further investigated during this RI.

1.2 SCOPE OF WORK

In order to achieve the project objectives, the RI will focus on collecting soil and groundwater data from the following primary areas of interest at the SSA including:

1. Buildings where hazardous materials were once stored and/or used.
2. Solid Waste Management Units (SWMUs) where hazardous materials were historically stored, managed, or potentially discharged.
3. Oven/Primer Pit Area (including Oven Pits) where munitions were once discarded by burning.
4. Former MEC Sites as identified during past MEC removal actions and recent NTCRA at the SSA.
5. The location where a single, discrete radiological item, a deck marker, was found and removed during an emergency MEC removal action in 1999.
6. Other Areas as necessary; these include those areas where underground tanks and buried drums were encountered during the MEC NTCRA completed in July 2013 (additional details regarding the NTCRA are provided in Section 2.4.7).

Specifically, soil samples will be collected from various depths at a total of 52 locations throughout the SSA. The sample locations have been selected to correspond with those areas where potential impacts from chemical contaminants are most likely to have occurred. In addition, nine groundwater monitoring wells will be installed and sampled to provide information relative to hydrogeologic conditions, potential contaminant impacts, and general water quality at the SSA, in part to support the request for an exception to the sources of drinking water policy for this area. Additional details regarding the methods, procedures, and approach to the soil and groundwater sampling activities planned for this RI are described in the sections that follow.

1.3 PROJECT POINTS OF CONTACT

The primary points of contact for the investigation are below.

Organization	Contact	Project Title
Base Realignment and Closure (BRAC) Program Management Office (PMO) West 1455 Frazee Road, Suite 900 San Diego, California 92108-4310	Heather Wochnick, PE (619) 532-0763 Fax: (619) 532-0780	Lead Remedial Project Manager
BRAC PMO West 1455 Frazee Road, Suite 900 San Diego, California 92108-4310	Brooks Pauly, PE (619) 532-0789 Fax: (619) 532-0780	Remedial Project Manager (RPM)

Organization	Contact	Project Title
Resident Officer in Charge of Construction (ROICC) San Francisco Bay Area 2450 Saratoga Street, Suite 200 Alameda, California 94501-7545	Izzat Amadea (510) 755-5876 (Office)	ROICC Representative
BRAC Caretaker Site Office 410 Palm Avenue, Building 1, Suite 161 San Francisco, California 94130	Patricia McFadden (415) 743-4720	Navy Caretaker Site Officer (CSO)
BRAC PMO West 1455 Frazee Road, Suite 900 San Diego, California 92108-4310	Janet Lear (619) 532-0976 Fax: (619) 532-0780	BRAC Environmental Coordinator (BEC)
NOREAS, Inc. 16361 Scientific Way Irvine, CA 92618	Jeff Brenner, PG (949) 467-9106 (Office) (949) 439-5402 (Mobile)	NOREAS Project Manager
NOREAS, Inc. 16361 Scientific Way Irvine, CA 92618	Vitthal Hosangadi, PE (949) 467-9099 (Office) (949) 300-9430 (Mobile)	NOREAS Technical Lead

1.4 PROJECT SCHEDULE

The current project schedule is provided as Figure 1-3.

1.5 DOCUMENT ORGANIZATION

This Work Plan has been structured to provide details regarding the major aspects of the RI and is divided into the following sections:

- Section 1.0 Introduction – Provides an introduction, describes objective and scope, project points of contact, schedule, and document organization.
- Section 2.0 Site Background and Previous Investigations/Actions – Provides relevant background for MINS as it pertains to the RI Work Plan.
- Section 3.0 Site Conditions – Describes the site geology/hydrogeology and other site conditions. Also includes a description of the Conceptual Site Model (CSM).
- Section 4.0 Remedial Investigation Approach – Provides information regarding the scope of the remedial investigation.
- Section 5.0 Implementation – Describes details regarding how the fieldwork will be implemented.
- Section 6.0 Project Required Plans – Describes the health and safety, waste management, and environmental protection procedures associated with the project.
- Section 7.0 Human Health Risk Assessment (HHRA) Methodology – Describes the approach to developing the HHRA.
- Section 8.0 Ecological Risk Assessment (ERA) Methodology – Describes the approach to developing the ERA.

- Section 9.0 Radiological Risk Modeling and MEC Hazard Analysis (HA) – Describes the methods and approaches used to conduct radiological risk assessment and MEC HA.
- Section 10.0 RI Report – Provides an outline of the RI Report that will be prepared based on methodologies described in this RI Work Plan.
- Section 11.0 References – Includes a list of documents used to compile this RI Work Plan.

This RI Work Plan also includes the following appendices:

- Appendix A Sampling and Analysis Plan
- Appendix B Environmental Protection Plan
- Appendix C Waste Management Plan
- Appendix D Accident Prevention Plan/Site Safety and Health Plan

This RI Work Plan also references the following reports issued under separate cover letter:

- RAD WP and related plans, including:
  - Radioactive Materials Management Plan (RMMP), and
  - Radiation Protection Plan (RPP)

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2.0 SITE BACKGROUND AND PREVIOUS INVESTIGATIONS/ACTIONS

The following subsections provide information regarding the site background and previous investigations, assessments, or actions. These include a site description and a brief summary of the history of MINS and the SSA. Discussions of previous investigations and information regarding applicable environmental programs are also provided below.

2.1 MARE ISLAND NAVAL SHIPYARD DESCRIPTION AND HISTORY

Mare Island is located in California, northeast of San Francisco, in Solano County. The Mare Island complex occupies 5,600 acres on a peninsula bound to the south by the Carquinez Strait, to the west by San Pablo Bay, and to the east by Mare Island Strait (Napa River), which separates it from the City of Vallejo, California. The City of Vallejo is located directly across Mare Island Strait. Land use types along the northeast shore of Mare Island Strait include residential, recreational, commercial, and industrial.

The primary mission of MINS was to build, maintain, and repair Navy ships and submarines. The southern portion of Mare Island was used for munitions storage and production operations from 1857 to 1975. The primary purpose of the Mare Island ordnance facility (designated as a "Naval Magazine" from 1857 to 1935) was to store explosives for Navy ships. The Naval Magazine was upgraded to a Naval Ammunition Depot in 1936 when ammunition manufacturing operations were initiated. Administrative control was transferred to Naval Magazine Port Chicago in 1942 and the facilities were consolidated into Naval Weapons Station Concord in 1957. The Mare Island ammunition facility remained an annex of Naval Weapons Station Concord until 1972 when operations were turned over to MINS. The Shipyard was closed in April 1996 after 139 years of service.

2.2 SOUTH SHORE AREA DESCRIPTION AND HISTORY

The SSA is located on the south end of Mare Island and includes portions of Investigation Area (IA) G and transfer parcel VII-B, along with a sliver of IX (Figure 2-1). The SSA has also been referred to as UXO 7. The SSA extends out from the base of the cliffs that define the southern boundary of the hills to the Carquinez Strait, and was created in several stages between 1930 and 1947. The material used to construct the SSA consisted primarily of rock and soil taken from the upland areas that was placed over the clays and silts that had been deposited at the edge of Mare Island. However, dredge materials may also have been used to expand portions of the SSA in the past. The SSA is bound on the west by dredge ponds and the IR05 area, on the south by Carquinez Strait, on the east by the Production Manufacturing Area (PMA), and on the north by the upland hills.

Originally, the entire southern portion of the former MINS was referred to as the ordnance facility. The ordnance facility included areas currently known as the Western Magazine Area, IR05, as well as the PMA and the SSA. The ordnance facility served a critical role as a munitions storage and production facility from 1857 until 1975. The purpose of the ordnance facility in the early years was to store and process the ammunition used aboard naval ships. Black powder munitions were emptied and refilled while ships were being repaired at the former MINS. Facilities for loading gun-cotton were built in the 1890s, and the loading of projectiles with ammonium picrate (Explosive D) was implemented by the beginning of World War I.

The ordnance facility was re-designated as the Naval Ammunition Depot in 1936 when ammunition manufacturing operations were initiated at the buildings located in the PMA. Many of the existing PMA production buildings were constructed during the period between 1936 and the beginning of World War II. Ordnance was received, maintained, refurbished, demilitarized, subjected to quality assurance (QA) testing, and loaded on and off ships at the PMA and SSA portions of the Naval Ammunition Depot. The SSA was used for the storage of general shipyard items as well as for the storage and handling of munitions. Ordnance was not manufactured in the SSA. The key buildings and features of the SSA are illustrated in Figure 2-1.

A wide variety of buried munitions items have been detected and removed from portions of the PMA and SSA, including propellants, munitions items filled with high explosives, small arms ammunition, fuses, primers, and small- to medium-caliber gun ammunition. A comprehensive MEC NTCRA was recently completed in the PMA and SSA. Despite this latest investigation and removal action, the potential exists for undetected munitions items to still be present in these areas. The MEC NTCRA is described in more detail in Section 2.4.7.

2.3 MUNITIONS TERMINOLOGY

As described in detail in Section 2.4, various munitions items have been identified as potential risks to human health and the environment at Mare Island. Several different terms have been used historically to describe munitions items. Historically, the terms UXO, ordnance, and explosives were used to describe various munitions items including medium-caliber gun ammunition, small arms ammunition, propellants, fuses, primers, and other items containing explosives. In December 2003, the United States Department of Defense (DOD) issued a memorandum clarifying the definition and use of munitions response items. For the purposes of consistency with the memorandum, the terms used to describe the munitions items most commonly found at the SSA are described below, and are graphically depicted in Figure 2-2.

Material Potentially Presenting an Explosive Hazard (MPPEH), Material Documented as Safe (MDAS), and Material Documented as an Explosive Hazard (MDEH)

MPPEH is defined as material potentially containing explosives or munitions (for example, munitions containers and packaging material; munitions debris remaining after munitions use, demilitarization, or disposal; and range-related debris) or material potentially contaminated with

a high enough concentration of explosives such that the material presents an explosive hazard (e.g., equipment, drainage systems, holding tanks, piping, ventilation ducts) associated with munitions production, demilitarization, or disposal operations. Excluded from MPPEH are munitions within the DOD-established munitions management system and other hazardous items that may present explosion hazards (e.g., gasoline cans, compressed gas cylinders, etc.) that are not munitions and are not intended for use as munitions. MPPEH items that can be positively determined to be free of energetic material are further classified as material documented as safe (MDAS) including fired small arms ammunition; otherwise they are classified as material documented as an explosive hazard (MDEH).

Munitions and Explosives of Concern (MEC)

This term distinguishes specific categories of military munitions that may pose a unique explosive safety risk, such as:

- Unexploded Ordnance (UXO),
- Discarded Military Munitions (DMM),
- Munitions Constituents (e.g., trinitrotoluene, nitroglycerin) present in high enough concentrations to pose an explosive hazard.

Unexploded Ordnance (UXO)

Military munitions that fulfill all of the following criteria:

- Have been primed, armed, or otherwise prepared for action,
- Have been fired, dropped, launched, projected, or placed in such a manner as to constitute a hazard to operations, installations, personnel, or material,
- Remain unexploded either by malfunction, design, or any other cause

Discarded Military Munitions (DMM)

Military munitions that have been abandoned without proper disposal or removed from storage in a military magazine or other storage area for the purpose of disposal. The term does not include UXO, military munitions that are being held for future use or planned disposal, or military munitions that have been properly disposed of consistent with applicable environmental laws and regulations. DMM have also not been armed or primed. However, live small arms are considered DMM.

Munitions Constituents (MC)

MC includes any materials originating from UXO, DMM, or other military munitions, including explosive and non-explosive materials, and emission, degradation, or breakdown elements of such ordnance or munitions.

Because there were no impact range facilities located at Mare Island (other than small arms ranges), and all encountered MEC items have been unfired, all MEC items recovered to date at Mare Island have been categorized as DMM. Potential sources for the recovered DMM at the SSA, as indicated in the Conceptual Site Model, include the following (Weston, 2008):

- Accidental or intentional disposal overboard into Mare Island Strait or Carquinez Strait,
- Inclusion of unwanted munitions and other debris with fill material used to expand the facility boundaries in adjacent wetland and tidal areas,
- Incidental loss during transportation or from handling within open storage areas,
- Intentional burial of unwanted munitions in disposal pits or trenches.

As a result of the long history of handling, storage, and disposal of munitions at Mare Island, the following investigations and removal actions have been completed at the SSA.

2.4 PREVIOUS INVESTIGATIONS/ACTIONS

A summary of the previous investigations, assessments, and removal actions conducted at the site are discussed in the following subsections.

2.4.1 Early Emergency Munitions Response Removal Actions

Four separate emergency munitions response actions were completed at the SSA by Explosive Ordnance Disposal Mobile Unit Nine (EODMU9) between August 1990 and May 1995 (Weston, 2011). The actions involved the mitigation of MEC hazards identified incidental to the former MINS maintenance actions being performed by DON and contractor personnel at five locations in the PMA and SSA.

A shoreline area just west of Dike 14 in the SSA was the site of two separate emergency munitions response actions in August and September of 1990. This location is depicted on Figure 2-3. On August 7, 1990, discovery of MEC exposed by former MINS maintenance workers resulted in the surface clearance of multiple items, including 20-millimeter (mm), 40-mm, and 3-inch/50 caliber anti-aircraft rounds, by EODMU9 personnel. On August 27, 1990, additional MEC items were observed at the same site in the bottom of a shallow fire pit that had been excavated by unknown persons.

A second munitions response action was completed by EODMU9 personnel after an initial inspection by the former MINS Explosives Safety Manager revealed additional buried MEC and related munitions items clustered together in a large conglomerate mass. Approximately 5,000 pounds of munitions dating from the Civil War through the post-World War II era were ultimately removed from the site and transported to China Lake Naval Air Warfare Center for disposal. Recovered MEC included small arms ammunition, projectile fuses, and many additional 20-mm and 40-mm anti-aircraft rounds.

Another SSA munitions response action took place on June 9, 1993, when EODMU9 responded to a report of a munitions item on the beach just west of Pier 34. EODMU9 personnel identified, evaluated, and transported two MK 58 Marine Markers to a disposal range where they were destroyed.

2.4.2 Preliminary Assessment Final Summary Report – Ordnance Sites (1995)

This Preliminary Assessment (PA) study was conducted to comprehensively address the nature and extent of potential unexploded ordnance contamination at MINS [PRC Environmental Management, Inc. (PRC), 1995a].

A number of buildings related to the SSA were assessed during the PA. For most of them, no further action was recommended. Exceptions included Building A227, the transformer house, for which it was recommended that investigation of polychlorinated biphenyls (PCBs) may be required. In addition, it was found that further investigation may be required at Building A259 to characterize the extent of petroleum contaminated soil from a former underground storage tank (UST) located adjacent to the building (PRC, 1995a). Additional discussion of Building A227 and Building A259 is provided in Section 4.1.1.

2.4.3 Preliminary Assessment/Site Inspection Final Summary Report – Non-Radiological Sites (1995)

A Preliminary Assessment/Site Inspection (PA/SI) for non-radiological sites was conducted at 95 SWMUs that were previously identified during a 1987 RCRA facility assessment (RFA) at MINS (PRC, 1995b). In addition to these 95 SWMUs, the work included assessment of 11 potential SWMUs, four areas of concern (AOC), and 19 additional potential sites with past or potential releases for which information had been requested by the EPA and DTSC. In total, the investigation included a PA/SI at 95 SWMUs as identified in the RFA plus 34 more sites. As such, 129 SWMUs and other sites were included in this PA/SI.

Of these sites, a total of five SWMUs are located within the SSA, including the following:

- SWMU 91 – Container Storage Area at Building A195
- SWMU 93 – Storm Sewer System
- SWMU 101 – Ordnance Sites including magazines
- SWMU 106 – Sanitary Sewer System
- SWMU 125 – South End of the Island

SWMU 91 is located entirely within the SSA. This SWMU is defined as the general hazardous waste container storage area in Building A195. The PA/SI indicates that wastes managed at this site included halogenated and non-halogenated solvents, flammable liquids, and corrosive liquids. The PA/SI also indicated that a 500-gallon UST containing solvent and diesel was

removed from the northwest corner of Building A195 in 1990. (Information contained in UST closure documents suggests that the tank was actually 1,000 gallons in capacity – refer to Section 4.1.1). Two soil samples were collected from shallow soil borings advanced adjacent to the tank and were analyzed for total petroleum hydrocarbons (TPH), purgeable aromatics, and purgeable halocarbons. All constituent concentrations were reported below detection limits (PRC, 1995b). SWMU 91 was subsequently closed under RCRA on June 3, 1996, as confirmed by DTSC concurrence dated August 17, 2011 (DTSC, 2011a). Additional information regarding SWMU 91 is provided in Sections 4.1.1 and 4.1.2.

SWMUs 93 and 106 are identified in the PA/SI as the storm sewer and sanitary sewer systems that consist of a network of catch basins and sewers that discharge excess surface runoff to Mare Island Strait and San Pablo Bay at 46 outfall locations across Mare Island. Five of these outfalls are located in SSA (Figure 2-1). The PA/SI Report indicates that until the Industrial Wastewater Treatment Plant was built in 1972, most of the industrial wastewater was discharged to Mare Island Strait and San Pablo Bay through the storm sewer system. As a result, hazardous wastes including solvents, coolants, oils, mercury, lead acids, and paint strippers were likely discharged through the storm sewer system. Rinse waters from sheet metal operations containing metal cleaning solutions, etching solutions, chromic acid, caustic soda, brightening compounds, and rust inhibitors were also likely discharged. As a result, the PA/SI Report recommended further investigation of the storm and sanitary sewer systems as part of the base closure activities (PRC, 1995b). Additional information regarding SWMU 93 and SWMU 106 is provided in Section 4.1.2.

SWMU 101 is defined in the PA/SI Report as the Concord Annex ordnance and additional sites located throughout MINS, although the PMA is indicated as the primary area of concern. The report indicates that contaminant-related ordnance sites should be investigated under the CERCLA/IR program, but does not provide additional information with respect to individual sites under this SWMU as they were addressed within the Preliminary Assessment Final Summary Report for Ordnance Sites (PRC, 1995b) summarized above. Additional details regarding the ordnance sites in the SSA are provided in Section 4.1.3.

SWMU 125 is described in the PA/SI Report as “contaminant-related ordnance sites” located in or near the “South End of the Island”, though specific locations or sites are not defined (PRC, 1995b). The report recommends that the contaminant-related sites “should be investigated under the Navy’s Installation Restoration Program”, but further indicates that the primary area of concern for SMWU 125 is the ordnance production area (PMA) (PRC, 1995b). Additional information regarding SMWU 125 is provided in Section 4.1.2.

2.4.4 SSA Unexploded Ordnance (UXO) Intrusive Investigations (1997-1999)

A UXO intrusive investigation at the SSA was conducted between August 1997 and May 1999, based on the presence of 1,093 geophysical anomalies that were identified during a previous

geophysical survey that was conducted for potential UXO in the SSA. During the intrusive investigations, a total of 1,810 MEC items were recovered from the SSA (Weston, 2003). The MEC items were removed down to a minimum depth of four feet bgs and up to ten feet bgs in locations near active or maintained utilities. None of the MEC items recovered showed evidence of having been fired and all were classified as DMM. Also recovered were 156,753 other live ordnance items (predominantly small arms ammunition), 767,373 inert ordnance items (munitions-related debris), and 688,419 pounds of scrap metal (Roy F. Weston, 2003).

Documented recoveries of MEC from the SSA included a small number of fuses and 20-mm rounds (totaling 43 items) recovered from the inland locations. However, the majority of MEC items recovered from the SSA (1,786 of 1,810 total discrete MEC items) originated from 4 locations at the Dike 14 area. The locations of these items are depicted on Figure 2-4. As discussed in Section 2.4.1, Dike 14 was the site of two 1990 emergency response actions and the shoreline area near Dike 14 was suspected to contain additional MEC items. The excavation of the Dike 14 site was complicated by its proximity to the shoreline and the susceptibility of excavations to tidal flooding.

In addition to the MEC items, a single $1^1/_2$-inch diameter radioluminescent deck marker, or radium button was found near Dike 14 on January 8, 1999. Radiological scanning of the deck marker indicated emissions of low-level radioactivity at a rate of 0.4 millirems per hour (Roy F. Weston, 2003). The item was identified during the screening of soil excavated near Dike 14 to remove ordnance. As a result of the finding, all of the soil removed from the excavation, several hundred cubic yards, was screened for radioactive material; no additional radioactive material was identified.

Although the exact origin of the deck marker could not be determined, no other radiological material was found during the investigation and therefore, it was not considered indicative of a more widespread problem. Based on the finding of the radium button, selected soil and groundwater samples from the Dike 14 area will be evaluated for the presence of radium-226 during the RI fieldwork according to the separate Work Plan for Radiological Screening and Survey Activities (RSRS and NOREAS, 2014).

During ordnance screening and clearing activities at the SSA, three discrete but closely located sites (designated as Primer Pit, Oven Pit No. 1, and Oven Pit No. 2) containing discolored soil and debris were discovered in September and October of 1999, approximately 650 feet south of Building A259, at the boundary between the tidal wetlands and upland areas (SSPORTS, 1997a; and Weston, 2008). The condition of the debris removed, along with observations of discolored soils, suggested that the pits were likely used for burning ordnance. The field sampling protocol required screening for pH, energetics [2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and methyl-2,4,6-trinitrophenylnitramine (Tetryl)], and ordnance-related

metals (copper, lead, and zinc) in the field whenever an unexplained change in the color, texture, or odor of soil or groundwater was noted.

Energetics (TNT, TDX, and Tetryl) were not detected during the field screening activities. However, the field screening results indicated elevated levels of copper, lead, and zinc in the soil, which is typical of an area used as a munitions burn site. A repetitive process of excavation and confirmation soil sampling was completed to ensure that all soils containing copper, lead, or zinc at concentrations above established action levels had been removed. It should be noted that the action levels used for the screening were based on industrial criteria and may not be applicable for a wetland setting. As a result, approximately 567 cubic yards of impacted soil were excavated from the three sites at the oven/primer pit area and disposed of at an appropriate offsite permitted facility. As described in Section 4.1.4, additional samples will be collected around the Oven/Primer Pits and evaluated as part of this RI.

2.4.5 Investigation for MEC at Mare Island Strait and Carquinez Strait (2003-2006)

Between 2003 and 2006, an investigation was conducted to characterize the nature and extent of MEC items in the shoreline (including nearshore and mudflat areas) and shallow water areas of the PMA, SSA, and IR 04 (ECC, 2010). This included a minimum overlap of five meters with the previous onshore geophysical surveys completed at the onshore portions of the PMA, SSA, and IR-04.

The investigation was completed in two phases, including a geophysical survey (Phase I) followed by excavation of selected geophysical anomalies (Phase II) identified during the first phase. For Phase I, a total of approximately 92 acres was surveyed in the summer of 2003 and summer of 2004, 85 acres of which were generally located in the shoreline and nearshore areas between Pier 34 and Dike 12 along the eastern boundary of IR 05. With respect to onshore areas, a total of approximately 15 acres of the exposed shoreline located within the SSA was surveyed using land based geophysical sensor equipment. As a result of the Phase I investigation activities, a total of 2,482 geophysical anomalies was identified in the shoreline and mudflat areas of the SSA (ECC, 2010).

Based on the Phase I results, a total of 765 geophysical anomalies in the SSA was selected for Phase II intrusive investigation. During the summer of 2006, the selected anomaly locations identified during Phase I were reacquired and excavated down to a depth of approximately four feet below ground surface (bgs), where possible. Excavation depths in some areas located in mudflats or with shallow groundwater were terminated at shallower depths due to infiltration and/or caving of the excavation.

Overall, a total of 38 MEC items and 236 items identified as inert munitions debris was recovered from the onshore areas between Pier 34 and Dike 12 during the Phase II investigation activities (ECC, 2010). All of the MEC items were classified as DMM. In addition,

approximately 1,237 pounds (lbs) of non-MEC related metallic scrap and debris were recovered from the area. The majority of the MEC items recovered (31 of 38 total) was found near the base of Dike 14. Moreover, two of the MEC items that were identified as being recovered from the SSA were found in the Dike 12 area. A graphical summary of the MEC items found during the 2006 anomaly excavations is provided in Figure 2-5.

As a secondary objective, the investigation also included a sedimentation study to evaluate the potential for subsurface MEC exposure and transport in the offshore areas of the SSA, PMA, and IR 04 due to the actions of waves or currents. The results of the sediment study indicated that any buried MEC items that may be present in the nearshore and mudflat areas of the SSA would likely remain buried even in the event of storm generated waves, tidal currents, or vessel traffic in Carquinez Strait.

The investigation report recommended continued investigation of the remaining anomalies in the shoreline areas of the SSA. This recommendation was based on the fact that not all exposed areas could be accessed safely by geophysical survey personnel at the lowest tide during the Phase II intrusive investigation conducted in the summer of 2006.

2.4.6 Digital Geophysical Mapping Investigation - PMA and SSA (2006)

A digital geophysical mapping (DGM) survey of all accessible areas within both the PMA and SSA was completed in 2006 (Weston, 2008). Wetland areas and debris piles within the boundaries of the PMA and SSA were excluded from the DGM survey. However, prior to the start of the MEC NTCRA, approximately 3.5 acres of accessible data gap area were subject to a DGM survey in 2012 and 2013 (ISR-JV, 2014). Additional details regarding the data gap survey are provided in Section 2.4.7. The 2006 PMA and SSA DGM surveys utilized a Geometrics G-858 magnetometer for all areas where there was an expectation of only ferrous components (PMA and most of SSA). The Geonics EM61 MK2 metal detector supplemented the G-858 magnetometer for areas of the SSA where non-ferrous components were recovered in the previous surveys.

The DGM survey included crawl spaces under three buildings, one of which is located in the SSA (Bldg. A163), to determine if geophysical data could be obtained. The building footprint areas (crawl spaces) represented extreme survey and positioning interferences due to the presence of steel reinforcement within the closely spaced concrete piers and flooring. For those reasons, the GeoVizor system was selected to conduct the building footprint survey. GeoVizor is a technology platform utilizing a standard G-858 magnetometer sensor that provides the ability to collect high resolution (high density) geo-registered data in environments with elevated interferences.

A total of 28,805 geophysical anomalies were identified by the 2006 DGM survey at the PMA and SSA: 13,938 anomalies in the PMA and 14,324 anomalies in the SSA (ISR JV, 2014). A

total of 543 anomalies were identified in the three surveyed building footprint areas, of which 207 anomalies were noted beneath Building A163 in the SSA.

2.4.7 Munitions NTCRA for PMA and SSA (2012-2013)

Based on the results of the 2006 DGM survey, an Engineering Evaluation and Cost Analysis (EECA)/Interim Remedial Action Plan (IRAP) was prepared by Weston Solutions Inc. for a Munitions NTCRA at the PMA and SSA (Weston, 2011). As part of the EECA/IRAP, the geophysical anomaly locations were categorized into separate sectors to prioritize the excavation process. The categorization was based on locations of previous MEC removal actions and an evaluation of historical records and photographs. These sectors were labeled as follows:

- Category A sectors - Areas considered most likely to contain additional MEC (high priority)
- Category B sectors - Areas where the likelihood of additional MEC is low (low priority)

The EECA/IRAP ultimately recommended excavation of 100 percent of the Category A sectors, and a minimum of 20 percent of the Category B sectors for the NTCRA at the PMA and SSA. Under this alternative, Category B sector geophysical anomaly locations would be selected for excavation based on geophysical anomaly characteristics typical of MEC items and locations with high geophysical anomaly densities that have the potential to represent disposal pits. Excavations at each targeted geophysical anomaly location would be limited to a depth of four feet bgs within an area having a two-foot radius if no MEC is encountered. If MEC or munitions debris (MD) items are identified at Category B sector anomalies, the excavation would be stepped-out in 25-foot increments to include the adjacent geophysical anomalies for MEC/MD. The 25-foot step-out distance was selected because most MEC items recovered at the former MINS have been discarded in clusters rather than as scattered individual items.

The selection of the remedial alternative recommended in the EECA/IRAP was finalized in the Final Action Memorandum for the NTCRA dated May 23, 2011 (DON, 2011), and the NTCRA was initiated in May 2012. Based on the planned future use of the SSA as a public park and recreational area, the NTCRA included excavation and screening of soils down to a depth of four feet bgs at each targeted geophysical anomaly location. Recovered MEC, MD, and scrap metal was screened and separated from the soil and evaluated for final disposition. Following screening of the soil for MEC and MD, soils that did not show evidence of discoloration, odors, or other indications of impacts were reused to backfill the excavation areas. No such evidence of impacts from MEC or MD was observed during the NTCRA. Six (6) soil samples were taken from sites in the SSA representative of the different types of munitions impacts seen during the NTCRA and analyzed for energetics and metals. The sampling results are described in a subsection below and indicated no impacts from energetics or metals from munitions.

Due to the size and scale of the removal action, the NTCRA activities were conducted by two separate contractors, Integrated Solutions for Remediation, JV (ISR-JV) and Battelle, working in different areas of the PMA and SSA. In addition, the removal activities expanded beyond the technical boundary of the SSA into portions of IA K along the shoreline. The NTCRA removal activities were completed in late July 2013, although one area within DGM Grid AF011 remains to be cleared. Munitions items were also found during the visual survey of the rip rap along the shoreline boundary between the IR05 and SSA (see below).

Data Gap Geophysical Surveys

Due to issues associated with accessibility or disturbances of critical habitat, several portions of the PMA and SSA were not included in the 2006 DGM survey. Therefore, in 2012 and 2013, prior to the initiation of the NTCRA, a total of approximately 5.3 acres of accessible data gap areas were subject to a DGM survey (ISR-JV, 2014).This included areas along the shoreline that could not be surveyed using the standard EM61-MK2™ system, but were therefore surveyed with hand-held equipment.

All of the accessible Category A anomaly locations were subsequently excavated. Category B anomaly locations were selected and excavated as appropriate, to achieve a removal rate of 20 percent, including step out requirements.

Munitions Items Found

During the NTCRA, approximately 36,000 munitions and munitions-related debris items were found and removed from the SSA, including primers, fuses, small arms ammunition, 0.50-caliber casings, projectiles bases, and primer flash tubes (ISR-JV, 2014, and Battelle, 2014). A graphical summary of the items recovered during the MEC NTCRA is provided in Figure 2-6. Figure 2-7 depicts the locations where the highest density of MEC items were recovered during the NTCRA, including significant munitions items. In particular, one Mark 6 depth charge with 300 lbs of trinitrotoluene (TNT) was found in the rip-rap along the shoreline in the southern portion of DGM Grid AB009.

In addition, several distinct areas described as disposal or burial pits were identified and excavated during the MEC removal activities in 2013. Based on information provided in the Final Removal Action Completion Report (RACR) for the NTCRA at the PMA and SSA (ISR-JV, 2014), the following disposal or burial pits were identified:

DGM Grid(s)	Location	Comments
AE010	South of Tyler Rd. and east of Jennings Rd.	Three pits identified Items found included empty propellant cans, small arms ammunition, and primers; one MEC item found

AE011	North of Tyler Rd., south of Bldg. A163	One pit identified Items found included MDAS, no MEC items
AH010 and AH011	Near Dike 14	Previously identified prior to NTCRA - mostly located in IA K Items found included MEC (predominantly fuses), small arms ammunition, and MDAS
AF011	West/Southwest of Bldg. A259	Two pits identified; western pit cleared, eastern pit partially excavated but extent not delineated Items found included empty propellant cans: no MEC found in western pit
AI015	Northeast of Bldg. A161	One pit identified Items found included small arms ammunition and MDAS; one MEC item found

At these locations, debris and soil was excavated to depths ranging from 4 to 12 feet bgs. Following the removal of the buried items and other debris, the excavations were backfilled with the original over burden soil (ISR-JV, 2014).

A total of three disposal pits were identified in DGM Grid AE010 where large quantities of MDAS (260 items), small arms ammunition, and one MEC item was recovered. The MDAS recovered here predominantly consisted of primers, and empty propellant cans. At the pit located in DGM Grid AE011, a small amount of MDAS (3 items) was recovered, no MEC items were found.

The disposal pit area originally identified in DGM Grid AH010, near Dike 14, was found to extend into adjacent grid AH011. The predominant munitions items found within AH010/AH011 appeared to be fuses and the area has been identified as a fuse dump. In addition, a significant amount of MDAS (more than 275 items) and small arms ammunition was found in the AH010/AH011 pit. The surface area of the disposal pit was estimated to measure approximately 11,700 square feet and was found to extend to depths exceeding 10 feet in some locations (ISR-JV, 2014).

Two disposal pits were identified within DGM Grid AF011 by ISR-JV in May 2013. Pit 1 (also identified as the western pit) was located at the intersection of Tyler Road and the unpaved service drive for Buildings A163 and A259 (Figure 2-7). Here, more than 25 empty propellant charge cans were first encountered at a depth of approximately 3 feet and were observed to

extend to depths of 5 to 6 feet. The debris was cleared down to approximately 6 feet in the area of this western pit. All of the debris removed from the western pit at AF011 was classified as MDAS.

Pit 2, also known as the eastern pit, was identified based on the encounter of additional empty propellant charge cans during the excavation of target anomalies located southwest of the corner of Building A259, east of Pit 1 (Figure 2-7). In this area, selected target anomalies were excavated down to a maximum depth of approximately 4 feet, although the vertical and lateral extent of the debris was not cleared as anomalies were documented as remaining in the floor and sidewalls of the pit in several locations (ISR-JV, 2014). In particular, the lateral extent of the AF011 Pit 2 may extend east of the excavated target anomalies by approximate 20 to 25 feet or more. The extent of AF011 Pit 2 will be delineated under this RI WP as described in Section 5.2.3.

At the disposal pit located in DGM Grid AI015, one MEC item was recovered along with a number of small arms ammunition and MDAS items, northeast of building A161. With the exception of the eastern pit identified in Grid AF011, all of the disposal pits were excavated and cleared of munitions items and munitions-related debris during the NTCRA (ISR-JV, 2014).

Munitions Constituent Sampling

During the excavation and clearing of soil for the NTCRA, no visual indications of discolored soils, unusual odors, or other indicators were observed (ISR-JV, 2014). However, to evaluate the potential for subsurface impacts from buried munitions items, a total of six soil samples was collected from biased locations where MEC, MDAS, and small arms ammunition was recovered during the removal action, including:

- DGM Grid AE008 – one sample location where expended small arms ammunition was recovered
- DGM Grid AF011 – two sample locations from the western disposal pit containing MDAS (Pit 1)
- DGM Grid AI012 – one sample location where live small arms ammunition was recovered
- DGM Grid AI015 – two sample locations from disposal pit containing MEC, MDAS, and small arms ammunition

These sampling locations are indicated on Figure 2-8. At each location, soil samples were collected from depths ranging from 2.0 to 3.5 feet bgs and analyzed for energetics and metals. Based on the analytical results, all detected metals concentrations were reported below ambient/background levels for Mare Island, and no energetics were detected (ISR-JV, 2014).

Non-Munitions Items Found

In addition to munitions-related items, several other non-munitions were found during the excavation and anomaly clearance activities completed as part of the 2012-2013 MEC NTCRA.

These items are depicted on Figure 2-8 and include:

- Six buried 55-gallon steel drums found in DGM Grid AI015 in July 2012 (Battelle, 2014),
- Three "USTs" connected to two dry wells through a series of perforated pipes, found in DGM Grid AJ015 in September 2012 (ISR-JV, 2014),
- A total of 30 buried 55-gallon steel drums found in DGM Grid AA009 in December 2012 and April 2013; 9 drums were initially found in December 2012 and an additional 21 drums were found in the same grid in April 2013(ISR-JV, 2014),
- Five additional 55-gallon steel drums found in the DGM AI015 disposal pit in May 2013 (ISR-JV, 2014).

Following their discovery, these items were investigated by Battelle and ISR-JV to evaluate potential impacts to the subsurface. Details of these investigations are included in the Draft RACRs (Battelle, 2014, and ISR-JV, 2014), brief summaries of which are provided below.

<u>Buried Drums in DGM Grid AI015</u>

In July 2012, a total of six 55-gallon drums were unearthed and removed by Battelle during the NTCRA MEC removal activities in DGM Grid AI015, approximately 250 feet east-northeast of Building A161 (Figure 2-8). The drums were found to be filled with soil at the time of their discovery and no information with respect to their contents at the time of burial was found.

Shortly after the discovery of the drums, two composite soil samples were collected from soil within the drums and analyzed for volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs) [including polycyclic aromatic compounds (PAHs)], extractable/purgeable total petroleum hydrocarbons (TPH), metals, herbicides, organochlorine pesticides (OCPs), PCBs, energetics, and dioxins/furans. The analytical results indicated that SVOCs, TPH, herbicides, PCBs, and energetics were not detected in either composite sample. All of the metals for both composite samples were reported below either the applicable ambient or residential EPA Regional Screening Levels (RSLs). VOCs and OCPs were either not detected or were reported in concentrations well below their respective residential RSLs (Battelle, 2014).

For the purposes of comparison, the Toxic Equivalency (TEQ) values for dioxin/furan results were calculated based on 2,3,7,8,-tetrachlorodibenzo-p-Dioxin (2,3,7,8-TCDD) TEQ and compared to both residential and industrial RSLs. The resulting sum of TEQ values for the dioxin/furan results for both composite soil samples from the drum areas were below the residential and industrial RSLs for those compounds (Battelle, 2014).

Following the removal of the drums, a total of six discrete soil samples were collected from the base of the excavation by Battelle, under the former locations of the drums, and analyzed for VOCs and OCPs only. The analytical results for VOCs indicated trace or estimated concentrations of benzene, 2-butanone, carbon disulfide, and methylene chloride. However, the reported concentrations were several orders of magnitude below their respective residential RSLs. Trace concentrations of the OCPs 4,4'-DDE and 4,4'-DDT were detected in all six of the soil samples from under the drums, though all of the reported concentrations were several orders of magnitude below the respective residential RSLs (Battelle, 2014).

In May 2013, ISR-JV conducted additional excavation of DGM Grid AI015 as part of their scope of work. During the excavation activities, five drums were found in the disposal pit. Following the removal of the drums, one soil sample was collected from four feet bgs and analyzed for VOCs, SVOCs (including PAHs), TPH, PCBs, and metals. The analytical results indicate that VOCs, SVOCs (including PAHs), TPH, and PCBs were not detected; all metals results were reported below their respective residential RSLs or background concentrations (Battelle, 2014).

Underground Storage Tanks and Dry Wells Found in DGM Grid AJ015

In September 2012, three previously unidentified USTs were uncovered and removed by ISR-JV during the Munitions NTCRA excavation activities in DGM grid AJ015, approximately 250 feet northeast of Building A161 (Figure 2-8). All three were documented as being steel tanks measuring 2 feet in diameter and 13 feet in length. Two of the tanks were found connected to two 18-inch diameter dry wells that extended to a depth of approximately 12 feet bgs. The tanks and dry wells were connected by a 40-foot length of 5-inch diameter perforated pipe (ISR-JV, 2014).

An additional length of solid 5-inch diameter conveyance pipe was also found leading away from the northwestern tanks, to the south/southeast. This pipe was cut and capped approximately 15 feet away from the tanks and no further investigation or evaluation of the conveyance piping was conducted under the NTCRA.

During a review/search for historical use regarding these tanks, ISR-JV indicated that two historical structures may once have been located in the vicinity of the tanks, but no records documenting the location of the suspected former buildings or tanks were available. However, based on the presence of the perforated pipe and dry wells associated with these tanks, it is likely that they were used for either rainwater infiltration or possibly a septic system and leach field.

Liquid samples were collected by ISR-JV from the first tank and dry well uncovered during the excavations and analyzed for TPH as diesel and motor oil (TPH-d and TPH-mo), PCBs, and metals. TPH-d, TPH-mo, and PCBs were not detected in the liquid samples collected from either the tank or dry well. The reported metals concentrations were compared to ambient concentrations in groundwater at Mare Island (Tetra Tech EM, 2002). None of the metals

detected in the liquid sample from the tank were reported in concentrations above their respective ambient concentrations. In the drywell sample, copper, lead, mercury, and nickel were reported in concentrations slightly above their respective ambient values for groundwater. All other metals were reported at or below their ambient concentrations.

Following the removal of the tanks, dry wells, and conveyance piping in December 2012, confirmation soil samples were collected from a total of 11 locations at depths of 4.5 to 6 feet bgs beneath the tanks and piping. All of the samples were analyzed for TPH-g, TPH-d, TPH-mo, SVOCs (including PAHs), and metals. The confirmation soil samples were collected from the following locations:

- Beneath each end of the removed tanks,
- Beneath every 20 linear feet of piping removed,
- Beneath the locations where tanks and piping were connected, and
- Adjacent to the dry wells.

TPH-g, TPH-d, and SVOCs (including PAHs) were not detected at or above their respective reporting limits. TPH-mo was detected in concentrations ranging from 7.4 mg/kg to 61 mg/kg in six of the 11 samples, but was not detected in the other five. The analytical results for all of the metals were reported below their respective ambient and residential RSLs, except for arsenic. The reported results for arsenic ranged from 4.6 mg/kg to 10 mg/kg, above the residential RSL value (0.39 mg/kg), but below the ambient arsenic concentration (36 mg/kg) for MINS (ISR-JV, 2014).

Buried Drums in DGM Grid AA009

In December 2012, a total of nine 55-gallon steel drums were unearthed and removed by ISR-JV during the NTCRA MEC removal activities in the location of DGM Grid AA009, approximately 150 feet south of Building A165 (Figure 2-8). The drums were found to be filled with soil at the time of their discovery and no information with respect to their contents at the time of burial was found.

Shortly after their discovery, the drums were removed and a total of four confirmation soil samples were collected from the bottom of the excavation at approximately six feet bgs. All of the samples were analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, metals, PCBs, OCPs, herbicides, MC, and dioxins/furans. Based on the analytical results, benzo(a)anthracene, benzo(a)pyrene, and benzo(b)fluoranthene were reported in concentrations above their residential RSLs in two of the four samples analyzed (ISR-JV, 2014). In addition, trace levels of dioxins and furans were also detected, though the resulting sum of TEQ values (based on 2,3,7,8-TCDD) were well below the residential RSL for 2,3,7,8-TCDD. All other

compounds analyzed were either not detected or were reported in concentrations below their respective residential RSLs and/or background levels (ISR-JV, 2014).

In April 2013, another 21 buried drums were found in DGM Grid AA009 during the NTCRA excavation activities.The drums were removed by ISR-JV and four additional confirmation soil samples were collected from the base of the excavation at a depth of 4 feet bgs.All of the samples were analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals. All compounds analyzed were either not detected or were reported in concentrations below their respective residential RSLs and/or background levels (ISR-JV, 2014).

Buried Cans in DGM Grid AE010

In January 2013, the tops of what were identified as roughly four 55-gallon steel drums were uncovered during the NTCRA MEC excavation activities in DGM Grid AE010. Due to scheduling priorities for excavation at other locations in the PMA, the drums at AE010 were not excavated right away. Once the excavation activities at grid AE010 were resumed in May 2013, the "drums" were unearthed and found to actually consist of empty propellant cans and not 55-gallon drums (ISR-JV, 2014). The cans were ultimately determined to be MDAS and based on the observed condition of the propellant cans, no sampling for chemical issues was performed during the NTCRA.

Items Found along IR05 Shoreline

During a visual inspection of the southern shoreline areas in February 2013, a number of munitions and non-munitions items were identified along the northeastern shoreline areas of IR05, directly adjacent to the SSA (see Figure 2-7). These items included two primer areas located in DGM Grids Z006 and Z007, large shell casings located in DGM Grid Z008, and a number of drums partially buried in the rip-rap in DGM Grid Z007. A large mass of metallic debris, munitions, and concrete was found along the shore in DGM Grid Z004. In terms of metallic debris, the mass appeared to contain steel rebar, valves, bolts, and other non-munitions items. Shell casings (20 mm) were also visible at the surface, though other munitions items may be buried within the interior of the mass. All of the debris in the mass appeared to be held together by concrete/cement or fusion of the materials over time, as was observed in similar masses found at dredge pond outfalls on other parts of the island.

At the time of this RI Work Plan, a response to the identification of these particular items has not been determined. As such, these areas are not planned for investigation under the SSA RI and it is anticipated that they will be addressed under a separate removal action. The boundary for the SSA now does, however, incorporate this shoreline area. While this area will not be included as part of this investigation, any information related to this area will be carried through and summarized in CERCLA documents for the SSA, including the RI Report.

Radiological Screening

As part of the NTCRA, the geophysical anomalies being cleared for MEC items were also scanned for potential radiation. Upon completion of the NTCRA activities in July 2013, no discrete radioactive items were found. In addition, radiological scan results did not indicate the presence of radioactivity in the excavated material (soils, debris, and munitions items) at levels above the established project investigation levels (Battelle, 2014 and ISR-JV, 2014).

As part of the RI activities, a final status survey (FSS) of the location of the former deck marker found in near Dike 14 in the SSA is planned. If additional radioactive items are found during the completion of the RI field activities, additional radiological surface scans and/or surveys may be conducted during the RI. All of the radiological data from the MEC NTCRA and RI field activities will be evaluated and incorporated into the RI Report. Additional information regarding the planned radiological screening for the RI is provided in the separate Work Plan for Radiological Screening and Survey Activities (RSRS and NOREAS, 2014).

2.4.8 Non-Munitions Related Investigations/Actions

2.4.8.1 UST Removals and Confirmation Sampling (2006-2009)

Historically, a total of four sites in the SSA have been associated with USTs. All of the USTs at these sites have either been removed or likely did not exist based on investigative efforts to confirm their presence.A brief summary of the status of these UST sites is included in the following table:

Location	ID	Capacity	Contents/Use	Comments
Bldg. A194	T-A194	Unknown	Unknown – reference to fuel oil in historical documents though no boiler ever present at A194	Presence of USTs never confirmed, Water Board case closure received on October 1, 2009
Bldg. A195	T-A195	1,000 gallons	Diesel fuel	Removed in 1990, Water Board case closure received on October 1, 2009
Bldg. A292	T-A292	420 gallons	Diesel/fuel oil	Removed in 1997, Water Board case closure received on December 5, 2006

Location	ID	Capacity	Contents/Use	Comments
Bldg. A296	T-A296	Unknown	Diesel/fuel oil	Water Board case closure received on October 22, 2009

Additional details regarding the UST removal and soil confirmation sampling activities at each of the individual sites is provided in Sections 4.1.1 and 4.1.2, which include the specific references to the individual Water Board closure letters for each site.

2.4.8.2 Confirmation Sampling for Polychlorinated Biphenyls (PCBs) (1997-2013)

A total of six of the 12 buildings in the SSA have been investigated as potential PCB sites under the TSCA program implemented by the DON at MINS. All six of these building have been closed for PCBs. A brief list of these buildings and their regulatory closure status is as follows:

Building	Description	TSCA Program Status	Date
A153	Sewer Pump Station	Closed – Meets criteria for unrestricted reuse	February 14, 2013
A161	Former Magazine	Closed – Meets criteria for unrestricted reuse	October 30, 2012
A162	Former Magazine	Closed – Meets criteria for unrestricted reuse	March 7, 2013
A163	Former Magazine	Closed – Meets criteria for unrestricted reuse	March 7, 2013
A194	Smoke Shack	Closed – Meets criteria for unrestricted reuse	September 12, 2013
A227	Transformer House	Closed – Meets criteria for unrestricted reuse	July 15, 2013

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3.0 SITE CONDITIONS

The regional (MINS) and local (SSA) conditions are described in the following subsections.

3.1 REGIONAL GEOGRAPHY AND CLIMATE

MINS is located on a peninsula that is approximately 3.5 miles long and one mile wide, bound by San Pablo Bay to the west, Carquinez Strait to the south, and Mare Island Strait (Napa River) to the east. The shipyard ranges in elevation from sea level at its extreme north end to 40 feet above mean sea level (MSL) in the south-central area. Sandstone and shale hills are located at the southern end of Mare Island, outside of the main areas of shipyard activity, and reach a maximum elevation of 287 feet above MSL. Of the total area of 5,613 total acres at MINS, approximately 3,031 acres are wetland areas and approximately 2,582 acres are dry land. More than half of the dry land areas was created by dredge and fill operations.

The climate is generally warm and dry in the summers, and cool and wet in the winters. The moderating influence of the marine air from the Pacific Ocean to the west is reflected in an average annual temperature of 58 degrees Fahrenheit (°F) in the vicinity of the strait. The summer temperatures range from approximately 55°F to 80°F on average in the San Pablo Bay area. The winter temperatures range from roughly 38°F to 53°F.

In the summer months, a steady marine wind blows from the Carquinez Strait. Wind speeds of 15 to 25 miles per hour (mph) or more are common in the afternoon and evening, but winds are generally 10 mph or less for the remainder of the day. Mean distribution of wind direction and speed is west to southwest at 12 mph. Rainfall as measured at MINS averages 17.41 inches per year (Ecology and Environment, Inc., 1983). Measurable precipitation falls 50 to 60 days per year. Approximately 95 percent of the total precipitation falls between October and April.

3.2 REGIONAL GEOLOGY AND HYDROLOGY

MINS is located at the mouth of the Sacramento River on San Pablo Bay between two major geographic provinces: the Coast Ranges and the Central Valley. Rocks exposed at and around MINS generally consist of micaceous shale and arkosic sandstones, part of the Cretaceous Great Valley Sequence. Underlying the Great Valley Sequence is the Cretaceous Franciscan Complex that is commonly dominated by graywackes, but also contains substantial quantities of cherts, greenstones, and shales, as well as limestones, serpentine, ultramafics, and blueschists. Basement rocks at MINS are commonly concealed by thick sequences of bay mud. Mare Island is geologically separated from Vallejo by the Franklin Fault, a southwest-dipping, high-angle reverse fault that is thought to strike north/northwest to south/southeast beneath Mare Island Strait.

The Mare Island peninsula has been profoundly altered by civilization, industry, and urban growth over the past 100 years. Many marshlands and lowlands have been filled, especially in the northern portion of the peninsula. Fill materials present several engineering problems such as subsidence, high shrink and swell potential, low strength, and high susceptibility to erosion.

3.3 LOCAL GEOLOGY

The SSA lies a few feet above sea level and is generally flat, extending from the Carquinez Strait shoreline to the base of the upland hills. The area is composed primarily of silty-clay and Younger Bay Mud bottom sediments originating in the waters adjacent to Mare Island and are made up of black to dark gray, soft clayey silt, and brown clay often containing thin lenses of fine sand. The SSA was created in several stages that began in 1930 and were substantially completed by 1950. The expansion operations utilized primarily rock and soil taken from upland areas of Mare Island that were placed over the clays and silts that had been deposited along the edge of Mare Island through natural and engineered accretion.

3.4 LOCAL HYDROLOGY/HYDROGEOLOGY

Apart from indications for shallow groundwater in the SSA, there is little information available with respect to the hydrologic conditions in this portion of MINS. Given the proximity to San Pablo Bay, it is expected that groundwater elevations, gradient, and flow are influenced by tidal fluctuations. Hydrologic data from the groundwater monitoring wells proposed for RI will be used to evaluate the hydrologic conditions at the SSA.

3.5 CURRENT CONDITIONS

With exception of Building A161, the area comprising the SSA is generally not in use currently and remains the property of the DON. Building A161 is currently used for storage of radiological items found during remedial actions conducted throughout MINS. The remaining manmade features on the site consist primarily of the buildings formerly used for the storage and handling of munitions, some of which were later used for office space. The site is generally in an undeveloped state and the infrastructure (roads, structures, utilities, etc.) has deteriorated from disuse and lack of maintenance, though the main road was resurfaced with recycled asphalt during the 2012-2013 NTCRA as part of the Navy's green and sustainable remediation (GSR) program.

A total of 13 buildings or structures at the SSA were evaluated for the development of the RI investigative approach. The locations of these buildings are illustrated on Figure 2-1. A list of these buildings and brief summary of their use is provided below. Detailed descriptions of past assessments or investigations are provided in Section 4.1.1.

- Building A153 – Sewer Pump Station, currently empty
- Building A161 – Former magazine, designated for temporary storage of radiological items found on MINS

- Building A162 – Former magazine, later used for general storage, currently empty
- Building A163 - Former magazine, later used for general storage, currently empty
- Building A164 – Former ordnance warehouse, later converted to office space
- Building A165 - Former ordnance warehouse, later used for general storage
- Building A193 – Former Mine Anchor Facility Annex (associated with Building 259, demolished prior to 1995
- Building A194 – Smoke Shack, used as a designated smoking area for work crews, currently not in use
- Building A195 – Ordnance segregation, historically used to segregate munitions and other ordnance items, later used to store hazardous wastes as a regulated SWMU (SWMU 91), details provided in Section 4.1.2
- Building A227 – Transformer house, currently not in use
- Building A259 – Mine Anchor Assembly and Advanced Weapon Container Maintenance, used to assemble mine anchors and renovate advanced weapons, currently not in use
- Building A292 – Former scale house, once housed a mechanical scale, building removed,
- Building A296 – High Explosive Safe Haven, used to temporarily stage rail cars with high explosives, structure remains in place

3.6 CONCEPTUAL SITE MODEL

The most current comprehensive Conceptual Site Model (CSM) for the SSA was prepared in 2008, following the completion of the final digital geophysical mapping of the PMA and SSA described in Section 2.4.6 (Weston, 2008). In general, the current CSM is largely based on information obtained from intrusive investigations and emergency removal actions for buried munitions items and related debris completed prior to 2008. As such, the current CSM is mainly focused on site contamination associated with MEC and was intended to provide the basis for the design and implementation of the NTCRA that was completed at the PMA and SSA in July 2013.

To date, very little information exists with respect to potential chemical contaminant impacts to the environment due to historical activities at the SSA. As outlined in Section 2.4, the current information available for evaluating potential chemical contamination issues is limited to the confirmation soil sampling results for a small number of sites where diesel or fuel oil USTs and drums have been removed and 6 soil samples analyzed for energetics during the 2012-2013 NTCRA.

3.6.1 Background Information and Current Conditions

The SSA was historically used for the storage and handling of munitions, as well as for the storage of general shipyard items. The site currently exists in an undeveloped state and the infrastructure (roads, structures, utilities, etc.) has deteriorated from disuse and lack of

maintenance. Remaining manmade features on the site consist primarily of the buildings formerly used for the storage of munitions.

Currently, only authorized personnel (maintenance workers, law enforcement, etc.) with a specific need to be in the area are currently allowed entry into the SSA. A brief summary of the history of the SSA is provided in Section 2.2. For the updated CSM, this information, along with any additional details regarding the background and or historical operations at the SSA will be evaluated.

3.6.2 Contaminants and Contaminant Sources

To date, a wide variety of buried munitions items have been detected and removed from portions of the SSA, as described in Section 2.4. In general, these include propellants, munitions items filled with high explosives, small arms ammunition, fuses, primers and minor to medium caliber gun ammunition. Of particular significance, a Mark 6 depth charge with 300 pounds of TNT was recovered near the shoreline area toward the western portion of the SSA. Projectile fuses and 20-mm anti-aircraft ammunition accounted for a majority of items recovered in the SSA.

Based on the completion of the NTCRA activities in July 2013, the updated CSM will assume that all Category A and selected Category B target DGM anomalies have been screened and cleared to a minimum depth of 4 feet or more in all accessible areas of the SSA. Overall, the excavation and anomaly removal at selected anomalies, MPPEH step-out locations, and disposal pits exceeded the requirements of the NTCRA Action Memorandum (DON, 2011) and have therefore achieved the Remedial Action Objective (RAO) of reducing the threat to human health, welfare, and the environment posed by MPPEH (ISR-JV, 2014).

A single, discrete radiological item was found in the SSA during a previous emergency MEC removal action in 1999. However, no additional radiological items or radioactive materials were encountered during the 2012-2013 NTCRA removal activities. The radiological screening data from the NTCRA, the RI field activities, and the unrestricted use survey associated with the former deck marker will be incorporated into the updated CSM in the RI Report.

With respect to chemical contaminants, only a few limited site investigations have taken place in the SSA to date and include:

- Analytical data for petroleum hydrocarbons in soil from 4 former UST sites,
- Limited analytical results for copper, lead, and zinc in soil and groundwater from one location (former Oven/Primer Pits) located near the southern portion of the SSA,
- Soil sample results for energetics and metals from six locations within the SSA (Section 2.4.7),

- Confirmation soil sample results for VOCs, SVOCs (including PAHs), TPH, PCBs, pesticides, herbicides, munitions energetics, metals, and dioxins/furans from buried drum locations in DGM Grids AA009 and AI015, and
- Confirmation soil sample results for SVOCs (including PAHs), TPH, and metals from excavation of underground tanks recovered from DGM Grid AI015.

The analytical results from the RI will be used to provide a basis for establishing the chemical contaminants of potential concern (COPC) at individual sites within the SSA and for evaluating the potential sources of contamination based on historical activities.

3.6.3 Release Mechanisms and Affected Media

Based on the current understanding of the CSM, the release mechanisms that describe how MEC items were introduced into the environment at the SSA include handling loss, open container spillage, disposal, loss through truck/railcar loading and unloading, and possible munitions burning (Weston, 2008). However, because very little is currently known with respect to potential chemical contamination, it is unlikely that these release mechanisms constitute the full range of possible means for chemical contaminants to have been introduced into the soil and groundwater. Other release mechanisms for the chemical contaminants that will be considered for the updated CSM include releases to soil and shallow groundwater by the following:

- Direct release of potential contaminants to subsurface (at depth) from leaking pipelines or tanks,
- Surface releases in areas where hazardous materials were once stored, and
- Disposal, burial, or burning of potential contaminants along with MEC items or other trash in disposal pits.

Consideration of these potential release mechanisms form the basis for the investigative approach and methods that will be applied to the RI. The analytical data obtained from the RI will be used to confirm these assumptions with regard to release mechanisms and may also identify other potential mechanisms that may apply to the SSA.

As indicated in Section 3.6.2 above, data from previous investigations and removal actions for munitions have provided a considerable amount of information with respect to the impacts of MEC and related debris to the soil at SSA. However, very little information is currently known regarding chemical impacts to the soil and groundwater conditions. The investigative approach for the RI is intended to provide information regarding the nature and extent of potential chemical contamination in the soil and groundwater at the SSA.

3.6.4 Future Use Scenarios and Potential Receptors

The area comprising the SSA remains the property of the U.S. Navy and is not currently in use. However, future plans for the site include transfer of the property from Navy control. Based on

the Mare Island Specific Plan (City of Vallejo, 2008), the current reuse planned for the SSA includes redevelopment as a recreational area (park) and a wildlife preserve (Weston, 2011). The current CSM identifies the following potential human receptors based on this planned reuse scenario:

- City and utility workers who access the areas,
- Construction workers performing ground intrusive work, and
- Recreational users of the area.

Based on the proximity of the SSA to Carquinez Strait and its planned use as a wildlife park, the updated model will also take ecological receptors, both marine and terrestrial, into consideration. Additional information regarding potential receptors at the SSA is provided in Sections 7.0 and 8.0.

3.6.5 Updated CSM

As part of the RI, the nature and extent of chemical contaminants and munitions will be assessed in soil and groundwater at the SSA. Results from the separate radiological investigation will also be evaluated separately in the RI. Soil data will be collected from those areas where information regarding historical activities and/or previous sampling data indicates that chemical impacts were most likely to have occurred. The results of the soil data will be used to evaluate the nature of the contaminants, potential source areas, and extent of the contamination. In addition, information obtained from the recently completed MEC NTCRA will also be used to update the CSM for the SSA. In particular, the following information or data will be used to update the CSM:

Data/Information from Previous Investigations and Removal Actions at SSA:

- Database information with respect to geophysical anomalies, munitions items, and related debris found during the investigation for MEC at Mare Island Strait and Carquinez Strait (ECC, 2010), including the results of the related sedimentation study (Section 2.4.5),

- Geographic Information System (GIS) data with respect to munitions items and related debris found and removed during the NTCRA (ISR-JV, 2014 and Battelle, 2014),

- Database information with respect to various quantities and types of munitions items and debris found and removed during the NTCRA (ISR-JV, 2014 and Battelle, 2014),

- Radiological screening data for the excavated soils and debris, as well as for the excavations (ISR-JV, 2014 and Battelle, 2014),

- Analytical data from soil sampling for chemical and munitions contaminants completed during the NTCRA (ISR-JV, 2014 and Battelle, 2014),

- Analytical data for soil sampling previously conducted during UST removal actions as summarized in Section 4.0, and

- Analytical data for soil sampling conducted during previous UXO intrusive investigation at the SSA (Roy F. Weston, 2003).

Data/Information from the RI Fieldwork:

- Soil data (lithology, stratigraphic configuration, etc.) obtained from soil borings,

- Analytical results for chemical contaminants of concern and energetics in soil and groundwater at various site features,

- Hydrogeologic data (groundwater elevations, flow direction, hydraulic gradient) obtained from the newly-installed groundwater monitoring wells,

- General groundwater quality information at the SSA with respect to potential exception to the sources of drinking water policy, and

- Radiological survey data from the location where the former deck marker was found near Dike 14, as well as data from the radiological screening of the soil samples and cuttings that will be conducted for health and safety purposes during the soil boring/well installation activities (RSRS and NOREAS, 2014).

Soil data from the RI will be used to evaluate the nature and extent of potential contamination, as well as to identify the possible source areas. Groundwater data will be collected from a number of permanent wells located across the SSA to assess and monitor hydrogeologic conditions that will be used in conjunction with analytical data to evaluate the fate and transport of potential contamination at the SSA. In addition, general groundwater quality data collected during the RI will also be used to support a future request for exception to the sources of drinking water policy.

Data obtained from the records review and RI fieldwork will be used to:

- Conduct Human Health Risk Assessments (HHRA),

- Conduct Ecological Risk Assessments (ERA),

- Conduct a Radiological Risk Assessment for the specific area designated in the Work Plan for Radiological Screening and Survey Activities (RSRS and NOREAS, 2014) and other areas if radiological items are discovered, and

- Conduct MEC Hazard Analysis.

Information obtained from these risk assessments and evaluations will be used to update the CSM and will provide a foundation for the subsequent Feasibility Study and Remedial Design efforts, with the ultimate goal of determining risk for current and future receptors and whether further action is required.

4.0 REMEDIAL INVESTIGATION APPROACH

In order to meet the RI objective to characterize the nature and extent of potential chemical contaminants in soil and groundwater at the SSA, the results of the previous site assessments, investigations, and removal actions (summarized in Section 2.0) were reviewed and evaluated to determine the overall approach for this RI. A summary of the previous assessments, investigations, and removal actions is provided in Table 4-1. In addition to the evaluation of previous investigation results, the IR, RCRA, Munitions Response Program (MRP), Petroleum, and TSCA environmental programs were considered during the development of the investigative approach.

Geophysical anomalies were cleared in accessible Category A (100%) and Category B (>20%) sectors to a minimum depth of four feet bgs in the upland and non-upland areas of the SSA as part of the 2012-2013 MEC NTCRA (even some inaccessible areas were cleared to 2 feet bgs). Because of this clearance, it is not expected that MEC will be encountered during this investigation. As a result, only CERCLA and petroleum chemical contaminants will be investigated for the RI.

A total of 52 soil borings and nine groundwater monitoring wells are proposed for this RI. The locations of all the proposed soil borings and groundwater wells are illustrated on Figure 4-1. Soil boring locations planned are depicted in Figures 4-1 through 4-6. Detailed descriptions of the soil and groundwater investigation approaches, including the proposed sample types and analytical parameters are provided in the following subsections. A summary of the proposed approach, including the number of samples, analytical parameters, and basis for the investigation at each site feature is summarized in Table 4-2.

It should be noted that soil samples will be collected from three discrete depth intervals at all locations except for those few associated with shallow features. As noted in Table 4-3, a shallow soil sample will be collected at approximately 0.5 feet bgs in all locations for the purpose of evaluating potential risks to ecological receptors. The depths for the deeper samples are currently planned for five and ten feet bgs, but will be adjusted in the field to provide adequate coverage below buried features (USTs, pipelines, etc.). In addition, the deeper sample depth intervals may also be adjusted based on evidence for potential contaminant impact (staining, elevated headspace readings, etc.) as observed in the field.

In the event that additional samples or sampling locations are required to evaluate the extent of a particular impact, based on field observations at the time of the investigation, additional soil borings and/or groundwater monitoring wells may be completed under this RI Work Plan at the discretion of the NOREAS field geologist and upon approval of BRAC PMO West.

4.1 INVESTIGATIVE APPROACH – SOIL SAMPLING

The soil sampling elements of the RI will focus on assessing the potential presence of chemical contaminants in vadose zone soils based on information regarding past uses/activities at a given location and/or the results of previous investigations. In general, historical use information and/or historical sample data (where available) were evaluated from each of the site features proposed for investigation. A summary of the number of soil boring/sampling locations proposed for each of the general features as part of the RI is as follows:

Location/Feature	Number of Site – Specific Soil Borings/Sampling Locations	Number of Additional/ Shared Sampling Locations	Comments
Building Areas/Structures	8	4	Samples collected from SWMU 93 and SMWU 106 will also be used to evaluate Building A195 and A259. Refer to Section 4.1.1
SWMUs	18	13	Samples collected for Buildings A193, A195, and A296 will also be used to evaluate SWMU 93 and SWMU 106. Refer to Sections 4.1.2 and 4.1.3
MEC Sites	6	11	Samples collected for SWMU 93 and SMWU 106 will also be used to evaluate MEC sites. Refer to Section 4.1.3
Oven/Primer Pit Areas	6	2	Samples collected for SWMU 106 will also be used to evaluate Oven/Primer pit area. Refer to Section 4.1.4
Other Areas	14	2	Includes USTs, dry wells, and piping found in DGM Grid AJ015; also includes 55-gallon drums found in DGM Grid AA009, refer to Section 4.1.5

Location/Feature	Number of Site – Specific Soil Borings/Sampling Locations	Number of Additional/ Shared Sampling Locations	Comments
Pilot Borings for Groundwater Monitoring Wells	9	NA	
Total	61		Includes 52 soil boring locations + 9 pilot boreholes for groundwater monitoring wells

Based on the information reviewed, a number of site features at the SSA were selected for soil sampling as part of this RI. A detailed description of the sampling locations selected, including proposed sample depths and analytical parameters, is provided in the following subsections and are summarized in Tables 4-2 and 4-3.

4.1.1 Building Areas/Structures

For the purposes of this RI, historical use information for a total of 14 buildings/structures in the SSA was evaluated. Historical sampling data was also evaluated for buildings and features where previous investigations or removal actions were completed. This section is organized into two main groupings; the first group describes those buildings and structures that are not proposed for investigation under the RI, and the second group is for those sites where investigation is proposed.

RI Status	Buildings/Structure
No Investigation Planned	A153, A161, A162, A163, A164, A165, A194, A227, A292, and Pier 35
Investigation Planned	A193, A195, A259, and A296

A total of eight soil boring/sampling locations to investigate the building/structure areas are planned for the RI. A detailed discussion of the rationale for the selection of those buildings/structures where soil sampling will not be conducted is provided in Section 4.1.1.1 below; descriptions of the detailed rationale for those features where soil sampling is proposed for the RI are provided in Section 4.1.1.2 and are summarized in Tables 4-1 and 4-2. The

proposed soil sampling locations associated with the buildings at the SSA are illustrated on Figure 4-2.

4.1.1.1 Buildings/Structures Not Proposed for Investigation as Part of the RI:

Sewer Pump Station (A153)

Building A153 is a 270 SF corrugated metal building attached to the east side of Pier 35, south of Building A194 (see Figure 2-1). The building is set on wooden piers and directly overlies the water of Carquinez Strait. The building is currently boarded up and not in use. Building A153 was not included in the 1995 PA/SI, therefore no additional information is provided in the 1995 PA Final Summary Report (PRC, 1995a). However, information provided in the Final Environmental Baseline Survey (EBS) Report (Mare Island Naval Shipyard, 1994) indicates that the pump station was connected to the sanitary sewer system. No reports of past leaks or releases at Building A153 were reported in the EBS.

Assessments conducted as part of the TSCA program between 1997 and 2003 did not reveal any historical documents or other evidence indicating that sources of PCBs existed in the building, but did confirm the presence of two pumps (ERS-JV, 2013b). As a result of the PCB sampling and investigations, Building A153 was closed with respect to PCB issues under TSCA on February 14, 2013.

Based on the lack of evidence for chemical (including energetics) impacts identified and the results of previous site assessments and investigations, including the site closure for PCB issues under the TSCA program, no further investigation of Building A153 is planned. Piping associated with the pump station will be addressed as part of the investigation planned for SWMU 106 (Sanitary Sewer System) as discussed in Section 4.1.2.

Magazine (A161)

Building A161 is a 5,151 SF transite building with a metal roof and concrete floor located approximately 250 feet west of Tyler Road and 200 feet east of Building A292 in the upland area of the SSA (see Figure 2-1). No tanks, sumps, floor drains, transformers, or air emissions controls are associated with this building. Based on information provided in the PA Final Summary Report (PRC, 1995a), no evidence of chemical or MEC impacts at Building A161 was identified and no further action was recommended.

The building was evaluated for PCBs under the TSCA program in 1997 and 2003 (ERS-JV, 2012a). As a result of this assessment, Building A161 was closed under the TSCA program on October 30, 2012 and meets the requirements for unrestricted reuse.

Based on the lack of evidence of chemical impacts identified in the results of previous site assessments and investigations, including the site closure under the TSCA program, no further investigation of Building A161 is planned for this RI. However, Building A161 is currently

being used for storage of radiological items found during investigations at other sites on Mare Island. A Baseline Radiological Survey (Weston, 2011) of the building was conducted prior to the items being stored in the building. A Final Status Survey will be conducted in the future prior to closure of the site.

Magazine (A162)

Building A162 is a 5,151 SF concrete building with a metal roof located approximately 70 feet west of Tyler Road and 370 feet south of Building A161 (see Figure 2-1). The building was formerly used as an ammunition magazine, but was being used for storage of inert materials in cardboard boxes on wooden pallets at the time of the PA/SI in 1995. No tanks, sumps, floor drains, transformers, or air emissions controls are associated with this building. Based on information provided in the PA Final Summary Report (PRC, 1995a), no evidence of chemical or MEC impacts at Building A162 was identified and no further action was recommended.

Assessments conducted as part of the TSCA program between 1997 and 2003 did not reveal any historical documents or other evidence indicating that sources of PCBs existed in the building. As a result of the sampling and subsequent assessments, Building A162 was closed under the TSCA program on March 7, 2013 (ERS-JV, 2013c) and meets the requirements for unrestricted reuse.

Based on the lack of evidence for chemical impacts identified in the results of previous site assessments and investigations, including the site closure under the TSCA program, no further investigation of Building A162 is planned.

Magazine (A163)

Building A163 is a 5,151 SF concrete building with a metal roof located north of Tyler Road; approximately 75 feet west of Building A259 (see Figure 2-1). No tanks, sumps, floor drains, transformers, or air emissions controls are associated with this building. Based on information provided in the PA Final Summary Report (PRC, 1995a), no evidence of chemical or MEC impacts at Building A163 was identified and no further action was recommended.

Assessments conducted as part of the TSCA program between 1997 and 2003 did not reveal any historical documents or other evidence indicating that sources of PCBs existed in the building. Building A163 was closed under the TCRA program on March 7, 2013 (ERS-JV, 2013d) and meets the requirements for unrestricted reuse.

Based on the lack of evidence of chemical impacts identified in the results of previous site assessments and investigations, including the site closure for PCB issues under the TSCA program, no further investigation of Building A163 is planned.

Ordnance Warehouse (A164)

Building A164 is a 5,151 SF concrete building located on Tyler Road near the southern end of the SSA (see Figure 2-1). The building was formerly used as an ordnance warehouse, but was vacant at the time of the PA/SI in 1995. The building is divided into three compartments, one of which was used as an office, the other two were used to store ordnance. No tanks, sumps, floor drains, transformers, or air emissions controls are associated with this building. Based on information provided in the PA Final Summary Report (PRC, 1995a), no evidence of chemical or MEC impacts at Building A164 was identified and no further action was recommended. Building A164 was not identified as a potential PCB site under the TSCA program.

Based on the lack of evidence for chemical impacts identified in the results of previous site assessments and investigations, no further investigation of Building A164 is planned.

Ordnance Warehouse (A165)

Building A165 is a 5,151 SF brick building with a corrugated metal roof located on Tyler Road near IR05 (see Figure 2-1). The building was formerly used as an ordnance warehouse, but was being used for storage of lube oils and cleaners at the time of the PA/SI in 1995. No tanks, sumps, floor drains, transformers, or air emissions controls are associated with this building. Based on information provided in the PA Final Summary Report (PRC, 1995a), no evidence of chemical or MEC impacts at Building A165 was identified and no further action was recommended. Building A165 was not identified as a potential PCB site under the TSCA program.

Based on the lack of evidence of chemical (including energetics) impacts identified in the results of previous site assessments and investigations, no further investigation of Building A165 is planned.

Smoke Shack/Warehouse (A194)

Building A194 is a 1,392 SF concrete building with a corrugated steel roof located near the southern end of Jennings Road, on the narrow strip of land that connects the SSA with Pier 35 (see Figure 4-1). The building included a small (82 SF) corrugated metal shed that is attached to the southeastern corner of the building. The main portion of the building was demolished sometime after 1995, though the exact date is unknown. A 1,310 SF concrete pad remains in place, as does the shed. Information provided in the Conceptual Site Model (CSM) indicates that the building was used as a designated smoking area where crews loading and unloading ordnance could smoke without concern of endangering the ordnance operations (Weston, 2008).

Information from earlier UST investigations noted the suspected presence of three USTs near A194 (ERM-West, 1988), but did not identify any specific information with respect to their use, capacity, or disposition. A subsequent investigation for the USTs was conducted in 1991 using

geophysical methods in an attempt to locate the tanks (PRC, 1991). In addition, two soil samples were collected southeast of the building. Evidence for the presence of the USTs could not be confirmed and no petroleum compounds or other potential chemical contaminants were detected in the soil samples (PRC, 1991, 1995a). Based on information provided in the PA Final Summary Report, no evidence of chemical or MEC impacts at Building A194 was identified and no further action was recommended (PRC, 1995a).

Building A194 received a no further action letter for the suspected USTs from the Water Board on October 1, 2009 (Water Board, 2009a). The letter indicated that USTs were initially included on a UST inventory list based on the observation of a suspected vent pipe located near the northern portion of the building. The letter acknowledges that no USTs were found during subsequent geophysical investigation and subsurface sampling did not identify evidence for TPH in the soil.

Information obtained during PCB assessments and investigations conducted after the PA/SI indicates that Building A194 was formerly used as a warehouse and for electrical distribution. A total of five PCB-containing transformers were once located within the building, three of which were documented as leaking (ERS-JV, 2013e). As a result, all five of the transformers inside Building A194 were removed between 1987 and 1992.

Building A194 was closed under the TSCA program on September 12, 2013. Based on the lack of evidence of chemical impacts identified in the results of previous site assessments and investigations, including the anticipated site closure under the TSCA program, no further investigation of Building A194 is planned.

Transformer House (A227)

Building A227 is an 81 SF transformer house that is located on the north side of Tyler Road, approximately 130 feet southeast of Building A195 and approximately 100 feet southwest of Building A163 (see Figure 2-1). One transformer was located inside the building but was removed in 1992. A second pad-mounted transformer and related rocker arm are located approximately 4 feet northeast of the building and remain active as of March 2013 (ERS-JV, 2013f). Built in 1943, it is likely that the transformers within it used oils containing PCBs. The PA/SI report contained a recommendation to obtain and verify documentation that the transformer used oils that did not contain PCBs (PRC, 1995a).

The site was evaluated for PCBs in 1997 and 2010. As a result of these evaluations, Building A227 was closed under the TSCA program on July 15, 2013. Based on the lack of evidence of chemical impacts identified in the results of previous site assessments and investigations, including the anticipated site closure under the TSCA program, no further investigation of Building A227 is planned.

Former Scale House (A292)

Building A292 was a 70 SF mechanical scale house located approximately 200 feet northwest of the shoreline in the southeastern portion of the SSA upland area (see Figure 2-1). The building was demolished sometime after the PA was completed in 1995 although the exact date of its removal is not known. No additional information was provided in the PA Final Summary Report, though it did provide a recommendation for no further action at this building (PRC 1995a).

A 420-gallon fuel oil/diesel UST was once located in the vicinity of Building A292, approximately 40 feet northwest of Building A292. The UST was removed in December 1997. During the removal/excavation activities, the tank was observed to be in good condition and no visual evidence of staining or odors were observed in the soil beneath the tank. One soil sample was collected from below the tank and analyzed for TPH and BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds. No TPH or BTEX compounds were reported in the sample results above laboratory detection limits. The UST case (Water Board case No. 48D9250) was closed on December 5, 2006 (Water Board, 2006).

Based on the lack of evidence for chemical impacts identified in the results of previous site assessments and investigations, no further investigation of former Building A292 is planned. It should be noted that the three USTs and related piping found in grid AJ015 during the MEC NTCRA excavation activities (see Section 2.4.7) were uncovered approximately 75 feet north of the former Building A292 location (Figure 2-8). Based on review of available information, it is unclear if the USTs were associated with the activities at the former scale house. However, as described in Section 4.1.5, the USTs and related piping will be investigated as part of the RI.

Pier 35

Pier 35, also known as the Mine Wharf Pier, extends southward from the SSA into Carquinez Strait, between Dike 12 (the IR05 shoreline) and Dike 14 (see Figure 2-1). Built in 1942, the pier was used historically to transfer mines from Building A195 to Navy ships (Battelle, 2009). The pier remains in place but is currently not in use.

Because of its location over the waters of Carquinez Strait, the potential for contaminant impacts associated with past activities at Pier 35 is being addressed as part of the offshore investigation at IA K (Figure 2-1). As such, no investigation of Pier 35 is planned for the SSA RI.

4.1.1.2 Buildings Proposed for Investigation as Part of the RI:

Mine Anchor Facility Annex (A193)

Building A193 was not specifically addressed under the PA/SI, though it was depicted as being located approximately 200 to 250 feet south of Building A164 (see Figure 2-1) in previous site documents. Information contained in the CSM (Weston, 2008) indicates that this building was constructed in 1942 and was likely associated with the Mine Anchor Assembly and Advanced

Weapon Container Maintenance operations conducted in Building A259. The building was demolished some time prior to 1995, though the exact date of its removal is unknown. No additional information regarding this building was available for review.

Based on the potential past use of Building A193 to support the Advanced Weapons Container Maintenance operations and lack of additional information, two soil borings (SSARI-B193B01 and SSARI-B193B02) are planned in the approximate location of the former building (Figures 4-1 and 4-2). The building may have been used for surface preparation (degreasing), painting, and cutting/welding activities. Soil samples at both locations will be collected from depths of 0.5, 5, and 10 feet bgs. The soil samples will be analyzed for VOCs, SVOCs (including PAHs), TPH as gasoline (TPH-g), TPH as diesel (TPH-d), TPH as motor oil (TPH-mo), and metals (Table 4-3).

Ordnance Segregation/Hazardous Waste Storage (A195)

Building A195 consists of an 8,874 SF concrete building constructed in 1942 and located approximately 100 feet north of Tyler Road, northwest of the location where Jennings Road terminates at Tyler Road, in the upland portion of the SSA (see Figure 2-1). Prior to 1988, the building was used for ordnance segregation activities of fleet return items, gun ammunition and high explosives items, bomb cabling, and MK 44 (Lazy Dog) modifications (PRC, 1995a). At the time of the PA/SI in 1995, the floor was documented as sealed concrete and no floor drains or sumps were observed within the building (PRC, 1995a and 1995b).

An air compressor and a boiler were observed in two outer buildings located outside of the northern end of the building, and a covered utility vault and electrical power boxes were also noted near the southern end of the building. Oil residue was observed on the boiler itself during the PA site inspections, but no indication of staining on the ground surface around the boiler was reported (PRC, 1995a). The PA Final Summary Report also identified two storm drains located near the southwest corner of the lot for the building. No indication, evidence, or documentation of potential chemical releases had been reported at Building A195 at the time of the PA/SI (PRC, 1995a).

After 1988, the Building A195 was subsequently used by the Defense Reutilization and Marketing Office (DRMO) for storage of general hazardous wastes such as oils, greases, corrosives, and flammables (PRC, 1995a and 1995b). As such, the building was regulated as a SWMU (SWMU 91) under a RCRA Part A permit. No indication, evidence, or documentation of potential chemical releases has been reported at this facility and SWMU 91 was closed on June 3, 1996 and confirmed on August 17, 2011 through DTSC correspondence (DTSC, 2011a). As a result of the closure, no additional investigation with respect to SWMU 91 is planned. (Additional information with respect to SMWU 91 at Building A195 is provided in Section 4.1.2).

A 1,000-gallon capacity UST was formerly located adjacent to the northwest corner of Building A195 and was used to store diesel fuel that was used by the boiler for heating the building. The UST was removed in July 1990. The Water Board closed the UST with a letter dated October 1, 2009 (GeoTracker No. T0609560708). Prior to the removal, soil samples were collected from two locations adjacent to the northeastern and southwestern edges of the tank. The samples were collected from depths of approximately 3 and 4 feet bgs and analyzed for TPH-d, TPH-mo, and BTEX compounds. One additional soil sample was collected from the base of the UST excavation at 3.5 feet bgs during the removal activities and was also analyzed for TPH-d, TPH-mo, and BTEX.

TPH-d, TPH-mo, and BTEX compounds were not reported in concentrations above the detection limit in any of the three samples, and the UST was granted regulatory closure by the California Water Board San Francisco Bay Region (Water Board Case No. 48D9240) on October 1, 2009 (Water Board, 2009b).

Although the site has been closed with respect to historical UST and SWMU issues, two soil borings and one groundwater monitoring well are planned at this location (Figures 4-1 and 4-2) based on the past presence of the boiler and hazardous material storage. Because soil sampling was previously conducted in the area of the former UST, adjacent to the northwest corner of the building, the soil borings will be advanced adjacent to the eastern and western sides of the building to provide additional information with respect to potential impacts to subsurface soil from historical activities at the site. Soil samples at A195 will be collected from the borings at all three locations at depths of 0.5, 5, and 10 feet bgs and analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals. In addition to these analytes, the soil samples collected from 0.5 feet bgs in the two soil borings will also be sampled for selected pesticides (Table 4-3).

In addition, two storm drains are located near the southwestern corner of the lot associated with Building A195. Based on the past use for hazardous storage at this building, the storm drains will be investigated as part of SWMU 93, as described in Section 4.1.2 (see Figure 4-3).

Mine Anchor Assembly and Advanced Weapons Container Maintenance (A259)

Building A259 is an 8,670 SF concrete building located just north of Tyler Road, approximately 75 feet southeast of Building A163 (see Figure 2-1). The building was constructed in 1943 and is separated into four rooms that were used for assembling mine anchors and maintaining advanced weapons containers. The building was equipped with an air compressor and air conditioning room for mine testing equipment. Six walk-in refrigerator units were located in the rear of the building for storing mine batteries. The building also contained a boiler room and mercury may have been used or stored at this location. The floor of the building consists of concrete and it contains no floor drains.

One 1,000-gallon diesel UST was removed from the west side of Building A259 in July 1990. Soil samples were collected adjacent to the tank and analyzed for TPH. The State Water Resources Control Board (SWRCB) GeoTracker database indicates that the UST at Building A259 (Water Board Case No. 48D9248) was closed on December 20, 2004. As a result of this closure, no additional investigation for this UST is proposed.

Based on the storage of marine batteries and the potential for metal surface preparation (degreasing), painting, and cutting/welding activities as part of the operations at A259, two soil borings are planned at this location (Figure 4-2) to provide additional coverage along the northeastern and southeastern portions of the building. The ultimate locations of these two soil borings will be based on observations of drain lines or other piping that may extend from the building, or other evidence of potential impacts to the surface soil (i.e. staining or odors) at the time of the sampling. Soil samples at A259 will be collected at depths of 0.5, 5, and 10 feet bgs and analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals. In addition to these analytes, two soil samples collected from 0.5 feet bgs will also be analyzed for selected pesticides (Table 4-3).

In addition, a storm drain associated with SMWU 93 is located just south of Building A259. Soil sampling will be conducted adjacent to this drain as part of the investigation for SMWU 93 (see Figure 4-3). Soil sampling will also be conducted for SWMU 106 near the southwest portion of Building A259 as part of SWMU 106 to evaluate the sanitary sewer line connection to the building (Table 4-3 and Figure 4-3). The analytical data from both of these locations will also be used to evaluate subsurface soil conditions south of A259. As such, a total of four sampling locations are planned at A259 to provide information with respect to those locations around the perimeter of the building.

High Explosives Safe Haven (A296)

Building A296 consists of a 200-foot long by 22-foot wide by 30-foot high concrete and soil barricade structure located south of Tyler Road and west of Jennings Road (see Figure 2-1). Originally constructed in 1941, this structure, known as the High Explosives Safe Haven, was designed to park two sets of railroad cars containing high explosives (Weston, 2008). The structure consists of two trapezoid-shaped structures arranged in an elongated east to west orientation and opening outward to the west.

The railroad tracks were removed in the 1970s and the eastern opening was bermed with dirt in the 1980s. After the dirt mound was built over the eastern opening, the safe haven was used for temporary parking of vehicles and trucks carrying high explosives. A former fuel oil/diesel UST was located just to the northeast of the structure. No further action for this UST was granted by the Water Board on October 22, 2009 (Water Board, 2009c).

This feature was not specifically addressed under the PA/SI and no additional information regarding historic use at the site was uncovered. Based on the fact that rail cars and other vehicles carrying high explosives were historically staged inside the Safe Haven, two soil borings are planned at this location (Figure 4-2). Soil samples at A296 will be collected at depths of 0.5, 5, and 10 feet bgs and analyzed for TPH-g, TPH-d, TPH-mo, and metals. In addition to these analytes, one soil sample collected from 0.5 feet bgs will also be analyzed for selected pesticides (Table 4-3).

4.1.2 Solid Waste Management Units (SWMUs)

A total of five SWMUs have been identified in the SSA. As summarized in Tables 4-2 and 4-3, soil samples will be collected from a total of 25 locations associated with the SWMUs at the SSA as part of the RI. Brief summaries of the SWMUs and the planned investigation for these features are provided below. The locations proposed for soil sample collection are illustrated on Figure 4-3.

SWMU 91 (Container Storage Area – Bldg. A195)

SWMU 91 is identified in the PA/SI report for non-radiological sites as the general hazardous waste container storage area in Building A195. According to information contained in the PA/SI (PRC, 1995b), wastes formerly managed at this SWMU included halogenated and non-halogenated solvents, flammable liquids, and corrosive liquids.

The container storage area consists of 14 individual containment cells, or units, approximately 6 inches in depth. During preparation of the PA/SI, PRC identified eight concrete bermed storage areas that measured approximately 15 feet by 30 feet in area (PRC, 1995b). The floor was noted as sealed concrete, and no sumps or floor drains were observed during the site inspection (PRC, 1995a and 1995b). Records have been maintained for this site since 1988 and no record of spills occurring at this SWMU have been documented.

The PA/SI also recommended no additional CERCLA investigation at this site as it was in the process of undergoing the RCRA closure process at the time of the report (PRC, 1995b). SWMU 91 was subsequently closed under RCRA on June 3, 1996 and confirmed on August 17, 2011 through DTSC correspondence (DTSC, 2011a). As such, no additional investigation for this SWMU will be performed.

SWMU 93 (Storm Sewer System)

SWMU 93 consists of the storm sewer system for the former MINS. It was designed to handle, collect, convey, and discharge excess surface water runoff into Mare Island Strait, Carquinez Strait, and San Pablo Bay at 46 different outfalls. Information provided in the PA/SI indicates that the domestic sanitary sewer system and storm sewer system at MINS were completely combined until 1959, after which a domestic wastewater sewage plant was built (PRC, 1995b).

The domestic wastewater sewage plant provided primary wastewater treatment, including aeration, grit removal, sedimentation, and chlorination prior to discharging treated water to San Pablo Bay.

In 1976, the MINS sanitary sewer system was connected to a publicly-owned treatment works (POTW) in the City of Vallejo, California. Until that time, most of the industrial waste water generated at MINS was discharged to Mare Island Strait and San Pablo Bay through the storm sewer system (PRC 1995b). Between 1959 and 1972, the storm sewer system and sanitary system were partially interconnected, and some raw wastewater (both sanitary and industrial wastewater) was discharged directly to Mare Island Strait. Before an industrial wastewater treatment plant (IWTP) was built in 1972, most of the industrial wastewater was discharged directly to Mare Island Strait and San Pablo Bay through the storm sewer system.

As depicted in Figures 4-1 and 4-3, the storm sewer system in the SSA consists of five separate lateral lines that convey storm water runoff captured in drains and catch basins located near buildings and roads in the upland areas to a series of outfalls along the shoreline. The storm sewer system in the SSA was not connected to other portions of the base where industrial wastes were generated and discharged as part of historical industrial activities at other part of MINS. Although large quantities of industrial wastes were not generated at the SSA during historical operations, some industrial wastes may have been discharged or released directly to the storm drains in the past. A total of five storm sewer outfalls that drain into Carquinez Strait are located in the SSA (see outfall numbers 40, 41, 42, 207, and 208 on Figures 4-1 and 4-3). Sediment samples from both the shoreline and the offshore areas in front of the outfalls were collected and analyzed for metals, organotins, PCBs, pesticides, SVOCs (including PAHs), and TPH (see Figure 2-8) as part of the RI for offshore Investigation Area K (Battelle, 2009). The analytical results of the outfall sampling at the SSA indicated that all of the chemicals analyzed were reported at or below ambient concentrations documented for sediments from the San Francisco Bay (Battelle, 2009). As such, no additional sampling of the SWMU 93 outfalls will be conducted for the RI.

However, for the purposes of the RI, soil samples will be collected from a total of 11 soil boring locations adjacent to storm drains and drain lines associated with SWMU 93 in the SSA to evaluate potential impacts to the subsurface. The total includes three sampling locations shared with Buildings A193, A195, and A296, as well as three locations shared with SWMU 106. The approximate locations of these soil borings are depicted on Figure 4-3 and are summarized in Table 4-3.

Although the results of the outfall sampling did not indicate evidence for discharge of industrial wastes through the storm sewer in the SSA, soil samples for the RI will be collected adjacent to the storm drains to evaluate the potential for discharges or releases of industrial or other hazardous wastes from historical activities. Given that extent of the storm sewer system in the

SSA limited and is not connected to other waste discharge systems that serviced the more active, upland portions of the shipyard, the storm drains are considered the most likely location where wastes could potentially have been discharged at the SSA in the past. In addition, at least one soil sample will be collected adjacent to each of the storm sewer lines approximately 100 to 150 feet downstream of the drains to provide additional information regarding potential impacts between the storm drains and outfall locations.

Soil samples from all 11 locations will be collected from depths of 0.5, 5, and 10 feet bgs and analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals. In addition, the samples from the soil boring located south of Building A259 will also be analyzed for metals to assist in the evaluation of the disposal pit located in the eastern portion of DGM grid AF011 (Figure 4-3 and Table 4-3).

SWMU 101 (Concord Annex Ordnance and Additional Sites)

SWMU 101 is designated as the Concord Annex Ordnance and Additional Sites and is intended to address ordnance disposal at additional sites throughout MINS. Information provided in the PA/SI Report indicates that contaminant-related ordnance sites should be investigated under the Navy's Installation Restoration Program under SWMU 101, although it notes that the primary area of concern is the ordnance production area or PMA (PRC, 1995b).

This SWMU was not designated at a specific location or set of locations at the SSA. Therefore, all investigations documented for the SSA are potentially applicable to this SWMU. For the purposes of the RI, the planned investigations at the former MEC sites (described in Section 4.1.3) will also serve to address contaminant-related issues at SWMU 101 as it pertains to the SSA.

SWMU 106 (Sanitary Sewer System)

SWMU 106 consists of the sanitary sewer system located throughout the former MINS installation. As depicted in Figures 2-1 and 4-3, the sanitary sewer consists of a main line that runs approximately 1,400 feet south from Tyler Road to pump station A153 located on the northeastern portion of Pier 35. Buildings A193, A195, and A259 connect to the main through a series of laterals that run approximately 900 feet between the buildings, in the central portion of the SSA (Figures 2-1 and 4-3). South of Tyler Road, another line extending a distance of approximately 1,800 feet comes out of the PMA and runs parallel to the shoreline to the point where it connects with the north/south running main line. A summary of the historical environmental concerns associated with the sanitary sewer at MINS was previously provided in the description of SMWU 93 and is not repeated here.

For the purposes of this RI, soil samples will collected from a total of 21 locations in the vicinity of the sanitary sewer lines to evaluate potential environmental impacts along each of the lines. This includes three sampling locations shared with Building A193, A195, and A296, as well as

four sampling locations associated with groundwater monitoring wells. Based on the total distance of the lines in the SSA, a soil sampling location is planned for approximately every 200 feet along the lines, with specific locations selected to correspond with connections and turns in the lines (Figure 4-3). The approximate locations of these soil borings are illustrated on Figure 4-3.

Soil samples from the 21 borings located near the SWMU 106 sanitary sewer line will be collected from depths of 0.5, 5, and 10 feet bgs. In some locations, the deepest sample may be collected from depths below 10 feet bgs to provide a sample from at least 1 to 2 feet below the bottom of the pipe. All soil samples associated with SWMU 106 will be analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals (Table 4-3). As indicated in Figure 4-3 and Table 4-3, soil samples from SWMU 106 borings will also be analyzed for metals based on their proximity to former MEC sites.

SWMU 125 (South End of Island)

SWMU 125 includes "contaminant-related ordnance sites" located in or near the South End of the Island, though specific locations or sites within the SSA are not defined (PRC, 1995b). Because this SWMU was not designated at a specific location or set of locations at the SSA, all investigations documented for the SSA are potentially applicable to this SWMU. For the purposes of the RI, the planned investigations at the former MEC sites (described in Section 4.1.3 below) will also serve to address contaminant-related issues at SWMU 125 as it pertains to the SSA.

4.1.3 MEC Sites

As summarized in Section 2.4, a large quantity of MEC items have been found at the SSA during the various site investigations and removal actions. A summary of the MEC items recovered across the SSA is provided on Figures 2-3 through 2-5.

For the purposes of this RI, soil samples will be collected from a total of 17 soil boring/sampling locations to investigate the potential for residual impacts associated with the former munitions items removed from the SSA during the historical removal actions conducted between 1990 and 2013. This total includes one shared sampling location with SWMU 93, seven locations shared with SMWU 106, and four locations associated with groundwater monitoring wells. The approximate locations proposed for soil sampling are illustrated on Figure 4-4 and described in Tables 4-2 and 4-3.

With respect to the proposed sampling for the MEC sites, particular focus is planned for those locations where the largest concentrations of munitions items and debris were found and removed during the NTCRA and previous removal actions. Specifically, a number of disposal or burial pits were identified during the NTCRA based on the high density of items found and

removed during the investigation of target anomalies, as described in Section 2.4.7. These pits were identified within DGM Grids AE010, AE011, AH010/AH011, AF011, and AI015.

Eight of the 17 soil boring/sampling locations are planned for the disposal pit areas in DGM Grids AE010, AE011, AH010/AH011, and AF011 that were not previously sampled during the NCTRA (Figure 4-4). Particular emphasis will be placed on grids AH010/AH011, near Dike 14, based on the number of items recovered during the NTCRA and previous removal actions. All of the soil samples for the former MEC sites will be collected from depths of 0.5, 5, and 10 feet bgs and analyzed for metals (Figure 4-4 and Table 4-3). Although the debris pit excavations were backfilled with reworked native soils following the debris removal, samples from the 0.5 feet bgs depth interval will be necessary to conduct risk assessment evaluations for current conditions.

As described in Section 2.4.7, the easternmost disposal pit in DGM Grid AF011 was not completely delineated during the NTRCA activities. Additional delineation of the easternmost pit in AF011 will be conducted during this RI as described in Section 5.2.3.

In addition to analyses for metals, soil samples from the four locations planned for grids AH010/AH011, near Dike 14, will be scanned in the field for gamma emissions using a portable sodium iodide (NaI) scintillation detector for worker health and safety purposes based on the recovery of a radiological item (radium button/former deck marker) in that area in 1999. This field screening will be conducted under the separate Work Plan for Radiological Screening and Survey Activities (RSRS and NOREAS, 2014). Based on the results of the field scan, soil samples from these locations may also be submitted for analysis for radium-226 (^{226}Ra).

4.1.4 Oven/Primer Pit Areas

A total of six soil boring and two groundwater sampling locations are planned to investigate the former oven/primer pits as part of the RI. Details regarding the historical analytical data and RI sampling rationale are described within this subsection.

As described in Section 2.4.4, three distinct areas were identified in the SSA where ordnance was disposed by burning. These areas were identified as the Primer Pit, Oven Pit 1, and Oven Pit 2. A total of 567 cubic yards of contaminated soil mixed with ordnance-related and other metallic debris was removed during the excavation of these three burn pits (Weston, 2003). Based on the observation of discolored soils and condition of the debris removed, confirmation sampling was conducted to verify the removal of impacted soils. The approximate outlines of the areas excavated for the Primer Pit and two Ovens Pits are depicted on Figure 4-5.

A total of 142 soil and 7 water samples were collected from within and around the pits as part of the confirmation sampling efforts. Of these, 24 soil samples and 5 groundwater samples were collected from within the Primer Pit and Oven Pit excavations, while 118 soil and 2 groundwater

samples were collected from around the perimeters of the excavations. All of the confirmation soil and water samples were analyzed for copper, lead, and zinc.

The results of the confirmation sampling were originally compared to the 1996 USEPA Preliminary Remediation Goals (PRGs) that were in place at the time of the investigation to determine the need for additional excavation of soil. As noted in the Confirmation Sampling Summary Report, the average concentrations of copper, lead, and zinc detected in the remaining surface and subsurface soils at the excavation sites were reported below their respective residential PRGs at the time (Appendix D of Weston, 2003). Following the completion of the confirmation sampling, the excavations were backfilled with clean soil (Weston, 2003).

For surface soils, the average concentrations of lead and zinc were reported below the respective comparison criteria for those metals, although the average value for copper was reported slightly above the background concentration, largely due to an elevated result from one sample location southeast of the Primer Pit.

As a result of the 2003 evaluation, the Confirmation Sampling Summary Report (Roy F. Weston, 2003) contained a recommendation for removing additional soil in the localized area around the elevated copper result due to the proximity of the wetlands and surface waters of Carquinez Strait and San Pablo Bay. For the purposes of this RI, additional soil sampling in the area of the Primer Pit and Oven Pits is proposed. Specifically, the confirmation sampling conducted during the UXO excavation activities was focused on three metals that are commonly associated with ordnance items.

Based on the potential for other hazardous non-ordnance materials (solvents, oils/grease, paints, etc.) to have been disposed in the burn pit operations, additional soil sampling will be conducted at eight boring locations (six soil borings and two monitoring wells) in the Oven/Primer Pit Areas (Table 4-2) Five of these borings will be placed outside the footprints of the former excavations to delineate the lateral and vertical extent of potential impacts outside the pits. At these five locations, soil samples will be collected from planned depths of 0.5, 5, and 10 feet bgs and analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals (Table 4-3).

Three boring locations will be placed with the footprints of the Oven and Primer Pits to confirm the vertical extent of potential impacts below the former excavations (one boring each within Oven Pit 1, Oven Pit 2, and the Primer Pit). Soil samples at these three locations will only be collected from a depth of 10 feet bgs to evaluate conditions in the native soils below the former excavations; samples will not be collected from the backfill materials in the shallower depth intervals. Samples from these three locations will be analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, metals, and dioxins/furans (Table 4-3).

In addition to the analytes described above, selected samples from the Oven/Primer Pit areas will also be analyzed for dioxins/furans given that visual evidence of discolored soils indicated that debris was once disposed by burning in these locations (Section 2.4.4). Although the affected (discolored) soil and debris within the pits was ultimately excavated and removed from the site (Roy F. Weston, 2003), soil samples from the three borings located in the wetlands surrounding the former pits, as well as though collected from beneath each of the three former pits, will be analyzed for dioxins/furans.

In particular, soil samples from all three discrete depth intervals (0.5, 5.0, and 10.0 feet bgs) at the three borings located in the wetlands surrounding the former pits will analyzed for dioxins/furans. In addition, at the borings located within the footprints of the former pits, the soil samples collected from beneath the bottom of the former excavations (at the 10 feet bgs interval) will also be analyzed for dioxins/furans. The final selection of samples for dioxins/furans analysis may be biased in the field based on observations of soil conditions at the time of sampling. Specifically, samples where visual evidence of burnt material (discoloration) is observed may be selected for analysis for dioxins/furans. The approximate locations of the soil samples proposed for this area are depicted on Figure 4-5.

4.1.5 Other Areas

Other areas considered for investigation under this RI include those locations where items were uncovered during the 2012-2013 MEC NCTRA removal activities, as described in Section 2.4.7, including:

- A total of 11 buried 55-gallon steel drums found in DGM Grid AI015 (six found in July 2012, and five found in May 2013),
- Three “USTs” and related piping found in DGM Grid AJ015, and
- A total of 30 buried 55-gallon steel drums found in DGM Grid AA009 (nine found in December 2012 and another 21 found in April 2013).

Brief descriptions of these items, including the sampling approach proposed under the RI, are provided below. The approximate locations of these items are depicted on Figure 2-8.

Buried Drums in DGM Grid AI015

As described in Section 2.4.7, the analytical results for the confirmation soil sampling conducted following the removal of the drums indicate that VOCs, SVOCs (including PAHs), TPH, herbicides, OCPs, PCBs, energetics, and dioxins/furans were either not detected or were reported in concentrations below their respective residential RSL values. In addition, all of the sampling results for metals were reported in concentrations below their respective residential RSLs or ambient/background values.

Based on the extent of the confirmation sampling and analytical results, no additional investigation of this area is planned. However, the analytical results of the confirmation sampling conducted during the NTCRA activities will be addressed and incorporated in the RI Report.

Underground Storage Tanks and Dry Wells Found in DGM Grid AJ015

Although the results of the confirmation soil samples do not indicate impacts associated with TPH, SVOCs, or metals due to the past use of tanks and dry wells, the exact use and history of these features remain unknown. In the event that tanks and dry wells were once used as part of a septic system or clarifier of some type, additional data would be required to rule out impacts from other chemicals commonly used at MINS. Given the proximity of these tanks to the former diesel/fuel oil UST associated with former Building 292 (T-A292), as well as to the former hazardous waste storage for the SSA at nearby Building A195, it would be prudent to have analytical data for VOCs in the soil to address the possibility that solvents may have been disposed in either the tanks or the dry wells.

As such, a total of three shallow soil borings are planned for the area where the former USTs, dry wells, and piping are planned for this RI. The soil samples collected from this location will be sampled for VOCs (including BTEX) and PCBs to evaluate the potential for impacts related to the tanks and dry wells. SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo and metals have already been sampled in soil beneath the removed tanks. The locations of these soil borings are illustrated on Figure 4-6.

In addition to the samples collected from the locations of the former tanks and dry wells, an estimated six additional soil borings will be advanced along the remainder of the 5-inch diameter conveyance piping that was left in place during the NTCRA activities. The samples will be taken at joints and at least every 20 feet. Based on review of geophysical results from the original DGM Investigation (Weston, 2008), it appears that the conveyance piping extended approximately 40 feet south/southeast of the tanks, at which point it may have connected to another line that appears to run parallel to the tanks from northeast to southwest for roughly 120 feet (see Figure 4-6).

At the time of the field activities, geophysical methods and/or hand-digging in selected locations will be used to delineate the remaining conveyance piping to the extent possible. For the purposes of this Work Plan, it is assumed that the remaining pipeline extends approximately 120 linear feet. As such, the six additional borings will be advanced in spacing of approximately 20 feet along the length of the pipeline, including the location where it connects to the shorter run from the tanks. Soil samples from these six borings locations will be collected from depths of 2 and 5 feet bgs (Figure 4-6) and will be analyzed for VOCs (including BTEX), SVOCs (including PAHs), PCBs, TPH-g, TPH-d, TPH-mo, and metals (Table 4-3).

Buried Drums in DGM Grid AA009

Although the results of the confirmation sampling indicate that the presence of the buried drums in DGM Grid AA009 did not result in a significant impact to the environment, benzo(a)anthracene, benzo(a)pyrene, and benzo(b)fluoranthene were reported in concentrations above their residential RSLs in two of the four confirmation samples collected after the removal of the original nine drums in December 2012 (ISR-JV, 2014). As such, two soil sampling locations where the drums were removed are planned for this RI to provide additional evaluation and potential confirmation of the previous sampling results (Figure 4-6). Soil samples at these locations will be collected from depths of 0.5, 5, and 10 feet bgs and analyzed for SVOCs (including PAHs), TPH-g, TPH-d, and TPH-mo, and metals (Table 4-3).

Buried Propellant Cans in DGM Grid AE010

Because no drums were ultimately identified in DGM Grid AE010 and previous sampling of soil where propellant cans were found did not indicate impacts by energetics or metals, no sampling for chemical issues is planned for these items during the RI. Moreover, a total of three soil boring/sampling locations is already planned in this grid to address the potential for energetics and metals impacts to the soils in the area due to the historical burial of propellant cans and other munitions-related materials found during the NTCRA activities.

4.1.6 Pilot Borings for Groundwater Monitoring Wells

In addition to the soil borings advanced for the purpose of soil sampling only, soil samples will also be collected from depths of 0.5, 5, and 10 feet bgs during the advancement of the pilot borings for the groundwater monitoring wells (see Figures 4-1 and 4-7). The actual depth of the two deeper soil samples at these pilot borings may be adjusted in the field based on observations of evidence of contaminant impacts (staining, odors, elevated PID readings, etc.) or variations in lithology (bias for higher-permeability zones). At all nine locations, the soil samples will be analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals (Table 4-3).

4.1.7 Abrasive Blast Material (ABM)

Abrasive blast material (ABM) was identified in the SSA during the recent excavation and removal activities conducted as part of the MEC NTCRA. As indicated in the Final Removal Action Completion Report (ISR-JV, 2014), the majority of the ABM was found along the edges of roads, along buried utility corridors. The locations of the ABM found in the SSA during the MEC NTCRA are depicted in Figure 4-1.

As can be seen on Figure 4-1, several of the planned soil sampling locations coincide with where ABM was found during the MEC NTCRA activities. In the event that ABM is found in the soil core or cuttings samples, the Navy will be notified immediately. In addition, the following information will then be documented in the appropriate field forms and log book:

- Location where ABM was recovered,
- Date and time,
- Depth at which ABM was encountered,
- Estimated thickness of zone where ABM was recovered, and
- Approximate volume of ABM recovered.

For those locations where ABM or soils mixed with possible ABM are observed, a sample of the soil located just below the ABM will be collected and analyzed for metals, PCBs, and organotins (monobutyltin, dibutyltin, and tributyltin). The locations of the ABM found during the RI sampling activities will be combined with those documented during the MEC NTCRA to evaluate the nature and extent of the ABM at the SSA and update the current CSM for the RI Report.

A human health and ecological risk assessment of ABM was previously conducted at IR Site 4 to evaluate the risks posed by exposure to ABM in backfill material placed around utility lines (Tetra Tech, 1999). The results of the evaluation, as provided in a technical memorandum, indicated that the ABM used to backfill utility trenches does not pose a significant risk to human or ecological receptors at Mare Island (Tetra Tech, 1999). However, the analytical results of ABM sampling completed as part of the RI will be evaluated at part of the risk assessment activities and will be incorporated into the RI Report.

4.2 INVESTIGATIVE APPROACH – GROUNDWATER

The main objectives of the groundwater investigation will be to (1) determine if chemical contaminants are present in groundwater and, if present, then determine the nature and extent, (2) investigate hydrogeologic conditions, and (3) to evaluate the general quality of shallow groundwater at the SSA.

To achieve these objectives, a total of nine 4-inch diameter groundwater monitoring wells installed to total depths of up to 20 feet bgs are planned for this RI. Based on groundwater monitoring data from wells located at IR05, the approximate depth to groundwater is anticipated between 2.5 to 6 feet bgs at the SSA. Where possible, the wells will be installed such that the top of the screen interval will be located approximately one foot above the water table as observed at high tide. Upon completion, the newly installed groundwater monitoring wells will be developed using standard well development procedures.

The proposed locations of the groundwater monitoring wells are depicted on Figure 4-7. The rationale for each of the groundwater monitoring wells is described in Table 4-4.

4.2.1 Potential Chemical Contaminants

Groundwater samples will be collected from each of the nine proposed groundwater monitoring wells and analyzed for potential impacts from chemical contaminants. As groundwater gradient

and flow patterns are not well established at the SSA, upgradient and downgradient areas within the SSA cannot yet be determined. However, it is anticipated that groundwater in the SSA generally flows from the upland areas toward Carquinez Strait at a relatively low (flat) gradient.

As such, the groundwater samples collected from all nine wells during the RI will be analyzed for VOCs, SVOCs (including PAHs), TPH, PCBs, and dissolved metals. In addition, one sample collected from the well near the oven/burn pit areas (SSAMW05) may be analyzed for dioxins/furans in the event that they are detected above their respective screening levels in soil samples collected from the Oven/Primer Pit areas (see Section 4.1.4). Additional details regarding the groundwater sampling methods and analytical procedures are provided in Section 5.3.3 and the Sampling and Analysis Plan (SAP) included in Appendix A.

4.2.2 Hydrogeologic Conditions

Currently, there are no groundwater monitoring wells located in the SSA. As part of the evaluation of contaminant impacts to groundwater and their potential risks to human health and the environment, general hydrogeologic conditions such as hydraulic gradient and flow patterns beneath the site will be evaluated. The locations of the proposed groundwater monitoring wells were, in part, selected to provide information with respect to the hydrogeologic conditions at the SSA.

Following their installation and development, groundwater elevation data will be collected from the proposed wells to determine the water table elevations, hydraulic gradient, and predominant flow directions. Given the proximity to Carquinez Strait and San Pablo Bay, groundwater elevations at the SSA are expected to fluctuate in response to tidal influences.

4.2.3 General Water Quality – Beneficial Use for Drinking Water

As part of the RI sampling activities, the groundwater samples collected from the newly installed monitoring wells will also be analyzed for pH and total dissolved solids (TDS). The results of these analyses will be used to evaluate the general water quality of the groundwater at the SSA and are expected to provide support for the preparation of a request for an exception to the sources of drinking water policy for the SSA that will be submitted to the Water Board.

In addition to the assessment of general water quality parameters, pump testing to evaluate well yields at the SSA will also be conducted. Based on the historical use of hydraulic fill (dredge materials) and native Bay Muds at the SSA, very low flow rates and/or well yields are anticipated for the new wells. Pump rates and well responses in the newly installed groundwater wells at the SSA will be used to calculate well yield data that will be used to support the request for an exception to the sources of drinking water policy for shallow groundwater.

4.3 INVESTIGATIVE APPROACH – RADIOLOGICAL MARSSIM FINAL STATUS SURVEY AND UNRESTRICTED RELEASE SURVEY

As part of the overall effort to determine the nature and extent of all potential risks to human health and the environment from historic activities at MINS, potential radiological impacts will also be investigated in conjunction with the soil and groundwater investigations described in this Work Plan. To date, only one discrete radiological item, a deck marker (radium button), has been found at the SSA. The deck marker was identified near Dike 14 in 1999 during the previous site investigations and removal actions at the SSA. The item was removed at that time and the area will be surveyed during the RI field activities under the separate radiological work plan (RSRS and NOREAS, 2014) for unrestricted future use (free-release).

Deck markers used by the Navy in the past consisted of small 1- to 2–inch diameter radioluminescent disks that would be affixed to the deck of the ship to provide a small amount of light. Depending on the amount of luminescence desired, the buttons typically contained ^{226}Ra in the amount of 5 to 15 microCuries (µCi).

Based in part on the finding of the deck marker during the previous MEC removal actions, radiological scans of the ground surface and excavations for worker safety were also conducted during the recent MEC NTCRA at the SSA that was completed in July 2013. At the time of the completion of the NTCRA activities, no discrete radiological items were found and radiological scan results did not indicate the presence of radioactivity in the excavated material (soils, debris, and munitions items) at levels above the established project investigation levels (ISR-JV, 2014).

In the event that evidence of radiological impacts or radiological items are found during the RI field activities, radiological surveying and/or sampling to support unrestricted future use will be performed. However, because no radioactive items were found and no evidence of radioactivity above the project investigation level (three standard deviations above the site background) was encountered during the scanning of the soil and debris excavated during the recent MEC NTCRA, it is anticipated that radiological items or materials will not be encountered during the RI field activities. However, the results of the field scans from the NTCRA will be summarized in the RI Report. Radiological data and information from the field scans and soil sampling will also be modeled and evaluated for human health and ecological risk and incorporated into the RI.

For the location where the former deck marker was found and removed near Dike 14 in 1999, the area will be subjected to a Final Status Survey (FFS) designed as a Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM) survey (DoD et al., 2000). This method will allow the use of the survey data to support future unrestricted use for the area if no residual radioactivity is found to exceed the release criteria.

Details regarding the FSS, and radiological screening activities for worker protection during the RI are provided under a separate Work Plan for Radiological Screening and Survey Activities

(RSRS and NOREAS, 2014). This Radiological Work Plan includes a Radiological Materials Management Plan (RMMP) that provides detailed descriptions of the survey methods, scans, sampling, handling, transport, and disposal of radiologic items (if encountered) that will be used during the RI. Also included is a Radiological Protection Plan (RPP) that describes the radiological screening criteria that will be applied to ensure protection of worker health and safety during completion of the RI field activities

5.0 IMPLEMENTATION

5.1 PREMOBILIZATION

Prior to mobilization, NOREAS will complete all procurement and field planning activities; this includes coordination among the team including the Navy, ROICC, CSO, subcontractors, and vendors. Work will be performed in accordance with applicable and relevant federal, state, or local laws, regulations, and permits for protection of the environment.

5.1.1 Permits

In addition, NOREAS will obtain all boring and well permits from the Solana County, Department of Resource Management, Environmental Health Division, where applicable. It is anticipated that permit fees will not be required, under CERCLA exemption rules; however, substantive permit requirements will apply.

5.1.2 Geophysical Survey (Utility Clearance)

Buried utilities or other underground infrastructure could be located within the project boundaries. Underground Service Alert will be contacted to assist in the locating of underground utilities in the project area. The ground surface over areas of identified or suspected underground utilities will be staked or flagged. NOREAS will also retain a geophysical utility locating company to map the area. Proposed boring and well locations will be repositioned as necessary to avoid conflict with underground utilities. Prior to drilling and sampling, the nearest shut-off valves for all utilities that may be encountered will be identified, and access to those shut-off valves will be ensured during all field activities.

5.1.3 Site Preparation

Site preparation includes mobilization, establishment of temporary facilities and construction control, personal and equipment decontamination areas, waste stockpile and loading areas, utility identification and lockout, and site security. Preparatory activities will include appropriate notification and a kickoff meeting with BRAC, the ROICC, and the CSO. The project team will receive site-specific training in health and safety awareness, a temporary staging area will be established, and the pre-design investigation area will be surveyed for underground utilities.

5.2 SOIL INVESTIGATION

5.2.1 Soil Boring and Lithologic Characterization

For this RI, a total of up to 46 soil borings will be advanced to depths of up to 20 feet bgs at the SSA. The soil samples will collected by advancing a 1.5-inch diameter borehole using a DPT drilling rig. The DPT rig will be capable of providing a continuous sample of soil for visual

observations and sampling. All DPT drilling operations will be conducted by a California C-57 licensed drilling subcontractor.

Continuous soil cores will be logged by the field geologist. Soil cores will be: 1) visually inspected for potential chemical impacts, 2) field screened for organic vapors using a photoionization detector, and 3) used to generate lithologic soil boring logs. Copies of the NOREAS field forms are included in Appendix E. Soils will be logged in accordance with the Unified Soil Classification System (USCS) visual-manual procedure American Society for Testing and Materials (ASTM) D2488-90 and Munsell, or equivalent, color designations. Lithologic soil boring logs generated during field work will be signed by a State of California Professional Geologist (PG).

5.2.2 Soil Sampling Procedures

For VOC analysis, laboratory-prepared TerraCore® sampling kits will be used to collect and preserve the soil samples for transportation to the laboratory. After the VOC samples have been collected, samples for the remaining analyses will be collected in clean glass jars with minimal headspace using a clean scoop. All samples will be labeled, placed in self-sealing plastic bags, and placed on ice in a cooler for transport to the analytical laboratory. The samples will be maintained and transported under strict chain-of-custody protocols at all times.

Nitrile gloves will be worn and will be disposed of after each sample is collected, and a new pair will be worn before the next sample is collected to avoid possible cross-contamination.

5.2.3 Additional Delineation of Disposal Pit – DGM Grid AF011

As described in Sections 2.4.7 and 4.1.3, the extent of the easternmost disposal pit in DGM Grid AF011 was not fully delineated during the completion of the NCTRA (ISR-JV, 2014). To delineate the approximate lateral extent of the pit, a limited non-intrusive geophysical survey will be conducted using a combination of methods, including EM (all-metals detector and magnetometer) and ground-penetrating radar (GPR) techniques. As the western portion of the pit has already been delineated and excavated, the objective of the geophysical survey is limited to delineating the lateral extent of the remaining debris to the east for order of magnitude quantification for incorporation into the Feasibility Study if appropriate to protect human health and the environment. It is not intended to constitute a DGM survey.

In the event that the pit cannot be sufficiently delineated from the results of the geophysical surface survey, several potholes in the area surrounding the pit location will be excavated in a step-wise manner to depths of approximately four feet bgs to locate the top of the buried debris. The potholes or excavations will be conducted in approximate 6-inch lifts by hand-digging or use of a small excavator (if necessary).

All intrusive activities will be conducted under the direct supervision of a qualified UXO technician in accordance with the MPPEH avoidance procedures described in Section 5.6. Following the completion of each lift, the base of the excavation/pothole will be screened with a magnetometer to determine if buried metallic anomalies are present. This procedure will proceed to the planned depth of the excavation until an anomaly is detected or debris is encountered.

At a given location, excavation activities will cease upon the first encounter of debris and the material will be left in place; no attempt will be made to remove, classify, or otherwise handle the debris. The location and depth of the debris will be documented to allow for further delineation of the disposal pit area, and the excavation will be backfilled.

5.3 GROUNDWATER INVESTIGATION

5.3.1 Well Drilling and Installation

A total of nine groundwater monitoring wells will be installed to depths of up to 20 feet bgs as part of this RI. The groundwater monitoring wells will be drilled and installed by a C-57 licensed drilling subcontractor using a hollow-stem auger (HSA) drilling rig. The HSA rig will be used to advance a 6- to 8-inch diameter pilot borehole to the target depth at each location. The augers will consist of carbon steel and will be free of paint or other materials that could impact water sample results.

The target depth for each well location will be determined based on the approximate depth of groundwater encountered at the time of drilling. Based on groundwater monitoring data from wells located at IR05, the approximate depth to groundwater is anticipated between 2.5 to 6 feet bgs at the SSA, depending on the proximity to the shoreline or uplands. The approximate depth to water at the time of drilling will be determined based on observations of continuous sections of soil core recovered during the advancement of the monitoring well boreholes. Where possible, the wells will be installed such that the top of the screen interval will be located approximately one foot above the water table as observed at high tide. Upon reaching target depth at a given location, the well casing will be constructed and hung in the borehole.

Each groundwater monitoring well will consist of a 15-foot length of nominal 4-inch diameter, Schedule 40 polyvinyl chloride (PVC) factory-slotted screen with 0.010-inch slots. The bottom of each screen will be completed with a flush-threaded end cap. The riser casing will consist of nominal 4-inch diameter, flush-threaded, Schedule 40 PVC. A schematic diagram of the well construction is provided as Figure 5-1.

Once the casing has been assembled and set into the borehole, a filter pack of clean #2/16 sand (or equivalent) will be tremied from the bottom of the borehole to approximately 1 foot above the top of the screen. The filter pack will then be settled by swabbing inside the screened interval for several minutes with a surge block prior to installing the well seal. This will aid in the packing of sand material within the annular space and improve the overall development of the

well. After swabbing, the top of the filter pack will be measured and additional sand will be added if necessary.

Once the filter pack has been set, a minimum 2-foot bentonite seal consisting of bentonite pellets will be placed above the top of the filter pack and hydrated. The seal will then be allowed to set up for approximately 30 to 60 minutes prior to adding additional backfill materials into the borehole. The remaining annular space will be backfilled with a grout mixture up to approximately 0.5 feet bgs. The grout mixture will consist of 95% Portland cement and 5% bentonite. In the event that groundwater is encountered at depths of less than 5 feet bgs during drilling, the filter pack sand will be installed to a minimum of 6 inches to 1 foot above the top of the screened interval, and a minimum 1-foot thick bentonite seal will be maintained.

At the surface, an 8- to 12-inch-diameter, steel monument with a locking cap will be placed around the well for protection, and a 4-foot by 4-foot concrete slab will be poured around the monument. The monument will be installed such that the top extends approximately 3 to 4 feet above grade. A concrete crash post or bollard (approximately 4 feet tall) will then be placed in each of the four corners of the slab to protect the well from potential contact with vehicular traffic.

Once the surface elements of the well are in place, the well monument and crash posts will be painted with high-visibility yellow paint. A lock will then be placed on the lid, and well identification numbers will be affixed to the monument. In addition, a small notch will be placed in the rim of each PVC well casing to identify the reference point for the elevation survey and all water level measurements. The notches will be placed at the portion of the rim that corresponds to direction north for each location. Depths including total depth of hole, depth to bottom of screen, depth to top of sand pack and seal thickness will be measured using a weighted tape and documented in the field logbook and on the well construction log.

5.3.2 Well Development Procedure

The monitoring wells will be developed to settle and establish the filter pack materials and clear fine-grained materials from the well casing, sand pack, and formation adjacent to the well. The purpose of well development is to ensure the well is in hydraulic connection with the formation and that it produces groundwater samples representative of the aquifer.

Well development will begin no sooner than 48 hours after final grout placement. Development will be initiated by bailing sediment from the well bottom and swabbing the screening interval using a surge block or swabbing tool. Following the swabbing activities, a submersible pump will be used to surge and pump the well. Well development will continue until the purge water turbidity is 50 nephelometric turbidity units (NTUs) or less and a minimum of five casing volumes have been removed. If the well does not properly develop within four hours, the well development data will be reviewed with the supervising hydrogeologist who will determine if

development should continue and for how long or if alternative development methods should be employed.

Well development will be performed by the drilling or well sampling subcontractor under supervision of a NOREAS field geologist.

5.3.3 Groundwater Monitoring and Sampling

For this RI, each groundwater monitoring well will be sampled once for the analytical parameters listed in Section 5.4 below and TDS. Field parameters (dissolved oxygen [DO], oxidation/reduction potential [ORP], pH, temperature, and electrical conductivity) will also be measured during each event.

Prior to sampling, groundwater level measurements will be collected from all monitoring wells first. Once groundwater levels have been measured in all of the wells, groundwater purging and sampling activities will be initiated.

Groundwater level measurement and sampling procedures are described below:

1. Arrive at the monitoring well and confirm the well identification number.
2. Unlock the well.
3. Open well monument lid.
4. Install the water level indicator probe through a hole in the sampling cap.
5. Measure the groundwater from the surveyed measuring point to the nearest 0.01 foot.
6. Record the measurement on the Well Sampling Log (Appendix E) to the nearest 0.01 foot.
7. Complete water level measurements at all wells prior to initiating purge and sampling activities.
8. To avoid possible cross-contamination, place the flow-through cell and purge water container in a plastic tub or equivalent.
9. Attach the flow-through cell tubing and pressure hose to the discharge and air lines of the pump.
10. Begin pumping the well at 0.1 to 0.5 liter per minute (100 to 500 milliliters per minute). Use of a bladder pump is required. Check the water level in the well, and measure the discharge rate of the pump by using a graduated cylinder every minute for the first 5 minutes. Ideally, the pumping rate should equal the well recharge rate with little or no water level drawdown in the well. (Drawdown shall be less than 0.3 feet.)
11. Measure and record the water level, discharge rate, and water quality indicator parameters in the well on the Well Sampling Log (Appendix E) every 5 minutes during purging.

12. Check the discharge tubing for air bubbles during the purging process. If bubbles are visible, pluck the tubing where the bubble is to enable the bubble to pass through the tubing and into the flow-through cell.
13. During purging, monitor pH, temperature, turbidity, specific conductance, ORP, and DO approximately every 5 minutes with a calibrated water quality meter.
14. The groundwater should be purged until indicator parameters have stabilized. The well will be considered stabilized and ready for sample collection when the indicator parameters have stabilized for three consecutive readings, as follows:
    - Consecutive readings within ± 0.1 standard units for pH
    - Consecutive readings within ± 1 degree Celsius (ºC) for temperature
    - Consecutive readings within ± 10 percent for turbidity (when turbidity is greater than 10 NTUs)
    - Consecutive readings within ± 3 percent micromhos per centimeter for specific conductance
    - Consecutive readings within ± 10 millivolts for oxidation/reduction potential
    - Consecutive readings within ± 0.3 milligram per liter for dissolved oxygen

    If stabilization is not occurring and the procedure has been strictly followed, then sample collection can take place once three (minimum) to six (maximum) casing volumes have been removed. Record the specific information during purging in the field logbook or on the groundwater sampling log.
15. Once the water quality parameters have stabilized, disconnect the flow-through cell from the pump discharge tubing.
16. Collect samples for analysis of VOCs first, followed by TPH-g. Next, collect samples for all other parameters (SVOCs, TPH-d/TPH-mo, PCBs, metals, and dioxins/furans). Sampling is to be performed in accordance with the containerization and preservation requirements listed on WS #19 of the SAP (Appendix A).
17. Prior to collecting samples for VOCs and TPH-g, reduce the flow rate to approximately 100 mL/min . Fill volatile organic analysis vials by initially tilting the vials, allowing the pump discharge to flow gently down the inside of the vial with minimal turbulence. Decrease the flow rate, if necessary, to reduce sample agitation. Fill each vial until a meniscus is formed at the top of the volatile organic analysis vial. After the vial is full, cap immediately, invert the vial, tap the side lightly, and check for the presence of air bubbles. If air bubbles are present, discard the sample, and resample using a new vial.
18. Do not allow containers with preservative to be overfilled to the point where overflow occurs, as overfilling may result in loss of preservative.
19. Containers should be kept capped except when they are being filled.
20. Affix a completed sample label to the sample container and cover with clear packaging tape.

21. Wrap glass bottles in bubble-wrap packaging material, place into re-sealable bags, and place sample containers into a cooler containing ice.
22. Record sample number, time and date, and requested analysis on chain-of-custody form.

Based on the presence of silts and other hydraulic fill materials in the SSA, it is anticipated that the recharge at some wells may be so poor that the maximum drawdown criteria for the method may be exceeded, even under the lowest of low-flow purge rates. For those wells where drawdown criteria cannot be met at even the lowest achievable/sustainable flow rates, the well will be purged at the lowest sustainable flow rate until such time as the well is dry. The well will then be allowed to recover to a minimum of 80% of its pre-purge level before groundwater samples are collected.

Disposable nitrile gloves will be worn during sampling. Nitrile gloves will be disposed of after each sample is collected, and a new pair will be worn before the next sample is collected to avoid possible cross-contamination.

5.4 LABORATORY ANALYSIS

All soil and groundwater samples collected during the RI will be submitted to a State of California-certified environmental laboratory for analytical testing. The analytical laboratory will also have current DOD Environmental Laboratory Accreditation Program accreditation for all analytical methods used for this RI. Additional detail regarding the analytical laboratory, procedures, methods, QA/QC, and DQOs are provided in the SAP (Appendix A). A list of the potential analytical methods that will be used during the RI is provided below.

For soils:

- VOCs by EPA Method 5035/8260B
- SVOCs (including PAHs) by EPA Method 8270C
- TPH-g by EPA Method 5035/8015B modified
- TPH-d/mo by EPA Method 8015B modified
- PCBs by EPA Method 8082
- Metals by EPA Method 6010B/7471A
- Dioxins/furans by EPA Method 8290A
- Organochlorine pesticides by EPA Method 8081
- Organotins by National Oceanic and Atmospheric Administration (NOAA) Status and Trends Program Method (NOAA 1993)

For groundwater:

- VOCs by EPA Method 8260B
- SVOCs (including PAHs) by EPA Method 8270C
- TPH-g by EPA Method 8015B modified
- TPH-d/mo by EPA Method 8015B modified
- PCBs by EPA Method 8082
- Dioxins/furans by EPA Method 8290A
- Metals by EPA Method 6010B
- Organochlorine pesticides by EPA Method 8081
- TDS by EPA Method 160.1

5.5 BIOLOGICAL MONITORING AND AVOIDANCE

Due to the potential for wildlife species, including the Salt Marsh Harvest Mouse (SMHM) and California Clapper Rail, to be present in the SSA, NOREAS has described biological monitoring and avoidance in the Environmental Protection Plan included as Appendix B.

5.6 MPPEH AVOIDANCE

Anomaly avoidance measures will be required during all intrusive activities associated with the collection of environmental samples. Because the environmental sampling for the RI is being completed after the completion of the DGM and subsequent NTCRA, the probability of encountering an anomaly during borehole advancement will be very low. In the event that hand-digging or potholing is necessary to complete the additional delineation of the eastern disposal pit in DGM Grid AF011, anomaly avoidance will be required during all intrusive activities for that effort.

Prior to any intrusive activities at the SSA, detector-aided surface sweeps will be performed in accordance with all local, state, and federal regulations, including all applicable DoD requirements. All detectors (magnetometers) will be checked for proper operation according to the manufacturer's instructions prior to use at each boring location.

The objective of the detector-aided surface survey is to determine if an anomaly which may represent MPPEH exists on the ground surface at the proposed soil boring and/or groundwater monitoring well locations. If a surface anomaly is discovered on the site while employing anomaly avoidance techniques, the location and description of the item will be reported immediately to the RPM. The specific boring location will then be moved to an area that is free of metal anomalies. The anomaly will not be excavated or handled.

During the advancement of each borehole (by hollow stem-auger method for monitoring wells and direct-push technology [DPT] method for soil samples), the boring will be checked at one-foot intervals for anomalies using a down-hole detector. If an anomaly is detected prior to the completion of the boring, the boring will be terminated and the depth of detection and location of the boring will be recorded. The anomaly will not be excavated for purposes of identification. The boring will then be relocated, and anomaly avoidance measures will resume.

As described in Section 5.2.3, excavation or potholing activities associated with delineation of the AF011 disposal pit, if necessary, will progress in approximate 6-inch lifts. Following the completion of each lift, the base of the excavation/pothole will be screened with the down-hole detector to determine if a buried anomaly is present. This procedure will continue to the planned depth of the excavation (up to four feet bgs) until an anomaly is detected or debris is encountered.

In the event that an anomaly is detected or debris is encountered, all excavation/potholing activities will cease and the material will be left in place. The debris will not be removed, handled, or otherwise disturbed. The location and depth of the debris will be documented to allow for further delineation of the disposal pit area, and the excavation will be backfilled.

If MPPEH are encountered during the implementation of the RI field activities, additional MPPEH management will be addressed under a separate work order at the direction of the Navy KO.

UXO Personnel Qualifications

All anomaly avoidance measures will be performed by a UXO Technician III meeting the requirements of Department of Defense Explosive Safety Board (DDESB) TP-18, *Minimum Qualifications for Unexploded Ordnance Technicians and Personnel.* MPPEH reclassification and disposal, if required, will be performed by two UXO Technician III personnel. One technician will act as Site UXO Supervisor (SUXOS) and the other will act as UXO Quality Control (QC)/Safety Officer. UXO personnel have stop work authority on site.

5.7 MANAGEMENT OF MPPEH

Based on the avoidance measures discussed in section 5.5, only MPPEH identified on the surface of the site is subject to the procedures in this section. Other anomalies that may represent MPPEH will be below ground surface and will not be excavated for identification and disposition. Based on the scope and extent of the current MEC removal action, the probability of surface encounters with MPPEH is considered low.

5.7.1 Summary of MPPEH Risk

The risk of encountering MPPEH on the site should be negligible based on the extensive history of removal actions at the site discussed previously in this work plan.

5.7.2 MPPEH Reporting

MPPEH will be recorded and included on daily reports. Records will include location, type, size, physical condition, fusing, and filler condition if possible. Photographs will also be obtained of the MPPEH. The MPPEH will be clearly marked with pin flags in the field.

5.7.3 MPPEH Identification

No MPPEH will be moved without positive identification of the item and evaluation of its condition by UXO personnel.

5.7.4 MPPEH Classification

MPPEH, including small arms, will be inspected and classified as MDEH, MEC (UXO, DMM [including live small arms], energetics) or MDAS (including spent small arms). Items will also be evaluated to determine if they are "acceptable to move". Items which are classified as MDAS will be relocated to building A169 for storage and future disposition. Items evaluated as "not safe to move" will be managed on site by the contractor. A 24-hour guard will be posted at the item until proper disposition can be provided. Non-ordnance related scrap will be sent off site for recycling.

5.8 LAND SURVEYING

All soil boring/sampling and well locations will be surveyed for elevation and location coordinates by a California-licensed Professional Surveyor. The survey will be accurate to 0.01 feet vertically above mean sea level and will be surveyed to the State Plane Coordinate System based on the North American Vertical Datum (NAVD) 88; horizontal coordinates will be surveyed to the State Plane Coordinate System North American Datum (NAD) 83. The surveyor will also report the horizontal data as feet in California State Plane NAD 1927; vertical data as feet msl in National Geodetic Vertical Datum 1929. The final survey data will be provided in Navy Electronic Data Deliverable (NEDD) format and uploaded into Naval Installation Restoration Information Solution.

5.9 INVESTIGATION-DERIVED WASTE

Purged groundwater and rinsate from equipment decontamination will be collected and placed into Department of Transportation-approved 55-gallon drums. The wastewater will be transported to an appropriate off-site permitted facility for treatment and/or disposal. Investigation-derived waste will be characterized based upon sampling results.

Soil cuttings will be contained in 55-gallon Department of Transportation-approved drums or 20-yard roll-off containers and stored at a designated staging area at the site pending waste classification. Soil cuttings and other investigation-derived wastes will be transported by an appropriately licensed carrier and disposed of at an appropriately licensed transport storage and

disposal facility. Soil samples for waste classification will be collected from the drums and analyzed in accordance with the waste receiving facility requirements.

Any ABM recovered in the soil core and/or cuttings will be segregated from the other soils and placed in 5 gallon buckets at the work sites. The ABM will then transferred to a dedicated 55-gallon drum for disposal at an appropriate off-site permitted facility pending waste characterization results.

All waste will be handled and disposed consistent with the procedures described in the Waste Management Plan (Appendix C).

5.10 EQUIPMENT DECONTAMINATION

Non-disposable equipment used to drill and sample groundwater will be decontaminated between boreholes and prior to leaving the site. All downhole equipment will be thoroughly decontaminated using steam cleaner/pressure washing equipment supplied by potable water. If required, brushes will be used to aid in the removal of gross contamination prior to steam/pressure-washing. A decontamination trailer will be used to facilitate collection of the wastewater. In the event any small downhole equipment is used that is not practical to steam/pressure wash, such equipment shall be decontaminated using the following steps: 1) Thoroughly wash using a non-phosphate detergent in potable water in a bucket, brushing/agitating as necessary; 2) Thoroughly rinse in potable water; 3) Thoroughly rinse in a second water rinse bucket containing distilled/deionized water. The source containers for the distilled/deionized water shall be used for equipment rinsate samples.

5.11 DEMOBILIZATION/SITE RESTORATION

Demobilization will consist of decontamination and removal of all equipment used to conduct the investigation, as well as collection and disposal of all contaminated material, including decontamination water and disposable equipment for which decontamination is inappropriate. Waste transport and manifestation will be coordinated with the ROICC and/or CSO representative. All waste management activities, such as on-site staging, waste minimization and characterization, and on- and off-site transport and disposal, will adhere to the existing protocols developed and maintained by the Navy for all waste activities at MINS.

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6.0 PROJECT REQUIRED PLANS

As part of this RI Work Plan, several other key planning documents have been prepared to describe the methods and procedures that will be implemented during the course of the RI. Brief descriptions of these planning documents are provided in the subsections that follow.

6.1 SAMPLING AND ANALYSIS PLAN

The investigation will be performed in accordance with the project SAP that is provided as Appendix A to this Work Plan. The SAP includes all the required elements of a Field Sampling Plan and a Uniform Federal Policy Quality Assurance Project Plan. Accordingly, extensive details are included on sample collection procedures, sample handling and chain-of-custody procedures, analytical requirements, QC and QA protocols, and data validation and management requirements. The SAP has been approved by the project Quality Control Manager, and will be reviewed and approved by the Naval Facilities Engineering Command Southwest (NAVFAC SW) Quality Assurance Officer prior to performing any sampling activities.

Data Handling and Management

This section provides an overview of the data handling and management procedures for record-keeping, technical data review, reporting, and data validation. A more detailed description is provided in the project-specific SAP.

During this project, field data will be recorded in permanently-bound field logbooks with consecutively-numbered pages or on preprinted forms. All entries will be recorded in indelible black or blue ink. Corrections will be made by drawing a single line through the erroneous entry and initialing and dating it. The analytical laboratory will review and verify completeness and accuracy of the sample receiving records upon sample receipt at the laboratory. Environmental samples will be assigned a unique identification number and recorded in the laboratory's internal chain-of-custody system, which will be carried through the data generation and reporting processes.

All analytical data generated by the laboratory in support of this project will be reviewed prior to reporting to ensure the correctness and completeness of reported data. The laboratory data review process will consist of data reduction, three levels of documented review, and reporting. Review processes will be documented using appropriate checklist forms or logbooks, which will be signed and dated by the reviewers. All analytical data generated by the laboratory will, at a minimum, undergo reviews by (1) the analyst performing the test, (2) a technical review by a peer qualified to perform the test or a technical supervisor, and (3) by the project manager to ensure that all project-specific analytical requirements are met. In addition, the laboratory QA manager will perform reviews on 10 percent of the data reported for this project. This review may be conducted after the data have been reported, however, all errors identified will be

corrected and documented and a revised report must be provided to the NOREAS Project Chemist.

All data calculations will be verified by laboratory personnel generating and approving them. All relevant laboratory raw data, including but not limited to logbooks, data sheets, electronic files, data review check sheets, nonconformance records, and any correspondences will be maintained for a minimum of seven years. In addition, all reports will be held client confidential. NOREAS must be notified 30 days before disposal of any project records.

Data Reporting

The laboratory will provide hard-copy reports and electronic data deliverables (EDDs). For this project, 90 percent of the data will be submitted in an EPA Level III-equivalent data report, and 10 percent submitted in an EPA Level IV-equivalent data report. All data will be reported by the analytical laboratory within the specified data turnaround times. The NOREAS Project Chemist will review preliminary and final analytical data prior to releasing data to project technical personnel to verify that the sampling and analytical procedures are in accordance with the procedures included in this Work Plan and SAP and data that produced are consistent with the project-specific DQOs.

Electronic Data Deliverables

In addition to the hard-copy reports, laboratory will submit EDDs compliant with the Navy electronic data deliverable (NEDD), which will be uploaded to the Naval Installation Restoration Information Solution database as specified in the Environmental Work Instruction (EWI) #6. An electronic data file (EDF) compatible with the State Water Resources Control Board GeoTracker database will also be provided by the analytical laboratory. The laboratory will be responsible for verifying that the EDD/EDF files are consistent with the final hard-copy reports. All field sampling locations, except for waste characterization samples, will be surveyed in accordance with the EWI EVR.6, Environmental Data Management and Required Electronic Delivery Standards (SWDIV 2005). The analytical data files will be checked for required values and project-specific requirements by the database. In the event that discrepancies are identified, the laboratory will resubmit revised EDDs and EDFs. Ten percent of the data will be checked by the Project Chemist against the hard-copy data package. If errors are found in the electronic data, the Project Chemist will contact the laboratory to request corrected data. The electronic data in NEDD format will be submitted to the DON 30 calendar days after the validation report is received.

All manually-generated data tables included in the project report will be QC reviewed by the Project Chemist against final hard-copy reports. Key field data from chain-of-custody forms (date and time collected, sample identification, etc.) to be included in data tables will also be reviewed for transcriptions errors.

Data Validation and Review

All analytical data generated for this project, with the exception of waste profile samples, will be validated by an independent data validation company. The Project Chemist will review all of the data validation reports to ensure that the data qualifiers are applied correctly and that data usability is in accordance with this project requirements specified in the RI SAP.

6.2 ENVIRONMENTAL PROTECTION PLAN

In order to protect the environmental and biological resources in the SSA during the RI field activities, a comprehensive Environmental Protection Plan (EPP) has been prepared and is provided as Appendix B of this Work Plan.

6.3 WASTE MANAGEMENT PLAN

The Waste Management Plan (WMP) (Appendix C) describes procedures for handling investigative derived waste (IDW) generated from the RI at the SSA. NOREAS will coordinate with the CSO representative, ROICC, and Navy RPM to ensure all IDW is properly characterized, stored, labeled, and hauled offsite in accordance with basewide procedures and applicable federal, state, and local regulations. Waste minimization procedures will be implemented to reduce the amount of waste generated at the worksite with emphasis on recycling where applicable. IDW generated during the RI will include soil, purge and decontamination water, concrete and trash.

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7.0 HUMAN HEALTH RISK ASSESSMENT METHODOLOGY

The Baseline Human Health Risk Assessment (BHHRA) Work Plan presented herein identifies the overall approach for evaluating potential human health impacts at the SSA resulting from impacts to soil and groundwater that are identified during the RI. The BHHRA will be submitted as part of the RI documentation, and will be prepared under the regulatory requirements of CERCLA and under the procedural requirements specified by the *U.S. Navy Human Health Risk Assessment Guidance* (NAVFAC, 2008).

As identified by the U.S. Navy (Navy, 2001), the preparation of a BHHRA represents a Tier II human health risk assessment which is a site-specific quantitative analysis of potential adverse health effects (current or future) related to site-related chemicals.

7.1 BHHRA CONCEPTUAL SITE MODEL

As previously identified in the "Engineering Evaluation Cost Analysis (EECA)/Interim Remedial Action Plan (IRAP)" (Weston, 2011) and in the current CSM described in Section 3.6, potential human receptors for residual contamination at the SSA would include:

- City and utility workers who access the areas,
- Construction workers performing ground intrusive work, and
- Recreational users of the area.

In addition to the receptors identified above, the BHHRA will also evaluate a hypothetical residential land use scenario. Recognizing the potential for exposure, and the potential for the presence of COPC, the BHHRA CSM is presented as Figure 7-1. As described in Section 3.6, this model will be re-evaluated and updated with the information obtained during the RI to provide a more complete understanding of the human health risks based on the most current data available.

7.2 TOXICITY ASSESSMENT

The purpose of the toxicity assessment is to identify current and relevant toxicity criteria and information for the identified COPCs necessary to quantify potential health impacts. Specific toxicity values are developed, published, and updated by regulatory agencies for many compounds. The toxicity values are used in the quantitative estimation of carcinogenic risk and noncarcinogenic hazard. For the HHRA, two sets of risks will be calculated: one set using federal (EPA) toxicity criteria, and the other set using the State of California (DTSC) toxicity criteria. The hierarchy of sources used to obtain federal and California toxicity criteria are described below.

Toxicity information will be obtained from the following hierarchy of sources, in order of priority:

- USEPA *Integrated Risk Information System* (IRIS) (USEPA, 2012a). Available online at www.epa.gov/iris/
- USEPA Provisional Peer Reviewed Toxicity Values (PPRTVs) (USEPA, 2012b). Available online at http://hhpprtv.ornl.gov/index.html
- Cal-EPA Office of Health Hazard Assessment (OEHHA) *Toxicity Criteria Database* (TCD) (Cal/EPA, 2012). Available online at http://oehha.ca.gov/tcdb/index.asp

The second set of risk estimates will be calculated using a similar toxicity criteria hierarchy, except the State of California toxicity criteria, where available, will be used preferentially over federal criteria for assessing cancer effects.

In the event that toxicity information is not available for specific chemicals, the identification of toxicity surrogates may be necessary. If additional surrogates are necessary, they will be identified and discussed in the BHHRA.

7.3 DATA EVALUATION

The data evaluated for the BHHRA will include those obtained under the RI as well as from previous investigations and removal actions at the SSA, including the 2012-2013 NTCRA. Data will be evaluated to select COPCs that are appropriate and representative of site conditions.

In general, it is important that the data used in the BHHRA represents site conditions. Towards this end, there are several issues related to data quality and its ability to fairly represent concentrations of site-related chemicals to which a receptor may be exposed. These issues include, but are not limited to, consideration of reported detection limits, coded data, blank sample results, and frequency of occurrence of detected chemicals. These issues are discussed further in the sections below.

7.3.1 Evaluation of Analytical Reporting Limits

The chemical data obtained during the RI sampling activities will be reviewed and evaluated. In cases where no chemicals were detected above their method reporting limits (RLs) it will be necessary to evaluate those RLs to determine if their levels are suitable for such comparisons.

7.3.2 Evaluation of Qualified and Coded Data

Data qualifiers and codes pertain to QA/QC issues and indicate questions concerning chemical identity, chemical concentration, or both. Some data are initially qualified and coded by the analytical laboratories consistent with EPA Contract Laboratory Program (CLP) protocol.

Additional qualifiers and codes are provided, as necessary, during the data validation process by project chemists and data reviewers.

Common qualifiers that may affect the risk assessment process are typically the "J", "U" and "R" qualifiers. These qualifiers and their impacts to the risk assessment process are described below:

J-Qualified Data – The "J" qualifier indicates that the reported concentration is an estimate. J-qualified data will be considered in the BHHRA. However, as with all data, the uncertainty and representativeness of the data must be evaluated. For example, if all or nearly all results for a compound that has been detected are J-qualified, then its presence may be suspect. This is especially true if that compound is among those typically considered a laboratory contaminant. Therefore, J-qualified data will be evaluated to assess their representativeness. The BHHRA will include a discussion of the rationale for including or excluding J-qualified data.

U-Qualified Data – The "U" qualifier indicates that an analyte is considered not present above its RL. When an analyte is undetected, the reported value represents the sample RL. Data qualified as "U" will be used in the risk assessment process as follows.

- Case 1 – Analyte in all samples reported as "U" or "Not Detected"

  In this case, the risk assessment will assume that the analyte is undetected at the RL. Because this analyte is “undetected”, there will be no quantitation of public health impacts for this analyte.

- Case 2 – Analyte in <u>some</u> samples reported as "U" or " Not Detected"

  The BHHRA will assume that the analyte is present at one-half the RL in those samples in which it is reported as not detected. This is a health protective assumption, and assumes that although a particular chemical may be reported as "U" or "Not Detected", the detection of the analyte in other samples may indicate that the analyte is present but at a level between the RL and zero. If a chemical detection is infrequent and determined to represent an isolated condition, the BHHRA will discuss the findings and implications to the BHHRA.

R-Qualified Data – The "R" qualifier indicates that quality control issues render the results unusable. Accordingly, the risk assessment process will not consider "R"-qualified data in the COPC selection process.

7.3.3 Evaluation of Chemicals in Blanks

For the risk assessment process, chemicals that are detected in both laboratory blanks and field samples will be subjected to the decision rules specified in “Appendix VII, Summary of Common Laboratory Contaminants, Concentrations, Concentration Requirements, and Risk Assessment Implications” of the “USEPA Guidance for Data Usability in Risk Assessment” (USEPA, 1992).

7.4 COPC SELECTION PROCESS

Following a review of data qualifiers, the detected chemicals will be considered as COPCs for further evaluation in the BHHRA. In general, chemicals found to be laboratory or sampling artifacts will not be considered COPCs.

7.4.1 Screening Levels

Consistent with the Screening Level HHRA, the following screening levels will be used to evaluate potential COPCs for BHHRA evaluation.

- Applicable USEPA RSLs based on residential use for CERCLA constituents and site-specific Tier 2 screening levels for TPH constituents, for soil and groundwater.

The screening levels will also be used to select analytical methods with detection and reporting limits low enough to support the HHRA evaluation. However, the screening levels will not be used to eliminate COPCs as all detected compounds will be carried through the HHRA evaluation.

For cases where background or ambient concentrations are available, the background value will be used as the screening level. In the event that RSLs are lower than background, the background value will be used.

7.4.2 Background Evaluation

Background information will be used to help select chemicals to be evaluated during the BHHRA process. In general, chemicals present at concentrations at or below naturally occurring levels will not be considered COPCs.

Metals are likely to be present in soil and groundwater at some concentration that is characteristic of naturally occurring levels. Where applicable, ambient/background concentration values for metals at Mare Island (Tetra Tech EMI, 2002) will be identified for use in the BHHRA.

7.5 EXPOSURE ASSESSMENT

For purposes of the BHHRA work plan, it is assumed that both soil and groundwater may be impacted by site-related COPCs. The following sections discuss the potential exposures associated with these potential impacts.

7.5.1 Potential Exposure Media

Based on the current understanding of the SSA and knowledge of future development, the following exposure media are discussed. In addition to exposures that may occur as a result of planned reuse, a hypothetical residential exposure scenario will also be evaluated as part of the BHHRA to evaluate an unrestricted reuse scenario.

Soil

While the 2012-2013 NTCRA should substantially reduce the potential for humans and wildlife to be exposed to MEC, all surface soil excavated during the NTCRA was screened for debris, reworked, replaced in the excavation, graded, and compacted. These existing/reworked soils were not noted at the time to contain any COPCs. As part the RI field activities, samples will be collected and analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, dioxins/furans, and metals to characterize soil.

The soil at the SSA may be a potential exposure media for industrial and construction receptors. Soils may also be contacted by recreational visitors and by hypothetical residents at the SSA. The extent of contact by recreational visitors will be determined on the overall planned use of the area.

Groundwater

The groundwater beneath the SSA is expected to range in depth from 2.5 to 6 feet bgs. Due to the shallow depth to groundwater, it is reasonable to assume that contact can occur in the event of construction or infrastructure installation and repair.

Under the hypothetical residential scenario, groundwater may be contacted if used for potable purposes. Although, no groundwater production wells exist on Mare Island, the evaluation of ingesting groundwater may be necessary for risk management purposes. The BHHRA will further identify potential groundwater designated uses, which may affect the assessment of residential groundwater exposures.

Outdoor Air

Outdoor air may also be impacted from VOCs potentially in soil and groundwater. Particulates in outdoor air may also contain nonvolatile COPCs. Outdoor air can be considered an exposure media based on current and future site usage.

Indoor Air

If VOCs are detected in groundwater and/or soil, they may have the potential to upwardly migrate through the vadose zone and impact indoor air via the vapor intrusion (VI) pathway. The BHHRA will evaluate the likelihood of vapor migration to existing and future (including the hypothetical residence) buildings.

7.5.2 Exposure Scenarios

Based upon the anticipated exposure setting and future use of the SSA, the most likely exposure scenarios are:

- City and utility workers who access the areas,

- Construction workers performing ground intrusive work, and
- Recreational users of the area.

In addition to the most likely exposure scenarios, the BHHRA will also address a hypothetical residential scenario at the SSA.

City and Utility Workers

This scenario is descriptive of workers who may be present at the SSA to either repair or maintain the property. This scenario is not unlike an industrial scenario, as it does not imply major excavation or construction activity. Under this scenario, it is likely that the worker may come into casual contact with site soils and air impacted by site related COPCs.

Construction Workers

This scenario is descriptive of workers who may need to excavate the soil at the SSA for construction projects and/or infrastructure installation and repair. Under this scenario, it is likely that the workers may come into contact with site soils and air impacted by site related COPCs. Although this scenario will result in higher daily exposures, such activities are generally short-term (e.g., less than a year). Because the depth to groundwater is relatively shallow at some areas of the SSA, it is not unreasonable that construction may result in contact with groundwater, potentially containing site-related COPCs.

The Navy developed a model approved by the DTSC during the IA FI RI (Chadux Tt, 2012) to simulate migration of chemicals in groundwater through the soil into a trench to estimate the vapor concentrations in the trench. The model consists of two parts: (1) calculation of volatile emission rates from groundwater into a trench, using the VLEACH model (Ravi and Johnson 1996), and (2) calculation of vapor concentrations in the trench air using the calculated emission rates and simple air dispersion (box) model. A full description of the model used to estimate volatilization into a construction trench will be provided in the RI Report.

Recreational Users

The planned land use for the SSA is as a recreational area and wildlife preserve. Under this land use, it is reasonable that off-site visitors will frequent the SSA. Under this scenario, it is likely that the visitors may come into casual contact with site soils and air impacted by site related COPCs.

Hypothetical Residential Land Use

Although not currently a planned use for the SSA, a hypothetical residential land use scenario will be evaluated for baseline purposes. Under this hypothetical land use, it can be assumed that residents may come into contact with site soils, air impacted by site related COPCs (outdoor and indoor), and groundwater potentially containing site related COPCs.

7.5.3 Estimation of Exposure Point Concentrations

Exposure point concentrations are representative of concentrations that a human receptor may be exposed to. In this case, it is expected that receptors may be exposed to concentrations of VOCs in both indoor and outdoor air. In order to derive both indoor and outdoor air estimates of potential health impacts, it will be necessary to understand the data obtained as part of the RI process.

Statistical Analysis of Data

A statistical evaluation of the data for the COPCs will be completed as part of the BHHRA to estimate representative concentrations in soil and groundwater. Such statistical evaluations are more likely to be representative of environmental conditions than single point estimates. Data will be grouped based on potential exposure zones, which will be determined based on project SWMUs, site-specific areas of investigation (based on the characterization of the RI), and possible future site building plans.

The COPC data will be input to the USEPA ProUCL v5.0 (USEPA 2013) statistical model to determine summary statistics and the UCL for each COPC. The ProUCL statistical model is peer reviewed and designed to assist in the statistical evaluation of data consistent with CERCLA guidance (USEPA 2013). As such, the model features parametric and nonparametric UCL computational methods that can be used on full-uncensored data sets without nondetects and also on data sets with below detection limit observations (BDLs). Some of the methods (e.g., Kaplan-Meier method, regression on order statistics) are applicable on left-censored data sets having multiple detection limits. To account for BDLs, ProUCL performs statistical routines using the limit of detection to estimate values for censored data. The UCL methods cover a wide range of skewed data sets with and without the BDLs (USEPA 2013).

For the BHHRA, ProUCL calculations will be based on the 95% UCL of mean. As a starting point, the choice of a 95% UCL to represent COPC exposure point concentrations is consistent with the “Risk Assessment Guidance for Superfund (RAGS), Part C” (USEPA 1992), and is the preferred statistic unless ProUCL calculations support the recommendation for an alternative confidence level. All calculated UCLs, and their confidence levels, will be summarized in the BHHRA.

The output from ProUCL identifies the recommended UCL calculating method, as well as calculated value. The ProUCL recommendations are based on decision rules that recognize data-set specific factors such as distribution, skewness, and censoring proportions. These decision rules are provided in the ProUCL Version 5.0 Users Guide, Chapter 18 (USEPA 2013).

In some cases, especially when data sets are small, the calculated UCL may exceed the maximum detected value. In such cases, an alternative UCL recommended by ProUCL will be used as the EPC. For example, when a 95% UCL exceeds the maximum detected concentration,

ProUCL recommends the use of an alternative UCL computation based on the Chebyshev inequality (USEPA 2013). If it becomes necessary to use the maximum detected value, the project team shall be advised of the situation and additional estimations, based on site-specific knowledge and experience, may be made on a case by case basis. All data and EPC determination assumptions will be included in the BHHRA.

All ProUCL output will be provided as an appendix to the BHHRA. Summary statistics (e.g., number of samples, number of detections, range of detections, etc.) will be provided in tables to the BHHRA.

Estimation of Outdoor Air Concentrations

Outdoor air may be impacted as 1) VOCs in groundwater migrate through the vadose zone, 2) VOCs volatilize from soil, and 3) particulate emissions from site soil.

Volatile Organic Compounds

The estimation of outdoor air concentrations of VOCs requires the estimation of 1) vapor concentrations at the source; 2) flux rate of the VOC at the surface soil; and 3) outdoor air concentration.

Per Johnson, et al (1991), vapor concentration from groundwater concentration can be calculated as:

$$C_{source,gw} = H'C_w$$

Where:

$C_{source,gw}$	=	Vapor concentration at equilibrium with groundwater concentrations, mg/m^3
H'	=	Henry's law constant, dimensionless
C_w	=	Groundwater concentration, micrograms per liter (µg/L)

All calculations of $C_{source,gw}$ will be presented in the BHHRA.

Following the estimation of $C_{source,gw}$ it will be necessary to estimate the flux rate. The flux rate is the rate of chemical emission per area, and will be calculated using the Farmer model (USEPA 1988) with site-specific data.

$$E_{sg,i} = \frac{C_{source,gw} \times D_i \, x \frac{\Theta_{as}^{3.33}}{\Theta_{tsoil}^{2}} \times 0.01 \, {}^{m}\!/_{cm}}{L}$$

Where:

$E_{sg,i}$	=	Flux rate of chemical i, milligrams per square meter per second [(mg/m^2)/s]
$C_{source,gw}$	=	Source soil gas concentration of chemical i, milligrams per cubic meters (mg/m^3)
D_i	=	Diffusion coefficient of chemical i in air, square centimeters per second (cm^2/s)
θ_{as}	=	Air-filled porosity of soil, unitless
θ_{tsoil}	=	Total porosity of soil, unitless
L	=	Depth between soil gas source and soil surface, centimeter (cm)

All flux rate calculations will be presented in the BHHRA.

Following the estimation of potential flux rate, it will be necessary to estimate the concentration of volatile COPCs in air following dispersion into the breathing space. This requires the use of atmospheric dispersion models. The simplest dispersion model, known as the box model, equates ambient concentrations to the mass of volatile COPCs within a specified volume of the atmosphere (Shen 1993). A steady-state assumption is inherent to the box model, and means that the processes affecting the mass balance do not change with time.

The box model is defined by the following equation:

$$C_{air} = \frac{E_{sg,i} \times A}{u \times H \times W}$$

Where:

C_{air}	=	Air concentration of chemical (mg/m^3)
u	=	Wind speed [meters per second (m/s)]
H	=	Height of mixing box [meters (m)]
W	=	Width of mixing box (m)
$E_{sg,i}$	=	Flux of chemical *i* (mg/m^{2}s)
A	=	Area of emission [square meters (m^2)]

For the purposes of the BHHRA, the height (H) will be assumed to be two meters and the width will correspond to the site-specific width of either the investigated area (e.g., SWMU, AOC) or future planned area where exposures are likely. The area of emission will also correspond to site-specific values. The median wind-speed for the SSA will be used for variable u. All outdoor air calculations will be presented in the BHHRA.

Particulates

To estimate particulate concentrations in air, the particulate emission factor (EF_{part}) methodology will be used. The EF_{part} is representative of the relationship between soil concentrations and particulate concentrations as follows:

$$C_{soil}/EF_{part} = C_{air}$$

Where:

C_{soil} = Concentration in soil (mg/kg)
EF_{part} = Particulate emission factor [cubic meters per kilogram (m^3/kg)]
C_{air} = Concentration in air (mg/m^3)

For the industrial and recreational scenarios, the EF_{part} will be 1.316×10^9 m^3/kg, and for construction activities the EF_{part} will be 1.0×10^6

m^3/kg. These values are consistent with the Cal/EPA-DTSC default HHRA values (DTSC 2011b). If, during the preparation of the BHHRA it is determined that the default EF_{part} values depict significantly different conditions than those at the SSA (e.g., vegetative cover, windspeed), the EF_{part} values may be modified. If modifications are made, the rationale for modifying each variable used to calculate EF_{part} will be provided in the BHHRA.

Estimation of Indoor Air Concentrations

The volatilization of contaminants from groundwater and the subsequent transport of these vapors into indoor spaces, constitute a potential inhalation exposure pathway.

Indoor air concentrations will be calculated using the Johnson and Ettinger (J&E) Vapor Intrusion Model. The J&E model further quantifies health impacts by integrating exposure factors and toxicity criteria to determine carcinogenic risks and noncarcinogenic hazards per the relationships described previously. At this time, it is expected that the EPA J&E models dated February 2004 will be used for the BHHRA (CalEPA, 2011). To assess the hypothetical residential scenario, the default residential building parameters will be used in J&E modeling unless site specific information becomes available that can substantiate reasonable deviations from the default parameters.

7.5.4 Exposure Factors

Exposure factors for the BHHRA will be representative of both Reasonable Maximum Exposures and Central Tendency Exposures. Per the NAVFAC 2008 guidance, Tables 7-1 and 7-2 identify the preliminary exposure parameters that will be used to assess the exposures for the SSA.

Exposure factors for the BHHRA will be obtained from the following sources:

- "U.S. Navy Human Health Risk Assessment Guidance" (NAVFAC, 2008),
- "Recommended DTSC Default Exposure Factors for Use in Risk Assessment at California Hazardous Waste Sites and Permitted Facilities" (DTSC, 2011b),
- "Exposure Factors Handbook" (USEPA, 2011),

- "Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E., Supplemental Guidance for Dermal Risk Assessment)" (USEPA, 2004), and
- "Risk Assessment Information System" (ORNL, 2012).

Future development plans will also be reviewed as part of the BHHRA to determine additional exposure parameters that may need to be considered to properly reflect future conditions.

7.5.5 Estimation of Intakes

For outdoor air, exposure factors are integrated into pathway exposure factors (PEFs). Once derived, the PEFs are multiplied by the exposure concentrations to estimate intakes.

Ingestion

For the ingestion of soil, the PEFs are calculated as follows:

$$\text{Lifetime PEF}_{\text{oral}}\,(\text{mg}_{\text{soil}}/\text{kg}_{\text{bodyweight}} - \text{day}) = \frac{\text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}}$$

Where:

IR	=	Soil ingestion rate, milligrams per day (mg/day)
ED	=	Exposure duration, years
EF	=	Exposure frequency, days per year
BW	=	Body weight, kilograms (kg)
AT	=	Averaging time, 25,550 days (365 days/year x 70 years)

$$\text{Daily PEF}_{\text{oral}}\,(\text{mg}_{\text{soil}}/\text{kg}_{\text{body weight}}\ \text{day}) = \frac{\text{IR}_{\text{soil}} \times \text{EF}}{\text{BW} \times \text{d/y}}$$

Where:

IR_{soil}	=	Soil ingestion rate (mg/day)
EF	=	Exposure frequency (days)
BW	=	Body weight (kg)
d/y	=	Days per year

Intakes are then calculated as follows:

$$\text{LADI} = C_m \times \text{LPEF}$$

Where:

LADI	=	Lifetime average daily intake (used to quantify carcinogenic health risks)
C_m	=	Concentration of chemical in exposure media

LPEF = Lifetime pathway exposure factor

and:

$$DADI = C_m \times DPEF$$

Where:

DADI = Daily average daily intake (used to quantify noncarcinogenic health hazards)
C_m = Concentration of chemical in exposure media
DPEF = Daily pathway exposure factor

Inhalation

For the inhalation of outdoor air, the PEFs are calculated as follows:

$$\text{Lifetime PEF}_{\text{inhl}}\ (\text{m}^3{}_{\text{air}}/\text{kg}_{\text{bodyweight}} - \text{day}) = \frac{FC \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}}$$

Where:

FC = Fraction from contaminated source (percent)
IR = Inhalation rate (mg/m^3)
ED = Exposure duration (years)
EF = Exposure frequency (days/year)
BW = Bodyweight (kg)
AT = Averaging time (25,550 days)

$$\text{Daily PEF}_{\text{inhl}}\ (\text{m}^3{}_{\text{air}}/\text{kg}_{\text{bodyweight}} - \text{day}) = \frac{\text{FC} \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}}$$

Where:

FC = Fraction from contaminated source (percent)
IR = Inhalation rate (mg/m^3)
ED = Exposure duration (years)
EF = Exposure frequency (days/year)
BW = Body weight (kg)
AT = Averaging time (365*ED)

Intakes are then calculated as follows:

$$LADI = C_m \times LPEF$$

Where:

LADI	=	Lifetime average daily intake (used to quantify carcinogenic health risks)
C_m	=	Concentration of chemical in exposure media
LPEF	=	Lifetime pathway exposure factor

and:

$$DADI = C_m \times DPEF$$

Where:

DADI	=	Daily average daily intake (used to quantify noncarcinogenic health hazards)
C_m	=	Concentration of chemical in exposure media
DPEF	=	Daily pathway exposure factor

In addition to the methods described, the estimation of inhalation intakes will also consider the alternative methods presented in the "Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment" (USEPA, 2009). The applicability of Part F guidance will be determined based upon the toxicity criteria obtained for each COPC. For example, when inhalation toxicity criteria derived from route-to-route extrapolations are used, the methods presented may be used. If inhalation toxicity criteria are based on the USEPA Inhalation Dosimetry Methodology, then Part F methods will be used. In either case, the calculation of intakes will be provided in the BHHRA.

For intakes associated with indoor air, the J&E model will be modified to reflect the selected exposure factors.

Dermal Absorption

The estimation of intakes based upon dermal absorption will utilize the methodologies of the "Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E., Supplemental Guidance for Dermal Risk Assessment)" (USEPA, 2004). This methodology is descriptive for exposures to both soil and water potentially containing organic and inorganic COPC.

All dermal absorption calculations will be provided in the BHHRA.

7.6 RISK CHARACTERIZATION

The purpose of the risk characterization process will be to provide deterministic quantitative estimates of carcinogenic risk and noncarcinogenic hazard. This is intended to be an estimate of

the relative magnitude or probability of potential adverse effects that may be incurred based on exposure to the COPCs under the conditions depicted in the BHHRA.

Risks will be estimated at each discretely characterized study area identified by the RI. In addition, future planning documents will be reviewed to identify areas of potential exposures in order to provide site-specific risk characterization.

The risk of cancer from COPC exposure is described in terms of probability that an exposed individual will develop cancer during his/her lifetime from that exposure (NAVFAC, 2008). All carcinogenic risks for COPCs for each scenario will be summed to yield a total carcinogenic risk.

Adverse noncarcinogenic health effects from exposure to a COPC are quantitatively expressed as a hazard quotient (HQ). The HQ is the ratio of a human's estimated intake to a particular chemical to a reference concentration, or dose (as determined in the Toxicity Assessment of the BHHRA), that represents a threshold level below which it is unlikely that even sensitive subpopulations would experience adverse health effects (NAVFAC, 2008). All relevant HQs will be summed for a total Hazard Index (HI). If the total HI exceeds unity (or 1), the HI may be separated based on toxicological endpoint.

In general, the quantification of potential carcinogenic risks requires that the chemical-specific intake rate [i.e., lifetime average daily intake (LADI)] and the toxicity factor (i.e. slope factor) for each chemical must be multiplied together. Thus, the formula for estimating the carcinogenic risk probability for an individual COPC along a single pathway is:

$$\text{Carcinogenic Risk Probability} = \text{LADI} \times \text{Slope Factor}$$

If more than one potential carcinogen is present the risks from all these COPCs and pathways will be summed to produce the total carcinogenic risk for exposure area evaluated.

A quantitative description of potential noncarcinogenic health impacts is a ratio defined as the HQ. The HQ is the ratio of the annualized, chemical-specific exposure rate [i.e., daily average daily intake (DADI)] divided by the route and chemical-specific Reference Dose (RfD).

$$\text{HQ} = \text{DADI}/\text{RfD}$$

Since there may be more than one chemical and more than one complete pathway for a given chemical, the sum of the independent HQs represents the total risk from noncarcinogenic chemicals for each separate site. The sum is called the overall cumulative HI.

$$\text{HI} = \text{Hazard Index} = \Sigma(HQ_1 + HQ_2 + \ldots HQ_n)$$

Where: HQ_1, HQ_2, HQ_n represent the HQs for each chemical, exposure pathway, and route.

For characterization of indoor air risks and hazards, the J&E model output will be used. The J&E model quantifies health impacts by integrating exposure factors and toxicity criteria to determine carcinogenic risks and noncarcinogenic hazards per the relationships described previously. All J&E modeling and output sheets will be included as an appendix to the BHHRA.

7.6.1 Target Organ Analysis

With respect to noncarcinogenic health effects, each chemical may impact a different target organ. While the total noncarcinogenic hazard provides a single risk management decision-making criterion, it may be helpful to understand the relative target impacts for a group of different chemicals. This will only be provided in cases where the total noncarcinogenic hazard is predicted to be greater than unity, which is the point of departure for risk management decision-making.

7.6.2 Presentation of Risks and Hazards

A summary of the risks and hazards, both incremental and cumulative, for the site across all investigated media and exposure scenarios will be presented in the BHHRA. All calculations of carcinogenic risk and noncarcinogenic hazard will be presented as an appendix to the BHHRA. The results from these calculations will be summarized in text-based tables that will list COPC-specific risks and hazards as well as total risks and hazards. These tables will identify exposure scenario, COPC-specific risks and hazards, and total risks and hazards.

7.7 IDENTIFICATION OF PRIMARY UNCERTAINTIES

By design, risk assessment procedures are based on health protective assumptions that will tend to overestimate potential health impacts. This fundamental principle is observed in an effort not to underestimate potential health impacts. However, in some cases, this practice may overestimate potential health impacts (or other assumptions may underestimate potential health risks) to a point where the uncertainties surrounding the estimates require identification and discussion to provide an understanding of how these assumptions affect the estimation of human health impacts. In some instances, the assumptions made in the risk assessment may also introduce uncertainties to the estimation of human health impact that may either under- or overestimate potential health impacts. Because of this, uncertainties must be identified and discussed.

The purpose of the uncertainties analysis is to identify those assumptions that may unduly influence the quantitative assessment of health impacts. Numerous assumptions must be made in order to prepare the BHHRA. Assumptions will be necessary regarding data selection, exposure parameters, and the choice of approach and inputs for modeling chemical fate and transport. To understand the impacts of uncertainties to the BHHRA results, a qualitative analysis of uncertainties will be performed to provide assistance in interpreting the risk characterization results.

Typically, uncertainties are associated with either exposure-related factors or toxicity assessment factors. These uncertainties may include, but may not be limited to, the items described in the following subsections.

7.7.1 Analytical Data

The data will be reviewed to determine the representativeness of the collected data. In many cases, the collected analytical data represent purposive sample locations. When this is the case, the data describe potentially contaminated areas only and may not necessarily fairly represent concentrations across an exposure zone. Therefore, such data may overestimate potential health impacts.

7.7.2 Use of Models

This outdoor air evaluation method assumes that the vapors at the source locations (i.e., groundwater) are available for direct migration into indoor air. The actual migration of the vapors, however, may be limited by site-specific subsurface features and phenomena, the presence of which may be unknown or difficult to account for using the model described above. For example, the transport of vapor from groundwater requires movement through the capillary zone and the unsaturated (vadose) zone. Both zones have the ability to limit the diffusive transport of the vapors due to the presence of discontinuous lenses of low permeability material.

Also, when site-specific information is not known, health-protective assumptions must be made in the BHHRA that may over estimate risk results. These assumptions will be identified and discussed in the BHHRA.

7.7.3 Toxicity Uncertainty

In some cases, it may be necessary to identify the uncertainty associated with the toxicity information used in the risk assessment process. Although the toxicity information for the BHHRA will be obtained from databases currently available to the regulatory agencies, this information may contain uncertainties that could influence the risk assessment result.

7.8 PRESENTATION OF UNCERTAINTY

At a minimum, uncertainty discussions will qualitatively describe how the uncertainties might be magnified or biased through the risk assessment methods used. According to the USEPA (1989), a qualitative approach is the most practical way to describe uncertainty. However, if adequate information is available, a semi-quantitative approach may be used. Such an approach can provide a potential range of uncertainty and describe the sensitivity of the parameters evaluated for uncertainty.

7.9 SUMMARY AND CONCLUSIONS

A summary of the BHHRA results will be presented that considers risk characterization results, uncertainties, and the risk levels relative to the risk management criteria of the USEPA and Navy and makes conclusions about human health risk at the SSA.

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8.0 ECOLOGICAL RISK ASSESSMENT METHODOLOGY

The primary objective of the RI is to characterize the nature and extent of potential CERCLA contaminants in soil and groundwater at the SSA. The RI will also include an Ecological Risk Assessment (ERA) if completed exposure pathways are identified. Navy policy for conducting ERAs identifies a three-tiered approach that incorporates different levels of complexity (Navy 1999, 2004). This approach consists of the following tiers:

- Tier 1 – Screening Level Ecological Risk Assessment (SLERA),
- Tier 2 – Baseline Ecological Risk Assessment (BERA), and
- Tier 3 – Evaluation of remedial alternatives.

The Tier 1 SLERA corresponds to Steps 1 and 2 of the EPA guidance (EPA 1997a, 2001). Sites identified in Tier 1 as posing potential unacceptable risks proceed to a Tier 2 BERA. The Tier 2 BERA corresponds to Steps 3 through 7 of the EPA guidance. The Tier 2 BERA is more technically rigorous, and much less conservative, than the Tier 1 SLERA. The Tier 2 BERA begins by refining the conservative exposure assumptions employed in Tier 1 and recalculating the risk estimates. This refinement is referred to as Step 3a (Navy 2004).

The objective of the Tier 1 SLERA, Step 1 is to determine if pathways are present that link site contaminants to ecological receptors. Step 1 includes an evaluation of the ecological setting and ecological characterization, identification of preliminary chemicals of potential environmental concern (COPECs), and development of a preliminary CSM. Step 2 is to determine if there are risks to ecological receptors at the site. Step 2 includes risk characterization and uncertainty and data gaps analysis.

The SLERA will identify proposed assessment endpoints, measures of effect for each endpoint, surrogate ecological receptors, literature-derived effects concentrations to estimate risk, and exposure scenarios for each assessment endpoint. Information in existing work plans and ecological risk assessments for other sites at MINS will be consulted to characterize biological conditions, select surrogate ecological receptors, select effects concentrations, and exposure scenarios to maximize continuity with the overall Navy IR program at MINS. Potential ecological risk will be evaluated by comparing soil data with the ecological soil screening levels (Eco-SSL) (EPA 2008b) and the lowest available ecological screening levels from Oak Ridge National Laboratory (Efroymson and others 1997a, 1997b) or Talmage and others (1999). Conservative assumptions will be used, including using the maximum detected soil and groundwater concentrations and a Site Persistence Factor (SPF) of 1.0 (meaning that wildlife will be assumed to spend 100 percent of their time at the site).

Two decision criteria control the outcome of the Tier 1 SLERA: 1) chemical concentrations that exceed the screening criteria used for comparison; 2) existence of a complete exposure pathway from the chemical from the receptor. There must be a complete exposure pathway and chemicals present that exceed the screening criteria in order to present an ecological risk. If a complete exposure pathway exists and chemicals are present that exceed the screening criteria, then a Tier 2, Step 3a refinement will be performed.

Step 3a, if required, includes generating revised ERA hazard estimates, using the soil and groundwater sample results and existing soil sample results that are relevant to ecological exposure at the Site. Because the CalEPA/DTSC soil interval of interest is 0 to 6 feet bgs for ecological receptors such as burrowing mammals, burrow-dwelling birds, and deep-rooting plants, soil sample results from greater than 6 feet bgs will not be used. A current site-wide exposure point concentration (EPC) will be estimated for each detected chemical, based on the 95% UCL on the mean, estimated using USEPA's ProUCL statistical software (USEPA, 2013). For groundwater data, a 95% UCL EPC will also be estimated and used as the EPC. In addition, realistic SPFs for modeled wildlife exposure will be used, based on the site area divided by the home range of the receptors. If inorganic hazard drivers are identified as COPECs, statistical comparisons to site-specific background will be performed, including the use of available background threshold values, as well as the performance of two-population statistical tests as available in ProUCL. Other Step 3 components will be to research any COPEC drivers that may have elevated risk, to make sure the most appropriate exposure and toxicity data are being applied. If Step 3 results in unacceptable ecological hazards, a risk management decision will be reached among all stakeholders as to whether further ERA work, including Steps 4 through 7 (as well as Risk Management Step 8) is warranted.

8.1 ECOLOGICAL SETTING AND SPECIAL STATUS SPECIES

The specific purpose of the ERA is to evaluate whether COPECs in surface soils or groundwater pose potential unacceptable risk to plants, terrestrial invertebrates, amphibians, and upper-trophic level species at the site. Ruderal plant communities are present at MINS, consisting primarily of sweet anise (*Foeniculum vulgare*), bristly ox-tongue (*Picris echioides*), willow herb (*Epilobium sp*.), scotch broom (*Cytisus scoparius*), common winter cress (*Barbarea vulgaris*), Russian thistle (*Salsola tragus*), vetch (*Vicia* sp.), oats (*Avena* sp.), hare barley (*Hordeum murinum ssp. leporinum*), coyote bush (*Baccharis pilularis*) and similar upland plants. The ruderal community is utilized by a variety of mammals including house mice, raccoons, opossums, jackrabbits, squirrels, skunks, and rats.

Wetland habitats within the SSA consist of tidal areas that support coastal salt marsh vegetation, which rotationally provide open water, mudflat and pickleweed marsh habitat. The tidal marsh areas and surrounding lands on MINS provide habitat for special-status species including the Salt Marsh Harvest Mouse (*Reithrodontomys raviventris*), California Clapper Rail (*Rallus longirostris obsoletus*), and a rare plant, California Mason's lilaeopsis (*Lilaeopsis masonii*).

8.2 ECOLOGICAL CONCEPTUAL SITE MODEL

The area comprising the SSA remains the property of the U.S. Navy and is not currently in use. However, future plans for the site include transfer of the property from Navy control. Based on the Mare Island Specific Plan (City of Vallejo, 2008), the current reuse planned for the SSA includes redevelopment as a recreational area (park) and a wildlife preserve (Weston, 2011).

Recognizing the potential for exposure, and the potential for the presence of COPEC, a preliminary ecological CSM is provided as Figure 8-1. The preliminary model includes the receptors that have been observed or may be present in the upland and wetland areas of the SSA that will be addressed during the risk assessment. In the upland areas, the preliminary model includes non-burrowing birds and mammals (Western meadowlark, northern harrier, ornate shrew, and gray fox) that may have potential for exposure to surface and shallow soils (0 to 0.5 feet), and burrowing receptors (California vole or California ground squirrel) that may be exposed to deeper soils (0-6 feet). For the wetland areas, plants, macro-invertebrates, birds, and mammals (mallards, salt marsh, harvest mouse, and gray fox) are considered as receptors for potential COPECs in shallow soils and sediments (0 to 0.5 feet bgs) in the marsh or tidal areas of the SSA. Example wildlife dose calculation parameters for COPEC exposure and a COPEC dose equation are presented in Table 8-1.

As very little information is currently known regarding the nature and extent of COPEC, this model will be re-evaluated and updated with information obtained during the RI to provide a more complete understanding of the ecological exposure. In addition, observations of plant and animal receptors made during biological monitoring of RI field activities may also be used to refine and update the Conceptual Site Model used for the evaluation of exposure pathways at the SSA.

8.3 CHEMICAL STRESSORS AND SELECTION OF COPECS

The soil sampling elements of the RI will focus on assessing the potential presence of chemical contaminants in vadose zone soils based on information regarding past uses/activities at a given location and/or the results of previous investigations. Analytical methods were selected for the proposed soil investigation and sampling locations to obtain the chemical information needed for making decisions on each site.

Target analytes at the various soil investigation locations within the SSA include, VOCs, SVOCs (including PAHs), TPH-g, TPH-d/mo, PCBs, metals, and dioxins/furans. Currently, no groundwater monitoring wells are present in the SSA. RI activities include the installation of nine groundwater monitoring wells. The groundwater samples collected from all nine wells during the RI will be analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d/mo, PCBs, metals, and dioxins/furans. Each detected target analyte, and for inorganics, those that have a maximum detected concentration above established background concentrations, will be considered a COPEC and will be evaluated in the ERA.

8.4 TOXICITY ASSESSMENT

The purpose of the toxicity assessment is to identify current and relevant toxicity criteria and information for the identified COPECs necessary to quantify potential ecological impacts. Specific toxicity values are developed, published, and updated by regulatory agencies for many compounds. The toxicity assessment and toxicity reference values (TRVs) used in the quantitative estimation of ecological risk will be obtained from, but will not be limited to, the following primary sources (in order of preference):

- TRVs recommended by EPA Region 9 Biological Technical Assistance Group (2002 and 2009 and DTCS Eco Note 4 (2000)
- USEPA *Guidance for Developing Soil Based Ecological Soil Screening Levels (Eco-SSLs),,* OSWER Directive 9285.7-555. (USEPA, 2005). With chemical-specific documents and TRVs available online at http://www.epa.gov/ecotox/ecossl/pdf/ecosslLos Alamos National Laboratory database that has recommended TRVs (2014)

ORNL Toxicological Benchmarks (TRVs) for Wildlife, ES/ER/TM-86/R3, Oak Ridge National Laboratory (ORNL) Health Sciences Research Division, Oak Ridge Tennessee (ORNL 1996).In the event that toxicity information is not available for specific chemicals, the identification of toxicity surrogates may be necessary. If additional surrogates are necessary, they will be identified and discussed in the ERA portion of the RI Report.

8.5 EXPOSURE ASSESSMENT

As part of the Tier 1 SLERA approach, an exposure assessment will be conducted to estimate the exposure of ecological receptors at the SSA to potential chemical stressors. For plants and invertebrates, exposure occurs primarily via direct contact with soil. For plant and invertebrate receptors, the estimated 95% UCL of the mean EPC of each COPEC from the soil samples collected from the 0 to 0.5 feet bgs depth interval will be used to assess exposure.

For small birds and small mammals, the SLERA will include food chain models to evaluate the exposure to COPECs ingested in food especially for those chemicals that have a potential for bioaccumulation, or incidentally during other activities, such as preening or grooming. The food chain models will focus on the ecological receptors that represent the main feeding guilds that are expected to occur at the site (e.g., carnivores, omnivores, herbivores). The estimated 95% UCL of the mean EPC of each COPEC from the soil samples collected from 0 to 0.5 feet bgs will be used in the food chain models for all vertebrate receptors, with the exception of the burrowing mammal (California vole or California ground squirrel) in which case the 0 to 6 feet bgs sample results will be used. Estimated COPEC concentrations in prey will be based on the soil (or sediment) concentrations and a bioaccumulation factor (BAF). The hierarchy of BAF selection will be as follows: (1) site-specific BAFs derived from other investigation areas at Mare Island (TetraTech, 2002b, where available), or (2) literature regression equations that scale with COPEC concentration, literature point values, or literature log Kow estimated values for

organics. Recommended site-specific BAFs for plants, terrestrial and aquatic invertebrates, and small mammals as applied at Investigation Area F1 (IA F1), adjacent to the SSA (TetraTech, 2002b), are summarized in Table 8-2. If site-specific BAFs are not available for a COPEC or medium, then literature-based BAFs will be used, with examples presented in Tables 8-3 through 8-6.

The total exposure from ingestion for each receptor of concern will be calculated as the sum of dietary exposure. For this calculation, the exposure for a given receptor will be calculated using the standard wildlife oral dose equation for soil or sediment ingestion as recommended in the EPA Wildlife Exposures Factors Handbook (EPA, 1993). Examples of the dose equation and input parameters for several ecological receptors anticipated at the SSA are summarized in Table 8-1.

8.6 RISK CHARACTERIZATION

Risk characterization integrates the results of the exposure assessment and the effects assessment, and is subject to the uncertainties associated with both of these assessments. Risk characterization includes estimation of risk (i.e., HQs) and evaluation of additional lines of evidence important for interpreting the risk results.

8.7 SUMMARY AND CONCLUSIONS

A summary of the ERA results will be presented that considers risk characterization results, uncertainties, the risk levels relative to the risk management criteria of the USEPA and Navy, and makes conclusions about ecological risks at the SSA.

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9.0 RADIOLOGICAL RISK MODELING AND MEC HAZARD ANALYSIS

In addition the Human Health and Ecological Risk Assessments, radiological risk modeling and MEC Hazard Analysis will be conducted as part of the RI. Brief descriptions of the overall approach and methods that will be used to conduct these assessments are provided in the subsections that follow. The results of the radiological risk modeling and MEC Hazard Analysis will be evaluated and described in detail in the RI Report.

9.1 RADIOLOGICAL RISK ASSESSMENT – RESRAD MODELING

Assessment of the risks associated with potential exposure to Radium 226 will be estimated using the RESidual RADioactivity (RESRAD) v6.5 model. This model was developed at the Environmental Science Division of the Argonne National Laboratories for the U.S. Department of Energy (DOE) and the U.S. Nuclear Regulatory Commission (NRC). Version 6.5 was developed in October 2009 (DOE, 2009). RESRAD 6.5 is a multifunctional model that allows consideration of site-specific factors in evaluating exposure types and scenarios.

A detailed description of the RESRAD model and the general approach that will be used to evaluate the radiological risks are provided in the Work Plan for Radiological Screening and Survey Activities (RSRS and NOREAS, 2014). The results of the RESRAD modeling and radiological risk assessment will be included in the RI report.

9.2 MEC HAZARD ANALYSIS

A MEC Hazard Assessment (HA) will be prepared for the SSA as part of the RI in accordance with the latest EPA guidance (EPA, 2008) using the MEC Hazard Assessment Workbook version 1.02 dated December 2007. Information on past munitions removal actions (including the current NTCRA) such as type of clearance, clearance depth, etc., and details of the recovered MEC items will be entered into the MEC HA spreadsheet template.

Other input parameters will include the current and anticipated future land use options, together with estimates of the number of man-hours per year that the site will be utilized for each type of activity. Site specific background information that will be entered into the HA spreadsheets that will be used to calculate MEC hazard scoring data for selected response actions that will be included in preparation of the Feasibility Study (FS).

9.3 SUMMARY AND CONCLUSIONS

A summary of the RESRAD and MEC HA results will be presented that considers risk characterization results, uncertainties, and the risk levels relative to the risk management criteria of the USEPA and Navy and makes conclusions about these risks at the SSA.

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10.0 RI REPORT

Following the completion of the RI field activities, an RI Report will be prepared describing the results of the investigation. In particular, at a minimum the report will include detailed descriptions of the following:

- Project and Site Background
- Evaluation of all Buildings, SWMUs, and PCB sites in the SSA
- Investigation methods and procedures
- Results of soil and groundwater sampling activities
- Results of radiological MARSSIM survey and NTCRA results (conducted under separate RAD WP)
- Nature and extent of potential contaminants
- Updated CSM
- QA/QC results
- Risk assessments to include:
  - HHRA
  - Ecological Risk Assessment
  - MEC Hazard Analysis (MEC HA)
  - Residual Radiation by RESRAD Modeling
- Conclusions and Recommendations

In addition, the results of the RI will be used to either support closure recommendations or provide the basis for further actions with respect to those sites that currently remain open under CERCLA, RCRA (SWMUs), UST, or other regulatory programs.

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11.0 REFERENCES

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TABLES

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TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
BUILDINGS				
Bldg. A153	Sewer Pump Station	Built in 1931, Building A153 is a 270 SF corrugated metal building attached to the east side of Pier 35, south of Building A194. The building set on wooden piers and directly overlies the water of Carquinez Strait. Historically, this building was used as a sewer pump station, but is currently boarded up and not in use. Building A153 was not included in the 1995 PA/SI. Assessments conducted as part of the TSCA program between 1997 and 2003 did not reveal any historical documents or other evidence indicating that sources of PCBs existed in the building, but did confirm the presence of two pumps. Two swipe samples were collected from the pumps in 1997 and were analyzed for PCBs. The analytical results indicated that PCBs were not detected at or above the reporting limit of 5 micrograms (µg)/swipe. Building A153 was closed for PCBs under the TSCA program on February 14, 2013.	No further Action for PCBs, (closed under TSCA on February 14, 2013).	Final PCB Site Closure Report for Building A153 (ERS-JV, 2013b)
Bldg. A161	Magazine	Built in 1934, Building A161 is a 5,151 SF concrete munitions magazine with a steel roof. At the time of the preliminary assessment (1995), the building was used for storage of inert materials in cardboard boxes on wooden pallets. No tanks, sumps, floor drains, or air emission controls were associated with the magazine. The floor was clean with no visible cracking at the time of inspection. No known spills or releases are known to have occurred inside or outside this building. No indication for the use of PCBs was identified but Building A161 was investigated under the TSCA program. PCBs were not detected in samples above 1.0 mg/kg and Building A161 was closed under the TSCA program on October 30, 2012.	No Further Investigation or Action Recommended in PA Final Summary Report No further Action for PCBs, (closed under TSCA on October 30, 2012)	Preliminary Assessment Final Summary Report Ordnance Sites (PRC, 1995a) Final PCB Site Closure Report for Building A161 (ERS-JV, 2012a)

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS
FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
Bldg. A162	Magazine	Built in 1934, Building A162 is a 5,151 SF concrete munitions magazine, with a steel roof. At the time of the preliminary assessment (1995), the building was used for storage of inert materials in cardboard boxes on wooden pallets. No tanks, sumps, floor drains, or air emission controls were associated with the magazine. The floor was clean with no visible cracking at the time of inspection. No known spills or releases are known to have occurred inside or outside this building. Assessments conducted as part of the TSCA program between 1997 and 2003 did not reveal any historical documents or other evidence indicating that sources of PCBs existed in the building, though several oil stains were noted on the concrete floor of the building during the initial PCB survey in 1997. Three exploratory concrete samples were collected from the stained areas. PCBs were not detected above the 1.0 mg/kg reporting limit in any of the three concrete samples. Building A162 was closed under the TSCA program on March 7, 2013	No Further Investigation or Action Recommended in PA Final Summary Report No further Action for PCBs, (closed under TSCA on March 7, 2013)	Preliminary Assessment Final Summary Report Ordnance Sites (PRC, 1995a) Final PCB Site Closure Report for Building A162 (ERS-JV, 2013c)
Bldg. A163	Magazine	Built in 1934, Building A163 is a 5,151 SF munitions magazine constructed of concrete with a steel roof. At the time of the preliminary assessment (1995), the building was used for storage of inert materials in cardboard boxes on wooden pallets. No tanks, sumps, floor drains, or air emission controls were associated with the magazine. The floor was clean with no visible cracking at the time of inspection. No known spills or releases are known to have occurred inside or outside this building. Assessments conducted as part of the TSCA program between 1997 and 2003 did not reveal any historical documents or other evidence indicating that sources of PCBs existed in the building. No visual evidence of staining was observed during the initial PCB survey in 1997 and subsequent Data Gap Assessment 2007. Building A163 was closed under the TSCA program on March 7, 2013	No Further Investigation or Action Recommended in PA Final Summary Report No further Action for PCBs, (closed under TSCA on March 7, 2013)	Preliminary Assessment Final Summary Report Ordnance Sites (PRC, 1995a) Final PCB Site Closure Report for Building A163 (ERS-JV, 2013d)

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
Bldg. A164	Ordnance Warehouse	Building A164 is a 5,151 SF concrete building, constructed in 1934 as an ordinance warehouse. The building was divided into three compartments that were empty at the time of the preliminary assessment (1995). One compartment appears to have been an office. No tanks, sumps, floor drains, or air emission controls are associated with this building. No known spills or releases are known to have occurred in or outside the building.	No Further Investigation or Action Recommended in PA Final Summary Report	Preliminary Assessment Final Summary Report Ordnance Sites (PRC, 1995a)
Bldg. A165	Magazine	Building A165 is a 5,151 SF brick building with a corrugated steel roof. The building was constructed in 1934 as an ordinance warehouse. At the time of the preliminary assessment (1995), the building was used for storage of materials such as expired lube oils and cleaners. No tanks, sumps, floor drains, or air emission controls were associated with the building, although asbestos may be present. No known spills or releases are known to have occurred inside or outside of the building.	No Further Investigation or Action Recommended in PA Final Summary Report	Preliminary Assessment Final Summary Report Ordnance Sites, September 1995 (PRC, 1995a)
Bldg. A169	Magazine	Building A169 is an 8,211 SF concrete building constructed in 1934. The concrete floor of the building rests on concrete piles. The building was used for ocean engineering storage before its most recent use as storage for Material Documented as Safe (MDAS) from the IR Site 05 removal action. At the time of the preliminary assessment (1995), the building had been cleaned and railroad tracks that once led up to the building had been removed. Building A169 is currently being used to store MDAS and other inert metallic debris recovered during the current MEC NTCRA at the SSA. Two transformers are associated with Building A169, one pad-mounted unit and one pole-mounted unit, both which were located outside the building. The pad-mounted transformer was removed in November 1992, but the pole-mounted transformer remains in place and is currently in active use. PCBs were not detected above the action level of 1.0 mg/kg. Building A169 was closed under the TSCA program on September 13, 2012.	No Further Investigation or Action Recommended in PA Final Summary Report No further Action for PCBs, (closed under TSCA on September 13, 2012)	Preliminary Assessment Final Summary Report Ordnance Sites (PRC, 1995a) Final PCB Site Closure Report for Building A169 (ERS-JV, 2012b)

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
Bldg. A193	Mine Anchor Facility Annex (associated with A259)	Building A193 was not specifically addressed in the 1995 PA Final Summary Report for Ordnance Sites (PRC 1995a) as it was likely demolished prior to 1995. Older site figures indicated that A193 located SW of Building A164, but is no longer depicted on current Base maps. Information contained within Table 3-1 of the Conceptual Site Model (CSM) indicates that activities at A193 were associated with the Mine Anchor Assembly and Advanced Weapons Container Maintenance operations conducted at Building A259. Building A193 was demolished some time prior to 1995.	Not addressed under PA – no prior recommendations Investigation of Bldg. A193 is planned under the RI. (See Table 4-2).	Revised Conceptual Site Model Production Manufacturing Area and South Shore Area (Weston, 2008)
Bldg. A194	Smoke Shack	Building A194 is a 1,392 SF building, constructed in 1942, located at the southern tip of filled land leading to Pier 35. Information contained in Table 3-1 of the revised CSM indicates that the building was used as a designated smoking area (Smoke Shack) where crews loading/unloading ordnance could smoke without endangering ordnance operations. No known spills or releases are known to have occurred inside or outside the building. An investigation was undertaken in 1991 in an attempt to locate three suspected USTs in the vicinity of Building A194. A geophysical survey was conducted and two soil samples were collected from the suspected area, SE of the building. The geophysical survey did not find evidence for the USTs and no chemical contaminants were detected in the soil samples. RWQCB granted closure for suspected T-194 in 2011. Five PCB-containing transformers were once located within the building, three of which were documented as leaking. As a result, all five of the transformers inside Building A194 were removed between 1987 and 1992. One dry transformer, located in the shed, remains active as of February 2013. After completion of several abatement and verification sampling events in 2010 and 2013, all of the verification sample results were reported below 1.0 mg/kg. Building A194 was recommended for closure under the TSCA program on March 20, 2013.	No Further Investigation or Action Recommended in PA Final Summary Report No Further Action Letter for Tank T-194 issued on October 1, 2009 (RWQCB, 2009a). No further Action for PCBs, (closure under TSCA recommended on March 20, 2013)	Preliminary Assessment Final Summary Report Ordnance Sites (PRC, 1995a); Revised Conceptual Site Model PMA and SSA(Weston, 2008); Draft PCB Site Closure Report for Building A194 (ERS-JV, 2013e)

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
Bldg. A195	Ordnance Segregation	Building A195 is an 8,874 SF concrete building with a steel roof and concrete floor. Historically, Building A195 was used to segregate munitions, high explosive items, bomb cabling, and other various ordnance items and related items. The building was equipped with an overhead rail system that included four monorail crane hoists (PRC 1995a). At the time of the PA in 1995, the building was used by the Defense Reutilization and Marketing Office (DRMO) to store hazardous wastes. The hazardous waste storage area of the building was regulated as a Solid Waste Management Unit (SWMU) under a RCRA Part A permit administered by Cal/EPA DTSC. Additional information about hazardous wastes stored at A195 is provided under the description for SWMU 91 below. No indication, evidence, or documentation of potential releases has been reported at this facility.	No Further Action or Investigation Recommended for ordnance-related activities. See SWMU 91.	Preliminary Assessment Final Summary Report Ordnance Sites (PRC, 1995a) See SWMU 91.
Bldg. A227	Transformer House	Building A227 is an 81 SF concrete building, constructed in 1943 to house an electrical transformer. No information regarding the condition of the transformer with respect to potential leaks or releases was provided in the PA Final Summary Report (PRC 1995a). One transformer was located inside the building but was removed in 1992. A second pad-mounted transformer and related rocker arm are located approximately 4 feet northeast of the building and remain active as of March 2013. Concrete samples were collected for PCBs on several occasions between 1997 and 2010. All of the sample results were reported below 1.0 mg/kg. Building A227 was recommended for closure under the TSCA program on March 20, 2013	Investigation for PCBs was recommended in in PA Final Summary Report No further Action for PCBs, (closure under TSCA recommended on March 20, 2013)	Preliminary Assessment Final Summary Report Ordnance Sites (PRC 1995a) Draft PCB Site Closure Report for Building A227 (ERS-JV, 2013f)

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS
FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
Bldg. A259	Mine Anchor Assembly and Advanced Weapon Container Maintenance	Building A259 is an 8,670 SF concrete building, constructed in 1943. The building was used to assemble mine anchors and renovate advanced weapons containers. It is separated into four rooms and was equipped with an air compressor and air conditioning room for mine testing equipment. One room was identified as an old boiler room. Six walk-in refrigerator units were located in the rear of the building for storing mine batteries and there was evidence for the use/storage of mercury at this location. No floor drains were observed in the building during the preliminary assessment. A 1,000 gallon UST used to store diesel was once located near the west side of the building. The UST was removed in 1990. No additional information regarding this tank was provided in the PA report. Refer to the UST section below for the description of the UST disposition.	Additional characterization (soil sampling) under UST program recommended in 1995 PA. See UST section below.	Preliminary Assessment Final Summary Report Ordnance Sites, September 1995 (PRC, 1995a)
Former Bldg. A292	Scale House	Building A-292 was a 70 SF building that housed a mechanical truck scale. The date of construction is unknown. The building was demolished sometime after the PA was completed although the exact date of its removal is unknown. No indication, evidence, or documentation of potential releases has been reported at this facility. A 420-gallon fuel oil/diesel UST was once located in the vicinity of Building A292, approximately 40 feet northwest of Building A292. The UST was removed in December 1997.	No Further Investigation or Action Recommended See UST section below.	Preliminary Assessment Final Summary Report Ordnance Sites, September 1995 (PRC,1995a)
Structure A296	High Explosive Safe Haven	Indicated as High Explosives Safe Haven in Table 3-1 of the CSM (Weston, 2008), though it was not addressed or indicated in the PA (PRC 1995a). Constructed in 1941, A296 consists of two 5-sided trapezoid-shaped concrete structures that open outward to the west, closed to east by dirt mound. Built wide enough to accommodate 2 sets of railroad tracks and designed as temporary parking for rail cars loaded with explosives. Railroad tracks removed in the 1970's.	No prior recommendations. Investigation planned under the RI. (See Table 4-2).	Revised Conceptual Site Model PMA and SSA (Weston, 2008)

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS
FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
		A 420-gallon fuel oil/diesel UST was once located approximately 3 feet east of Structure A296. The UST was removed in January 1998.	See UST section below.	Removal Summary Report for Underground Storage Tank Site A-296 (SSPORTS, 1998)
SWMUs				
SWMU 91	Container Storage Area	This SWMU was a general hazardous waste container storage area located within Building A-195. Wastes managed at this site included halogenated and non-halogenated solvents, flammable liquids, and corrosive liquids. Building A195 had been used to store hazardous wastes for at least 7 years, prior to 1995. Eight concrete bermed storage areas were observed during the site inspection in 1995, each approximately 15 feet by 30 feet (PRC 1995b). Containerized hazardous wastes were properly identified, packed, and labeled, and placed in the bermed cells. The floor was sealed concrete. No record of spills occurring at this site was found, going back to 1988 when records were first kept. The SWMU was closed in 2011.	No further CERCLA action recommended at this SWMU in PA/SI. SWMU 91 closed on 8/17/2011 (DTSC, 2011a).	Preliminary Assessment/Site Inspection Final Summary Report Non-Radiological Sites (PRC, 1995b)
SWMU 93	Storm/Sewer Outfalls	The domestic sanitary sewer system and storm sewer system were completely combined until 1959 and remained partially connected until 1972. Some of the industrial facilities that discharged to the storm sewer prior to 1972 included sheet metal operations (Bldgs. 52 and 116), the boiler shop acid tanks (Bldg. 814), the plating shop sump (Bldg. 225), the dip tanks at Building 900, the inside machine shop (Bldg. 680), and the center tool shop (Bldg. 678). Hazardous wastes that were likely discharged through the storm sewer system include solvents, coolants, oils, mercury, lead acids, and paint strippers. Rinse waters from sheet metal operations would have contained metal cleaning solutions, etching solutions, chromic acid, caustic soda, metal brightening compounds, and rust inhibitors.	Further investigation for VOCs, SVOCs, oil and grease, metals, and PCBs. Investigation planned under the RI. (See Table 4-2).	Preliminary Assessment/Site Inspection Final Summary Report Non-Radiological Sites (PRC, 1995b)

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS
FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
SWMU 101	Concord Annex Ordnance and Additional Sites	No specific information regarding these sites in the SSA was indicated in the PA/SI report, refers to numerous sites throughout MINS. PA/SI refers back to the PA for Ordnance sites to identify those areas or buildings that were considered under this SWMU. Information provided in the PA/SI Report indicates that contaminant-related ordnance sites should be investigated under the Navy's Installation Restoration Program under SWMU 101, although it notes that the primary area of concern is the ordnance production area or PMA (PRC, 1995b).	Table 6-1 in PA/SI Final Summary Report recommends investigation for contaminant-related ordnance sites under the IR Program. Also indicates that the PMA is primary area of concern for this SWMU. Planned investigations at MEC sites under RI will be used to address contaminant issues at SWMU 101 in the SSA.	Preliminary Assessment/Site Inspection Final Summary Report Non-Radiological Sites (PRC, 1995b)
SWMU 106	Sanitary Sewer System	No specific information in the PA/SI report, refers to numerous locations throughout MINS. The sanitary sewer line extends a distance of approximately 1,800 feet within the SSA, running generally parallel to the shoreline.	No further CERCLA action recommended at this SWMU in PA/SI. But investigation of sewer system under non-CERCLA BRAC compliance program recommended.	Preliminary Assessment/Site Inspection Final Summary Report Non-Radiological Sites (PRC, 1995b)

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS
FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
			Investigation planned under the RI. (See Table 4-2).	
SWMU 125	South End of Island	No specific information regarding these sites in the SSA was indicated in the PA/SI report, refers to numerous sites throughout MINS. PA/SI refers back to the PA for Ordnance sites to identify those areas or buildings that were considered under this SWMU. Information provided in the PA/SI Report indicates that contaminant-related ordnance sites should be investigated under the Navy's Installation Restoration Program under SWMU 125, although it notes that the primary area of concern is the ordnance production area or PMA (PRC, 1995b).	Table 6-1 in PA/SI Final Summary Report recommends investigation for contaminant-related ordnance sites under the IR Program. Also indicates that the PMA is primary area of concern for this SWMU. Planned investigations at MEC sites under RI will be used to address contaminant issues at SWMU 101 in the SSA.	Preliminary Assessment/Site Inspection Final Summary Report Non-Radiological Sites (PRC, 1995b)

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS
FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
HISTORICAL MEC SITES				
N/A	MEC Items – Various Locations	Various MEC items were recovered from the SSA during multiple removal actions and intrusive investigations between 1990 and 2006, including fuses and primers, gun ammunition larger than .50 caliber, high explosives, and miscellaneous explosive devices and hazards. More than 5,000 pounds of MEC items were removed near Dike 14 during the 1990 removal actions. Refer to Figure 4-2 for the approximate locations of the MEC items recovered during the 1990 emergency removal actions. Based on the findings of previous UXO/MEC investigations and removal actions, a digital geophysical mapping (DGM) investigation was conducted at the SSA in 2006. Based on the DGM results, a total of 14, 324 geophysical anomalies were identified in the SSA. Based on the results of the DGM investigation, a MEC Non-Time Critical Removal Action (NTCRA) was conducted between May 2012 and July 2013. A total of 358 MEC items were recovered from the SSA predominantly consisting of propellants and small arms ammunition. In addition, a total of 8,832 items classified as MDAS (including 3,878 expended small arms ammunition items) were also recovered during the NTCRA activities at the SSA. A total of 8 debris/disposal pits containing munitions items and other metallic debris were identified in several DGM Grids, one of which was not fully delineated during the NTCRA. A total of six soil samples were collected from several representative locations where MEC items were recovered. The samples were analyzed for energetics and metals. No energetics were detected, all metals were reported in concentrations below their respective screening or ambient concentrations. In addition to MEC items, buried drums and underground storage tanks were uncovered in several locations during the NTCRA excavation activities. Some sampling was conducted as described in Section 2.4.8. Additional investigation of several areas planned as described in Section 4.1.5.	No prior recommendations for CERLCA contaminants. Multiple sites to be addressed during the RI. No recommendations for CERCLA contaminants. No recommendations for CERCLA contaminants. Investigation of MEC sites and other areas where tanks and drums were uncovered is planned under the RI. (See Table 4-2).	Draft Final UXO Intrusive Investigation Summary Report (Weston, 2003) Final Investigation Summary Report for MEC at Mare Island Strait and Carquinez Strait (ECC, 2010) Final Geophysical Investigation PMA and SSA (Weston, 2008) Final Removal Action Completion Report for the Non-Time Critical Removal Action at the PMA and SSA (Battelle, 2014 and ISR-JV, 2014)

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
FORMER UST SITES				
UST A195	UST (Water Board Case No. 48D9240)	A 1,000 gallon diesel UST for heating Building A195 was removed from the northwest corner of the building in 1990. Information contained in the 1995 PA indicates that the tank had a 500-gallon capacity and may also have contained solvents. Soil samples were collected adjacent to the UST in 1988, before the tank was removed, and again in 1990, after the excavation. Samples were analyzed for TPH (diesel and motor oil) compounds and BTEX. All constituent concentrations were reported below detection limits. This UST case is also listed as being closed on October 5, 2009 on the RWQCB GeoTracker on-line database http://geotracker.waterboards.ca.gov/profile_report.asp?global_id=T0609592452	Closed as a Low-Risk Fuel Site on October 1, 2009 - No Further Action Required	SFB Water Board Case Closure and Site Closure Summary Letter dated October 1, 2009 GeoTracker website, GeoTracker ID#T0609592452
UST A259	UST (Water Board Case No. 48D9248)	A 1,000 gallon UST used to store diesel was located near the west side of building A259. The tank was removed in July 1990. This UST case is listed as being closed on December 20, 2004 on the RWQCB GeoTracker on-line database. http://geotracker.waterboards.ca.gov/profile_report.asp?global_id=T0609592455	Closed on December 20, 2004 - No Further Action Required	GeoTracker website, GeoTracker ID#T0609592455
UST A292	UST (Water Board Case No. 48D9250)	A 420 gallon fuel oil/diesel UST that was located in the vicinity of Building A292. The tank was removed on December 17, 1997. This tank was not mentioned in the information summary of the PA report (PRC 1995a). Based on comments on the closure summary report for this site, one soil sample was collected below the tank excavation and analyzed for TPH-d, TPH-mo, and BTEX. None of these compounds were reported as being detected above their respective reporting limits. This UST case is listed as being closed on December 5, 2006 on the Water Board	Closed on December 5, 2006 - No Further Action Required	SFB Water Board Case Closure and Site Closure Summary Letter December 5, 2006 GeoTracker website,

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS
FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
		GeoTracker on-line database. http://geotracker.waterboards.ca.gov/profile_report.asp?global_id=T0609592457		GeoTracker ID#T0609592457
UST A296	UST (Water Board Case No. 48D9251)	A 420 gallon fuel oil/diesel UST that was located adjacent to Structure A296. The tank was removed on January 9, 1998. The history of the tank is unknown but it was not connected to the shipyards fuel oil line system. Two soil samples were collected following the removal of the tank. One sample was collected from below the tank invert at approximately 4 feet bgs, another composite sample was collected from the excavation spoils piles. Both samples were analyzed for TPH-d, benzene, toluene, ethylbenzene, and xylenes (BTEX). None of the analytes were detected at or above the reporting limits in either sample. This UST case is listed as being closed on October 29, 2009 on the RWQCB GeoTracker on-line database. http://geotracker.waterboards.ca.gov/profile_report.asp?global_id=T0609592458	Closed on October 22, 2009 - No Further Action Required	SFB Water Board Case Closure Letter dated October 22, 2009 GeoTracker website, GeoTracker ID#T0609592458

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
PRIMER/OVEN PITS				
N/A	Primer Pit, Oven Pit 1, and Oven Pit 2	During excavation and screening for the two emergency UXO removal activities in 1990, three distinct areas were observed where discolored soil and the condition of the debris suggested that ordnance was disposed by burning in these locations. These areas were identified as the Primer Pit, Oven Pit 1, and Oven Pit 2. As a result of these observations, confirmation sampling specifically for copper, lead, and zinc was conducted to confirm that impacted soils associated with the disposal of MEC/UXO items in the burn pits were successfully removed. A total of 567 cubic yards of impacted soil mixed with ordnance-related and other metallic debris was removed from the Primer Pit (548 cubic yards), Oven Pit 1 (14.4 cubic yards), and Oven Pit 2 (4.2 cubic yards) areas. A total of 142 soil and 7 groundwater samples were collected from within and around the pits. Ultimately, soil from 48 of these soil sampling locations was excavated and removed. The remaining 94 samples represent sampling locations outside of the excavations. Average concentrations of copper, lead, and zinc were calculated from the results of those samples collected outside the excavations and were compared to Base-wide ambient concentrations and 1996 PRGs. The maximum concentrations of copper and zinc in the surface and subsurface samples were reported above their respective ambient values. The maximum concentration of lead in the subsurface samples was reported above its ambient concentration.	Appendix D of UXO Intrusive Investigation Summary Report recommends addition soil removal in localized area SW of Primer Pit to reduce risk based on elevated copper result for surface soil as reported in one sampling location. Additional sampling planned as part of the RI. (See Table 4-2)	Appendix D of UXO Intrusive Investigation Summary Report, (Weston, 2003).

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
OTHER AREAS (Buried Drums and USTs Found During MEC NTCRA)				
DGM Grid AI015	55-gallon drums	Six 55-gallon drums (tops with small corrosion holes, vertical, 1 foot bgs) were found in DGM Grid AI015 of the SSA in July 2012 during the excavation and MEC removal action under the MEC NTCRA. Two composite samples were collected, one from the soil within the drums and another from below the drums. The composite samples were analyzed for metals and dioxins/furans. The results of the composite samples for metals were reported within range of ambient concentrations; TEQ values for dioxins/furans below residential RSLs. Following the removal of the drums, six discrete soil samples were collected in from the bottom of the excavation below the drums for VOCs and organochlorine pesticides. Trace concentrations of several VOCs and pesticides were detected in the samples but all of the results were reported several orders of magnitude below their respective residential RSLs. Five additional drums found in grid AI015 in May 2013 and removed. One soil sample was collected from beneath the drums and analyzed for VOCs, SVOCs, TPH, PCBs, and metals. Based on the results, VOCs, SVOCs, TPH, and PCBs were not detected. All metals reported below residential RSLs or background levels.	No prior recommendations. No additional investigation of this area is planned as part of the RI.	Final Removal Action Completion Report for the NTCRA at the PMA and SSA (Battelle, 2014 and ISR-JV, 2014)

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
DGM Grid AJ015	USTs	Three buried 2-foot diameter tanks (13 feet in length) found during excavation activities associated with MEC removal action (NTCRA) in October 2012. Two of tanks were connected by a 40-foot run of 5-inch diameter perforated pipe to separate dry wells. A 5-inch diameter solid conveyance line running to the tanks was cut approximately 15 feet south of the tanks during the removal, leaving a run of approximately 120 feet in place. (See Figure 4-6 for detail). Samples of liquids collected from first tank and dry well uncovered were analyzed for TPH-d, TPH-mo, PCBs, and metals. The samples were not analyzed for VOCs at the time.TPH and PCBs were not detected in the liquid samples; lead was reported above EPA & CA MCL of 15 µg/L. After the removal of the tanks, 11 confirmation soil samples were collected for TPH-g, TPH-d, TPH-mo, SVOCs, and metals. TPH-g, TPH-d, and SVOCs (including PAHs) were not detected at or above their respective reporting limits. Trace concentrations of TPH-motor oil were detected in 6 samples, but was not detected in the other five. The analytical results for all of the metals were reported below their respective ambient and residential RSL criteria, except for arsenic. The reported results for arsenic ranged 4.6 mg/kg to 10 mg/kg, above the residential RSL value (0.39 mg/kg), but below the ambient arsenic concentration for MINS (36 mg/kg). Although the tanks and perforated pipe were sampled during the NTCRA, samples were not collected along the route of the 5-inch conveyance pipe that was left in place. Approximately 120 feet of conveyance pipe may still remain in place.	No prior recommendations. Additional investigation of the area where the tanks and dry wells were once located for VOCs and PCBs is planned under the RI. Investigation of the conveyance piping that was left in place is planned under the RI. (See Table 4-2).	Final Removal Action Completion Report for the NTCRA at the PMA and SSA (ISR-JV, 2014)

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature ID #	Feature Description	Comments	Status/Prior Recommendations	Reference
DGM Grid AA009	55-gallon drums	Nine 55-gallon drums were found in DGM Grid AA009 of the SSA in July 2012 during the MEC NTCRA. Following removal of the drums in January 2013, 4 confirmation soil samples were collected from the bottom of the excavation at approximately 6 feet bgs and analyzed for VOCs, SVOCs (including PAHs), TPH-gasoline, TPH-diesel, TPH-motor oil, metals, PCBs, organochlorine pesticides, herbicides, energetics, and dioxins/furans. VOCs, PCBs, organochlorine pesticides, herbicides, and energetics were not detected. Three PAHs were reported in concentrations above their respective residential RSL values (Section 2.4.7). Trace concentrations of several PAHs were detected, though all of the results were reported below residential RSLs. Trace levels of dioxins and furans also detected though the TEQ values were the residential and industrial RSLs for 2,3,7,8-TCDD. In April 2013, another 21 buried drums were recovered. Four additional soil samples were collected and analyzed for VOCs, SVOCs, TPH, and PCBs. All compounds were either not detected or reported in concentrations below their respective residential RSLs.	No prior recommendations. Additional investigation of this area is planned as part of the RI. (See Table 4-2).	Final Removal Action Completion Report for the NTCRA at the PMA and SSA (ISR-JV, 2014)

Notes:

bgs – below ground surface
BRAC – Base Realignment and Closure Program
BTEX – benzene, toluene, ethylbenzene, and xylenes
Cal/EPA – California Environmental Protection Agency
CERCLA – Comprehensive Environmental Response, Compensation, and Liability Act
CSM – conceptual site model
DGM – digital geophysical mapping
DRMO – Defense Reutilization and Marketing Office
DTSC – Department of Toxic Substances Control (Cal/EPA)
EPA – United States Environmental Protection Agency
MCL – Maximum Contaminant Level
MEC – munitions of explosive concern
mg/kg – milligrams per kilogram
PA – Preliminary Assessment
PA/SI – Preliminary Assessment/Site Inspection
PCB – polychlorinated biphenyl
PRG – Preliminary Remediation Goal (US EPA)
RCRA – Resource Conservation and Recovery Act
RSL – Regional Screening Level (US EPA)
RWQCB – Regional Water Quality Control Board (San Francisco Bay Region)
SF – square feet
SFB – San Francisco Bay
SSA – South Shore Area
SVOC – semi-volatile organic compound
SWMU – Solid Waste Management Unit (RCRA)
TSCA – Toxic Substances Control Act
VOC–volatile organic compound
UST – underground storage tank

TABLE 4-1

SUMMARY OF INFORMATION FOR SSA FROM PREVIOUS SITE ASSESSMENTS/INVESTIGATIONS FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

TEQ – toxicity equivalent
MINS – former Mare Island Naval Shipyard
mm – millimeter
N/A – not applicable
NTCRA – Non-Time Critical Removal Action
TPH-d – total petroleum hydrocarbons as diesel
TPH-mo – total petroleum hydrocarbons as motor oil
µg/L – micrograms per liter
UXO –unexploded ordnance

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TABLE 4-2

SUMMARY OF PROPOSED APPROACH TO SOIL AND GROUNDWATER SAMPLING RI AT SOUTH SHORE AREA, FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature Proposed for Investigation	Scope of Proposed Investigation	Analytical Parameters	Basis for Proposed Investigation
Building A193-Associated with Bldg. A259 Mine Anchor Assembly and Advanced Weapons Container Maintenance	Collect soil samples at 3 depth intervals from 2 soil borings located in the former building footprint.	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals	Information provided in the Revised Conceptual Site Model (Weston 2008) indicates that Building A193 was likely associated with the Mine Anchor Assembly and Advanced Weapons Container Maintenance operations at Building A259. Though this building was likely used for storage, limited soil sampling at this location is proposed to address the possibility that hazardous materials were once used or stored at this location.

TABLE 4-2

SUMMARY OF PROPOSED APPROACH TO SOIL AND GROUNDWATER SAMPLING RI AT SOUTH SHORE AREA, FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature Proposed for Investigation	Scope of Proposed Investigation	Analytical Parameters	Basis for Proposed Investigation
Building A195 – Ordnance Segregation/Hazardous Materials Storage	Collect soil samples at 3 depth intervals from 2 soil borings located adjacent to the building.	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals Analysis for selected pesticides will also be included for the 2 near surface samples at 0.5 feet bgs.	Former presence of UST (T-195, removed), boiler, and use as hazardous materials storage as SMWU 91. Although both T-195 and SWMU 91 have been closed under the respective UST and RCRA programs, additional soil sampling is proposed based on the nature and historical activities conducted at the building.

TABLE 4-2

SUMMARY OF PROPOSED APPROACH TO SOIL AND GROUNDWATER SAMPLING RI AT SOUTH SHORE AREA, FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature Proposed for Investigation	Scope of Proposed Investigation	Analytical Parameters	Basis for Proposed Investigation
Building A259 – Mine Anchor Assembly and Advanced Weapons Container Maintenance	Collect soil samples at 3 depth intervals from 4 soil borings located around the building.	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals Analysis for selected pesticides will also be included for 2 of the near surface samples at 0.5 feet bgs.	Information documented in the Preliminary Assessment Final Summary Report (PRC 1995a), indicates that past activities included maintenance of advanced weapons containers, assembly of mine anchors, and storage/maintenance of batteries. The report also indicates the presence of six walk in refrigerator units and a boiler room. Based on this information, the proposed investigation is intended to address potential environmental impacts associated with past use of metal cleaners/metal prep materials (solvents), paints, coolants/refrigerants, fuel oils, and metals (in particular lead and mercury) at Building A259.

TABLE 4-2

SUMMARY OF PROPOSED APPROACH TO SOIL AND GROUNDWATER SAMPLING RI AT SOUTH SHORE AREA, FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature Proposed for Investigation	Scope of Proposed Investigation	Analytical Parameters	Basis for Proposed Investigation
Structure A296-Explosives Safe Haven	Collect soil samples at 3 depth intervals from 2 soil borings from between the berms, where rail cars were once parked.	TPH-g, TPH-d, TPH-mo, and metals Analysis for selected pesticides will also be included for 1 of the near surface samples at 0.5 feet bgs.	The High Explosives Safe Haven was designed to park two sets of railroad cars containing high explosives (Weston, 2008). The structure consists of two 5-sided trapezoid-shaped structures arranged in an elongate east to west orientation and opening outward to the west. The railroad tracks were removed in the 1970s and the eastern opening was bermed with dirt in the 1980s. After the dirt mound was built over the eastern opening, the safe haven was used for temporary parking of vehicles and trucks carrying high explosives. A former fuel oil/diesel UST was located once located just the northeastern of the structure. No further action letter for this UST was granted by the Water Board on October 22, 2009 (Water Board, 2009c). This feature was not specifically addressed under the PA/SI and no additional information regarding historic use at the site was uncovered. Based on the fact that rail cars and other vehicles carrying high explosives (and possibly other hazardous cargos) were historically staged inside the Safe Haven, two soil borings are planned at this location.

TABLE 4-2

SUMMARY OF PROPOSED APPROACH TO SOIL AND GROUNDWATER SAMPLING RI AT SOUTH SHORE AREA, FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature Proposed for Investigation	Scope of Proposed Investigation	Analytical Parameters	Basis for Proposed Investigation
SWMU 93 – Storm/Sewer Drains	Collect soil samples at 3 depth intervals from 11 soil borings located around storm drains found adjacent or near buildings in upland areas. Soil samples from one boring for SWMU 93 (south of A259) will also be used to evaluate former MEC site.	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals	Information provided in the Preliminary Assessment/Site Inspection Report (PRC 1995b) indicates that the domestic sanitary sewer and storm drains at MINS were completely connected until 1959 and remained partially connected until 1972. Additional information indicates that industrial wastes were also discharged through the storm sewer system including solvents, coolants, oils, mercury, lead acids, paint strippers, rinse waters from sheet metal operations, metal cleaning solutions, etching solutions, chromic acid, caustic soda, metal brightening compounds, and rust inhibitors. The proposed scope of investigation is intended to address the concern for impacts of hazardous waste discharges to the soils in the vicinity of the storm drains located near the buildings in the upland areas. This includes a total of 5 storm drains located near Bldgs. A195 (2), A161 (1), A259 (1), and A292 (1). Sediment samples were collected from the SWMU 93 outfall locations (both onshore and offshore) and analyzed for SVOCs, TPH, metals, organotins, PCBs, and pesticides as part of the RI for Investigation Area K (IA K) (Battelle, 2009). The analytical results indicated that all constituent concentrations were consistent with ambient or background concentrations for San Francisco Bay sediments. Therefore, no additional sampling of the outfall locations is planned for the SSA RI.

TABLE 4-2

SUMMARY OF PROPOSED APPROACH TO SOIL AND GROUNDWATER SAMPLING RI AT SOUTH SHORE AREA, FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature Proposed for Investigation	Scope of Proposed Investigation	Analytical Parameters	Basis for Proposed Investigation
SWMU 106 – Sanitary Sewer System	Collect soil samples at 3 depth intervals from 20 soil boring/soil sampling locations. Based on their proximity to locations where MEC items have been recovered in the past, samples from 8 borings associated with SWMU 106 will also be used to evaluate potential impacts from MEC debris. These boring locations are identified in Table 4-2 and are depicted on Figures 4-3 and 4-4.	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals	The sanitary sewer system was connected to buildings A193, A195, and A259 in the SSA. Several lines connect these buildings to the main line that runs approximately 1,500 south, parallel to Jennings Road, to pump station A153 located on the end of Pier 35 (see Figure 4-1). Another line coming from the PMA to the northeast extends a distance of approximately 1,800 feet parallel to the shoreline, south of Tyler Road, and connects to the main line approximately 150 feet northeast of the intersection between Murphy Lane and Jennings Road. The proposed scope of investigation is intended to address the concern for impacts of hazardous waste discharges to the soils in the vicinity of the sanitary sewer line. Soil samples will be collected at lateral intervals of approximately 200 feet over the length of the line, with samples also being collected near the terminus and bend in the pipeline.

TABLE 4-2

SUMMARY OF PROPOSED APPROACH TO SOIL AND GROUNDWATER SAMPLING RI AT SOUTH SHORE AREA, FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature Proposed for Investigation	Scope of Proposed Investigation	Analytical Parameters	Basis for Proposed Investigation
Former MEC Sites – (includes debris pits and areas where MEC items were found during NTCRA and prior removal actions)	Collect soil samples at 3 depth intervals from 16 soil boring/sampling locations in the approximate locations where MEC items were previously found and removed (see Figure 4-4).	Metals	Based on the identification and removal of MEC and munitions debris from the SSA, soil sampling is proposed in the locations where the highest concentrations of MEC items and debris were found and removed. Particular emphasis will be focused on the areas where debris/disposal pits were found during all previous removal actions, including: • Debris/disposal pits identified in DGM Grids AE010, AF011, AE011, and AH010/AH011, and • Area southwest of Dike 14 Ten soil sampling locations used for SWMU 106 will also be used to evaluate locations were MEC items were recovered.

TABLE 4-2

SUMMARY OF PROPOSED APPROACH TO SOIL AND GROUNDWATER SAMPLING RI AT SOUTH SHORE AREA, FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature Proposed for Investigation	Scope of Proposed Investigation	Analytical Parameters	Basis for Proposed Investigation
Primer Pit/Oven Pits	Collect soil samples at 3 depth intervals from 6 soil borings and 2 pilot boreholes for groundwater monitoring wells located in and around the former burn pit areas. In addition, soil samples will also be collected at 1 location within the footprint of each of the 3 former pits (Oven Pit 1, Oven Pit 2, and the Primer Pit). At these locations, a soil sample will be collected from 10 feet bgs only.	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, metals, and dioxins/furans	Previous soil sampling focused on copper, lead, and zinc only based on evidence for historical burning and disposal of ordnance items in the pit areas. Based on the potential for the historical disposal of other hazardous materials in the pits, investigation for other common materials and/or chemicals known to have been used at MINS is proposed to supplement the copper, lead, and zinc data and support closure of this area. In addition to VOCs, SVOCs, TPH, and metals analysis for dioxins/furans is proposed for the soil samples collected from Primer/Oven pits based on past burn operations suspected at these locations. Samples collected from the 3 locations within the footprint of the former Oven and Primer Pits will be used to evaluate conditions beneath the former excavations only. Samples at these 3 locations will not be collected from depth intervals that correspond to the backfill.

TABLE 4-2

SUMMARY OF PROPOSED APPROACH TO SOIL AND GROUNDWATER SAMPLING RI AT SOUTH SHORE AREA, FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature Proposed for Investigation	Scope of Proposed Investigation	Analytical Parameters	Basis for Proposed Investigation
Former Underground Tanks and Dry Wells in DGM Grid AJ015	Collect soil samples at 2 depth intervals from 3 soil borings located in area where the tanks, perforated pipes, and dry wells were found and removed.	VOCs and PCBs	Following the removal of the tanks, piping, and dry wells in January 2013, a total of 11 soil samples were collected and analyzed for TPH, SVOCs, and metals. Although the results of the confirmation soil samples did not indicate impacts associated with TPH, SVOCs, or metals, the exact use and history of this feature remains unknown. The dry wells extended to a total depth of 5 feet bgs. n the event that tanks and dry wells were once used as part of a septic system or clarifier of some type, additional data would be required to rule out impacts from other chemicals including solvents.
	Collect soil samples at 2 depth intervals from 10 soil borings along the length of the conveyance piping located to the south of the tanks (see Figure 4-6)	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals	Samples to be collected at bend and at spacing of every 20 feet along the length of the conveyance piping located to the south of the former tanks. This assumes an approximate length of 200 linear feet of piping based on interpretation of geophysical data. Additional sampling may be required.
Drums found in DGM Grid AA009	Collect soil samples at 3 depth intervals from 2 soil borings located in area where the buried drums were removed from DGM Grid AA009.	SVOCs (including PAHs), TPH-d, and TPH-mo	Based on the presence of 3 SVOCs [Benzo(a)anthracene, Benzo(a)pyrene, and Benzo(b)fluoroanthene] reported above residential RLSs in 2 of the soil samples collected from underneath the drums in found in AA009, two additional samples will be collected and analyzed for SVOCs, TPH-d, and TPH-mo to provide additional evaluation and/or confirmation of samples results obtained following the removal of the drums.

TABLE 4-2

SUMMARY OF PROPOSED APPROACH TO SOIL AND GROUNDWATER SAMPLING RI AT SOUTH SHORE AREA, FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Feature Proposed for Investigation	Scope of Proposed Investigation	Analytical Parameters	Basis for Proposed Investigation
Groundwater at SSA	Install Groundwater Monitoring Wells in 9 locations at the SSA.	VOCs, SVOCs, TPH-g, TPH-d, TPH-mo, PCBs, metals, and TDS	Well locations selected to provide sufficient spatial coverage to evaluate both hydrogeologic (groundwater gradient and flow conditions) and potential contaminant impacts to groundwater at the SSA. Samples collected from the wells will provide information regarding potential contamination at individual areas of interest as well as across the SSA. Groundwater samples will also be tested for TDS and other general water quality parameters to provide support for anticipated application for exception to beneficial use determinations at the site.

Notes:

DGM – digital geophysical mapping
MEC – munitions of explosive concern
MINS – former Mare Island Naval Shipyard
PCBs – polychlorinated biphenyls
SSA – South Shore Area
SVOC – semivolatile organic compound
SWMU – Solid Waste Management Unit
TDS – total dissolved solids
TPH-g – total petroleum hydrocarbons as gasoline
TPH-d - total petroleum hydrocarbons as diesel
TPH-mo – total petroleum hydrocarbons as motor oil
VOC – volatile organic compound

TABLE 4-3

SUMMARY OF PLANNED SAMPLING LOCATIONS AND ANALYTICAL PARAMETERS

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]
BUILDINGS					
Former Bldg. A193 (Former Mine Anchor Facility Annex)	None	SSARI-B193B01-0.5	0.5[c]	Soil	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals
		SSARI-B193B01-5	5.0		
		SSARI-B193B01-10	10.0		
	SWMU 93 + SWMU 106	SSARI-B193B02-0.5	0.5[c]		
		SSARI-B193B02-5	5.0		
		SSARI-B193B02-10	10.0		
Bldg. A195 (Ordnance Segregation/Hazardous Waste Storage)	SWMU 93 + SWMU 106	SSARI-B195B01-0.5	0.5[c,d]		
		SSARI-B195B01-5	5.0		
		SSARI-B195B01-10	10.0		
	None	SSARI-B195B02-0.5	0.5[c,d]		
		SSARI-B195B02-5	5.0		
		SSARI-B195B02-10	10.0		
Bldg. A259 (Mine Anchor Assembly and Advanced Weapons Container Maintenance)	None	SSARI-B259B01-0.5	0.5[c,d]		
		SSARI-B259B01-5	5.0		
		SSARI-B259B01-10	10.0		
		SSARI-B259B02-0.5	0.5[c,d]		
		SSARI-B259B02-5	5.0		
		SSARI-B259B02-10	10.0		
Structure A296 Explosives Safe Haven	None	SSARI-B296B01-0.5	0.5[c,d]		TPH-g, TPH-d, TPH-mo, and metals,
		SSARI-B296B01-5	5.0		
		SSARI-B296B01-10	10.0		
	SWMU 93 + SWMU 106	SSARI-B296B02-0.5	0.5[c]		VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals
		SSARI-B296B02-5	5.0		
		SSARI-B296B02-10	10.0		

TABLE 4-3

SUMMARY OF PLANNED SAMPLING LOCATIONS AND ANALYTICAL PARAMETERS

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]
SWMUs					
SWMU 93	None	SSARI-S93B01-0.5	0.5[c]	Soil	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals
		SSARI-S93B01-5	5.0		
		SSARI-S93B01-10	10.0		
	Building A259 + Former MEC Site in Grid AF011	SSARI-S93B02-0.5	0.5[c]		
		SSARI-S93B02-5	5.0		
		SSARI-S93B02-10	10.0		
	None	SSARI-S93B03-0.5	0.5[c]		
		SSARI-S93B03-5	5.0		
		SSARI-S93B03-10	10.0		
		SSARI-S93B04-0.5	0.5[c]		
		SSARI-S93B04-5	5.0		
		SSARI-S93B04-10	10.0		
	Building A296	SSARI-S93B05-0.5	0.5[c]		
		SSARI-S93B05-5	5.0		
		SSARI-S93B05-10	10.0		
SWMU 106	SWMU 93	SSARI-S106B01-0.5	0.5[c]		
		SSARI-S106B01-5	5.0		
		SSARI-S106B01-10	10.0		
		SSARI-S106B02-0.5	0.5[c]		
		SSARI-S106B02-5	5.0		
		SSARI-S106B02-10	10.0		
	None	SSARI-S106B03-0.5	0.5[c]		
		SSARI-S106B03-5	5.0[b]		
		SSARI-S106B03-10	10.0[b]		
	Former MEC Site in Grid AI011	SSARI-S106B04-0.5	0.5[c]		
		SSARI-S106B04-5	5.0		
		SSARI-S106B04-10	10.0		
	Former MEC Site in Grids AH011	SSARI-S106B05-0.5	0.5[c]		
		SSARI-S106B05-5	5.0		
		SSARI-S106B05-10	10.0		

TABLE 4-3

SUMMARY OF PLANNED SAMPLING LOCATIONS AND ANALYTICAL PARAMETERS

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]
SWMU 106	SWMU 93	SSARI-S106B06-0.5	0.5[c]	Soil	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals
		SSARI-S106B06-5	5.0		
		SSARI-S106B06-10	10.0		
	Former MEC Site in Grids AF010/AG010	SSARI-S106B07-0.5	0.5[c]		
		SSARI-S106B07-5	5.0		
		SSARI-S106B07-10	10.0		
	Building A259 + Former MEC Site – disposal pits in Grid AF011	SSARI-S106B08-0.5	0.5[c]		
		SSARI-S106B08-5	5.0		
		SSARI-S106B08-10	10.0		
	None	SSARI-S106B09-0.5	0.5[c]		VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals
		SSARI-S106B09-5	5.0		
		SSARI-S106B09-10	10.0		
	Former MEC Site – disposal pits in Grid AE010	SSARI-S106B10-0.5	0.5[c]		VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals
		SSARI-S106B10-5	5.0		
		SSARI-S106B10-10	10.0		
	Former MEC Site in Grid AE009	SSARI-S106B11-0.5	0.5[c]		
		SSARI-S106B11-5	5.0[b]		
		SSARI-S106B11-10	10.0[b]		
	Oven/Primer Pits	SSARI-S106B12-0.5	0.5[c]		
		SSARI-S106B12-5	5.0		
		SSARI-S106B12-10	10.0		
	None	SSARI-S106B13-0.5	0.5[c]		VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals
		SSARI-S106B13-5	5.0		
		SSARI-S106B13-10	10.0		
		SSARI-S106B14-0.5	0.5[c]		
		SSARI-S106B14-5	5.0		
		SSARIS106B14-10	10.0		

TABLE 4-3

SUMMARY OF PLANNED SAMPLING LOCATIONS AND ANALYTICAL PARAMETERS

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]
FORMER MEC SITES					
Former MEC Site (disposal pit AH010/011 + former deck marker location)	None	SSARI-MECB01-0.5	0.5[c]	Soil	Metals
		SSARI-MECB01-5	5.0		
		SSARI-MECB01-10	10.0		
		SSARI-MECB02-0.5	0.5[c]		
		SSARI-MECB02-5	5.0		
		SSARI-MECB02-10	10.0		
		SSARI-MECB03-0.5	0.5[c]		
		SSARI-MECB03-5	5.0		
		SSARI-MECB03-10	10.0		
		SSARI-MECB04-0.5	0.5[c]		
		SSARI-MECB04-5	5.0		
		SSARI-MECB04-10	10.0		
Former MEC Site (disposal pit AE011)		SSARI-MECB05-0.5	0.5[c]		
		SSARI-MECB05-5	5.0[b]		
		SSARI-MECB05-10	10.0[b]		
Former MEC Site (disposal pit AE010)		SSARI-MECB06-0.5	0.5[c]		
		SSARI-MECB06-5	5.0		
		SSARI-MECB06-10	10.0		
OVEN/PRIMER PITS					
Oven/Primer Pit Area (wetlands)	None	SSARI-PPB01-0.5	0.5[c]	Soil	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, metals, and dioxins/furans
		SSARI-PPB01-5	5.0		
		SSARI-PPB01-10	10.0		
		SSARI-PPB02-0.5	0.5[c]		
		SSARI-PPB02-5	5.0		
		SSARI-PPB02-10	10.0		
		SSARI-PPB03-0.5	0.5[c]		
		SSARI-PPB03-5	5.0		
		SSARI-PPB03-10	10.0		
		SSARI-PPB04-10	10.0		
		SSARI-PPB05-10	10.0		
		SSARI-PPB06-10	10.0		

TABLE 4-3

SUMMARY OF PLANNED SAMPLING LOCATIONS AND ANALYTICAL PARAMETERS

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]
OTHER AREAS – TANKS (AJ015) AND DRUMS (AA009)					
Tanks/Dry Wells (DGM Grid AJ015)	None	SSARI-STB01-2	2.0	Soil	VOCs and PCBs
		SSARI-STB01-5	5.0		
		SSARI-STB02-2	2.0		
		SSARI-STB02-5	5.0		
		SSARI-STB03-2	2.0		
		SSARI-STB03-5	5.0		
Tank Conveyance Pipeline (DGM Grid AJ015)		SSARI-STB04-2	2.0		VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals
		SSARI-STB04-5	5.0		
		SSARI-STB05-2	2.0		
		SSARI-STB05-5	5.0		
		SSARI-STB06-2	2.0		
		SSARI-STB06-5	5.0		
		SSARI-STB07-2	2.0		
		SSARI-STB07-5	5.0		
		SSARI-STB08-2	2.0		
		SSARI-STB08-5	5.0		
		SSARI-STB09-2	2.0		
		SSARI-STB09-5	5.0		
		SSARI-STB10-2	2.0		
		SSARI-STB10-5	5.0		
		SSARI-STB11-2	2.0		
		SSARI-STB11-5	5.0		
		SSARI-STB12-2	2.0		
		SSARI-STB12-5	5.0		
		SSARI-STB13-2	2.0		
		SSARI-STB13-5	5.0		
Buried Drums (DGM Grid AA009)		SSARI-BDB01-0.5	0.5		SVOCs (including PAHs), TPH-d, and TPH-mo
		SSARI-BDB01-5	5.0[b]		
		SSARI-BDB01-10	10.0[b]		

TABLE 4-3

SUMMARY OF PLANNED SAMPLING LOCATIONS AND ANALYTICAL PARAMETERS

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]
SOIL SAMPLES FROM MONITORING WELL BORINGS					
SSA-MW01	Former drums and tanks in Grids AI015 and AJ015	SSARI-MW1SB-0.5	0.5[c]	Soil	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals
		SSARI-MW1SB-5	5.0		
		SSARI-MW1SB-10	10.0		
SSA-MW02	Former MEC Site AH011	SSARI-MW2SB-0.5	0.5[c]		
		SSARI-MW2SB-5	5.0		
		SSARI-MW2SB-10	10.0		
SSA-MW03	SWMU 106 + Former MEC Site AF011	SSARI-MW3SB-0.5	0.5[c]		
		SSARI-MW3SB-5	5.0		
		SSARI-MW3SB-10	10.0		
SSA-MW04	SWMU 106 + Former MEC Site AE010	SSARI-MW4SB-0.5	0.5[c]		
		SSARI-MW4SB-5	5.0		
		SSARI-MW4SB-10	10.0		
SSA-MW05	SWMU 106 + Oven/Primer Pits	SSARI-MW5SB-0.5	0.5[c,d]		
		SSARI-MW5SB-5	5.0		
		SSARI-MW5SB-10	10.0		
SSA-MW06	Former drums in AA009	SSARI-MW6SB-0.5	0.5[c]		
		SSARI-MW6SB-5	5.0[b]		
		SSARI-MW6SB-10	10.0[b]		
SSA-MW07	Building A195	SSARI-MW7SB-0.5	0.5[c]		
		SSARI-MW7SB-5	5.0[b]		
		SSARI-MW7SB-10	10.0[b]		
SSA-MW08	South of Oven/Primer Pit Area	SSARI-MW8SB-0.5	0.5[c]		
		SSARI-MW8SB-5	5.0		
		SSARI-MW8SB-10	10.0		
SSA-MW09	Southwest portion of SSA	SSARI-MW9SB-0.5	0.5[c]		
		SSARI-MW9SB-5	5.0		
		SSARI-MW9SB-10	10.0		

TABLE 4-3

SUMMARY OF PLANNED SAMPLING LOCATIONS AND ANALYTICAL PARAMETERS

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]
GROUNDWATER SAMPLE LOCATIONS					
SSA-MW01	Groundwater	SSA-MW01-001	TBD[e]	Water	VOCs, SVOCs (including PAHs), TPH-g, PCBs, TPH-d, TPH-mo, metals, and TDS
SSA-MW02		SSA-MW02-001	TBD[e]		
SSA-MW03		SSA-MW03-001	TBD[e]		
SSA-MW04		SSA-MW04-001	TBD[e]		
SSA-MW05		SSA-MW05-001	TBD[e]		VOCs, SVOCs (including PAHs), TPH-g, PCBs, dioxins/furans[f], TPH-d, TPH-mo, metals, and TDS
SSA-MW06		SSA-MW06-001	TBD[e]		VOCs, SVOCs (including PAHs), TPH-g, PCBs, TPH-d, TPH-mo, metals, and TDS
SSA-MW07		SSA-MW07-001	TBD[e]		
SSA-MW08		SSA-MW08-001	TBD[e]		
SSA-MW09		SSA-MW09-001	TBD[e]		

Notes:

a. Planned depth only, actual depth may be adjusted in the field based on observations of potential evidence for contaminant impact (staining, elevated head space measurements. etc.).
b. Organotins will be analyzed only in the event that ABM is encountered or identified.
c. No analysis for VOCs for the 0.5 feet bgs sample at this location.
d. Include analyses for organochlorine pesticides for the 0.5 feet bgs sample collected from this location.
e. Groundwater samples will be collected from the depth corresponding with the middle of the screened interval for each well, as determined from the total depth as installed.
f. Groundwater samples from well SSA-MW05 may be analyzed for dioxins/furans in the event that they are detected in the soil samples from the Oven/Primer Pit area.

Well/boring identification by location is shown on Figures 4-2 through 4-7.

ABM – abrasive blast material
bgs – below ground surface
Bldg. – building
DGM – digital geophysical mapping
MEC – munitions and explosives of concern
PAH – polycyclic aromatic hydrocarbon
PCB – polychlorinated biphenyl
SVOC – semi-volatile organic compound
SWMU – solid waste management unit
TBD – to be determined
TDS – total dissolved solid
TPH-d – total petroleum hydrocarbons as diesel
TPH-g – total petroleum hydrocarbons as gasoline
TPH-mo – total petroleum hydrocarbons as motor oil
VOC – volatile organic compound

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TABLE 4-4

SUMMARY OF RATIONALE FOR GROUNDWATER MONITORING WELLS
RI AT SOUTH SHORE AREA, FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CALIFORNIA

Well I.D.	Target Feature/Potential Contaminant Source Area Objective	Hydrologic Target/Objective
SSAMW-01	Former drums and debris pit in Grid AI015	Upland area in eastern portion of SSA
SSAMW-02	Debris pits in Grids AH010/AH011, Dike 14 area + south/southeast of Bldg. A259	Eastern shoreline area, wetlands to northeast
SSAMW-03	Bldg. A259 and debris pits in Grid AF011	Central upland area
SSAMW-04	Debris pits in Grid AE010 + Bldgs. A195 and A259	Central portion of the SSA
SSAMW-05	North of Oven/Primer Pits + south of central portion of SSA	Near central portion shoreline, just north of wetland areas
SSAMW-06	Bldg. A195	Upland area in central portion of SSA
SSAMW-07	Former drums and debris pit in Grid AA009	Shoreline area near western extent of SSA
SSAMW-08	Oven/Primer Pit area	Shoreline area near southern central extent of SSA
SSAMW-09	Former Bldg. A193 and High Explosives Safe Haven	Southwestern portion of SSA

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TABLE 7-1

SUMMARY OF PRELIMINARY EXPOSURE FACTORS FOR RECREATIONAL, INDUSTRIAL, AND CONSTRUCTION SCENARIOS

Exposure Parameters		Central Tendency			Reasonable Maximum Exposures		
		Recreational	Industrial	Construction	Recreational	Industrial	Construction
Event Frequency (events/day)		1	1	1	1	1	1
Exposure Frequency (days/year)		75[e*]	219[c]	20[e*]	75[e]	250[a]	20[e]
Exposure Duration (year)		9	9	1[e]	30	25	1[e]
Inadvertent Water Ingestion (mL/event)		NA	NA	16[b]	NA	NA	53[b]
Event Time (hour/day)	Adult	1	8[e]	8[e]	1	8[e]	8[e]
	Child	1	NA	NA	1	NA	NA
Skin Surface Area (cm^3)	Adult	5700[c]	3300[c]	5700[c]	5700[c]	3300[c]	5700[c]
	Child	2800[c]	NA	NA	2800[c]	NA	NA
Soil Adherence Factor (mg/cm^2)	Adult	0.01[c]	0.02[c]	0.3[e]	0.07[a]	0.2[a]	0.8[a]
	Child	0.04[c]	NA	NA	0.02[a]	NA	NA
Soil Ingestion Rate (mg/day)	Adult	20[b]	100[a]	330[a]	100[a]	100[a]	330[a]
	Child	50[b]	NA	NA	200[a]	NA	NA
Inhalation Rate (m^3/day)	Adult	20a	14a		20a		20a
	Child	10a	NA	NA	10a	NA	NA

Abbreviations and Acronyms:

mL – milliliter
cm – centimeter
mg – milligram
m – meter

References:

a - Recommended DTSC Default Exposure Factors for Use in Risk Assessment at California Hazardous Waste Sites and Permitted Facilities" (DTSC 2011).
b - "Exposure Factors Handbook." (USEPA 2011).
c - "Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E., Supplemental Guidance for Dermal Risk Assessment)." (USEPA 2004).
e - Oak Ridge National Labs. 2012 Risk Assessment Information System.,

Notes:

* - Exposure factor subject to change. Final exposure factors will documented in the BHHRA Report.

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TABLE 7-2

SUMMARY OF PRELIMINARY EXPOSURE FACTORS FOR HYPOTHETICAL RESIDENTIAL SCENARIO*

Exposure Parameter	Definition	Units	Child (0-6) CTE	Child (0-6) RME	Adult CTE	Adult RME
IR_{soil}	Ingestion Rate, Soil	milligrams	100	200	100	100
AF	Soil Adherence Factor	milligrams per square centimeter	0.4	0.4	0.06	0.06
SA	Skin Surface Area Exposed to Soil	square centimeter	2800	2800	5700	5700
IR_{gw}	Ingestion Rate, Groundwater	liters	1	1	1.4	2
FC_{air}	Air Fraction from contaminated source	%	30% outdoors; 70% indoors	30% outdoors; 70% indoors	30% outdoors; 70% indoors	30% outdoors; 70% indoors
IR_{air}	Inhalation rate, Air	cubic meters/day	7.5	7.5	20	20
ED	Exposure duration	years	3	6	9	30
EF	Exposure frequency	days/year	275	350	275	350
BW	Bodyweight	kilogram	15	15	70	70
AT_{nc}	Averaging time non-carcinogenic	days	1095	2190	3285	10950
AT_{carc}	Averaging time carcinogenic	days	25550	25550	25550	25550

Abbreviations and Acronyms:

CTE – Central Tendency Exposure
RME – Reasonable Maximum Exposure
* Recommended Default Residential Exposure Factors. Naval Facilities Engineering Command (NAVFAC). 2008. *U.S. Navy Human Health Risk Assessment Guidance*.

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Table 8-1
Example Dose Parameters for Measurement Receptors and Dose Equation

DOSE PARAMETERS FOR THE GREY FOX *(Urocyon cinereoargenteus)*

Parameter	Average Adult	Units	Reference/Notes
Ingestion $Rate_{food}$	1.82E-01	kg/day	Calculated with body weight of 5,000 grams using the equation for the food requirement for intake of dry matter for carnivores (food ingestion rate = [0.323[BW(grams)]^0.744]/1000 (Nagy 2001).
Ingestion $Rate_{mammal}$	1.82E-01	kg/day	Based on 100 percent of food ingestion rate.
Ingestion $Rate_{soil}$	5.11E-03	kg/day	2.8 percent of food ingestion rate based on red fox (Beyer and others 1994).
Soil Concentrations	95% UCL on the mean	mg/kg	Estimated using EPA's ProUCL software.
Food Concentrations	Food Chain Model	mg/kg	Food concentrations were estimated using uptake models using concentrations at the site or by multiplying concentrations in soil at the site by BAFs for small mammals.
Diet Composition[a]	100%	Small Mammal	Food will consist of 100 percent small mammal tissue because the grey fox was selected as representative species for carnivorous mammals.
Foraging Range	1.20E+02	Hectare	Average for four females in Davis, California (Fuller 1987 as cited in Zeiner and others 1990).
Area Use Factor	To be determined	Unitless	Will be estimated by dividing the area of specific subsites identified within the Mare Island South Shore Area by the foraging range (defaulting to 1.0 if greater than 1).
Body Weight	5.00E+00	kg	Median body weight from Davis and Schmidly (1994).

Notes:

[a] The grey fox feeds primarily on rodents and other animal matter (Zeiner 1990).

BAF	Bioaccumulation factor
bgs	Below ground surface
BW	Body weight
EPA	U.S. Environmental Protection Agency
ERA	Ecological Risk Assessment
kg	Kilogram
kg/day	Kilograms per day
mg/kg	Milligrams per kilogram

References:

Beyer, W.N., E.E. Connor, and S. Gerould. 1994. Estimates of Soil Ingestion by Wildlife. J.Wildl. Manage. 58(2): 375-382.

Davis, W.B. , and D.J. Schmidly. 1994. The Mammals of Texas. Austin, Texas,: Texas Parks & Wildlife, Nongame and Urban Program: Distributed by University of Texas Press, 338 pages.

Nagy, K.A. 2001. "Food requirements of wild animals: predictive equations for free-living mammals, reptiles, and birds." Nutrition Abstracts and Reviews, Series B. Volume 71. Number 10. Pages 2R-12R.

EPA. 1997. "Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments, Interim Final." Environmental Response Team, Edison, New Jersey.

Zeiner, D.C., W.F. Laudenslayer, Jr., K.E. Mayer, and M. White. 1990. "California's Wildlife: Volume III, Mammals." CWHR System. State of California, the Resource Agency, CDFG. Sacramento, California.

Table 8-1
Example Dose Parameters for Measurement Receptors and Dose Equation

DOSE PARAMETERS FOR THE RED-TAILED HAWK *(Buteo jamaicensis)*

Parameter	Average Adult	Units	Reference/Notes
Ingestion $Rate_{food}$	9.00E-02	kg/day	Calculated with body weight of 1134 grams using the equation for the food requirement for intake of dry matter for carnivorous birds (food ingestion rate = [0.849[BW(grams)]^0.663]/1000) (Nagy 2001).
Ingestion $Rate_{mammal}$	9.00E-02	kg/day	Based on 100 percent food ingestion rate.
Ingestion $Rate_{soil}$	5.13E-03	kg/day	5.7 percent of total ingestion rate, based on the 90th percentile result for the hawk determined for use in the Eco-SSL calculations (EPA 2005).
Soil Concentrations	95% UCL on the mean	mg/kg	Estimated using EPA's ProUCL software.
Food Concentrations	Food Chain Model	mg/kg	Food concentrations were estimated using uptake models using concentrations at the site or by multiplying concentrations in soil at the site by BAFs for small mammals.
Diet Composition[a]	100%	Small Mammals	Food will consist of 100 percent small mammal tissue because the red-tailed hawk was selected as representative species for carnivorous birds.
Foraging Range	5.31E+02	Hectare	Based on median of home range (78-984 hectares) provided in Zeiner and others (1990a).
Area Use Factor	To be determined	Unitless	Will be estimated by dividing the area of specific subsites identified within the Mare Island South Shore Area by the foraging range (defaulting to 1.0 if greater than 1).
Body Weight	1.13E+00	kg	Mean body weight for adult males and females (EPA 1993).

Notes:

[a] Red-tailed hawks are swooping, pouncing carnivores with a diet that consists of small mammals, insects, earthworms, reptiles, and amphibians (Ehrlich and others 1988; Zeiner and others 1990a).

BAF	Bioaccumulation factor
bgs	Below ground surface
BW	Body weight
EPA	U.S. Environmental Protection Agency
ERA	Ecological Risk Assessment
kg	Kilogram
kg/day	Kilograms per day
mg/kg	Milligrams per kilogram

References:

Ehrlich, P.R., D.S. Doobkin, and D. Wheye. 1988. The Birder's Handbook, A Field Guide to the Natural History of North American Birds. Simon and Schuster, Inc. New York, New York.

Nagy, K.A. 2001. "Food requirements of wild animals: predictive equations for free-living mammals, reptiles, and birds." Nutrition Abstracts and Reviews, Series B. Volume 71. Number 10. Pages 2R-12R.

U.S. Environmental Protection Agency (EPA). 1993. "Wildlife Exposure Factors Handbook." December. 1993

EPA. 1997. "Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments, Interim Final." Environmental Response Team, Edison, New Jersey.

EPA. 2005. Ecological Soil Screening Levels for Arsenic, Interim Final. March. Available online at: http://www.epa.gov/ecotox/ecossl/pdf/eco-ssl_arsenic.pdf

Zeiner, D.C., W.F. Laudenslayer, Jr., K.E. Mayer, and M. White. 1990a. "California's Wildlife: Volume II, Birds." CWHR System. State of California, the Resource Agency, CDFG. Sacramento, California.

Table 8-1
Example Dose Parameters for Measurement Receptors and Dose Equation

DOSE PARAMETERS FOR THE CALIFORNIA GROUND SQUIRREL *(Spermophilus beecheyi)*

Parameter	Average Adult	Units	Reference/Notes
Ingestion Rate$_{food}$	4.89E-02	kg/day	Calculated with body weight of 632 grams using the equation for the food requirement for intake of dry matter for rodents (food ingestion rate = [0.332[BW(grams)]^0.774]/1000) (Nagy 2001).
Ingestion Rate$_{plant}$	4.89E-02	kg/day	Based on 100 percent of food ingestion rate.
Ingestion Rate$_{soil}$	1.17E-03	kg/day	2.4 percent of food ingestion rate based on the meadow vole from EPA (1993).
Soil Concentrations	95% UCL on the mean	mg/kg	Estimated using EPA's ProUCL software.
Food Concentrations	Food Chain Model	mg/kg	Food concentrations were estimated using uptake models using concentrations at the site or by multiplying concentrations in soil at the site by BAFs for plants.
Diet Composition[a]	100%	Plant Tissue	Food will consist of 100 percent plant tissue because the California ground squirrel was selected as representative species for herbivorous mammals.
Foraging Range	1.00E-01	Hectare	Average range for adult males from Evans and Holdenreid 1948 as cited in DFG 2005.
Area Use Factor	To be determined	Unitless	Will be estimated by dividing the area of specific subsites identified within the Mare Island South Shore Area by the foraging range (defaulting to 1.0 if greater than 1).
Body Weight	6.32E-01	kg	Average mean weight for adults from Cal/EPA 2013.

Notes:

[a] The California ground squirrel eats seeds, nuts, fruits, bulbs, fungi, and stems and leaves of greasses and forbs. They also eat some insects, bird eggs, and carrion. (DFG 2005).

BAF	Bioaccumulation factor
bgs	Below ground surface
BW	Body weight
Cal/EPA	California Environmental Protection Agency
DFG	California Department of Fish and Game
EPA	U.S. Environmental Protection Agency
ERA	Ecological Risk Assessment
kg	Kilogram
kg/day	Kilograms per day
mg/kg	Milligrams per kilogram

References:

DFG. 2005. California Interagency Wildlife Task Group. California Wildlife Habitat Relationships version 8.1 personal computer program. Sacramento, California.

Cal/EPA. 2013. California Wildlife Exposure Factor and Toxicity Database. Office of Environmental Health and Hazard Assessment. Ecotoxicology Unit. Sacramento, California. www.oehha.org/cal_ecotox/default.htm

Nagy, K.A. 2001. "Food requirements of wild animals: predictive equations for free-living mammals, reptiles, and birds." Nutrition Abstracts and Reviews, Series B. Volume 71. Number 10. Pages 2R-12R.

EPA. 1993. "Wildlife Exposure Factors Handbook." December.

EPA. 1997. "Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments, Interim Final." Environmental Response Team, Edison, New Jersey.

Table 8-1
Example Dose Parameters for Measurement Receptors and Dose Equation

Example Wildlife Oral Dose Equation for Soil Ingestion Exposure (Wildlife Exposure Factors Handbook, Equation 4-23 [EPA, 1993]):

$$ADD_{pot} = \left(\left[\sum_{k=1}^{m} \left(\frac{C_k \times FS \times IR_{total}(dry\ weight) \times FR_k}{BW} \right) \right] \right)$$

Where:

ADD_{pot} = Potential average daily dose (e.g., mg/kg-day).

C_k = Average contaminant concentration in soils in the kth foraging area (e.g., in mg/kg dry weight).

FS = Fraction of soil in diet (as percentage of diet on a dry-weight basis divided by 100; unitless).

IR_{total} = Food ingestion rate on a dry-weight basis (e.g., in kg/day). Nagy's (2001) equations for estimating FI rates on a dry-weight basis can be used to estimate a value for this factor. If the equations equations for estimating FI rates are on a wet-weight basis are used, conversion to ingestion on a dry-weight basis would be necessary.

FR_k = Fraction of total food intake from the kth foraging area (unitless). This is also referred to as the Area Use Factor (site area/wildlife species home range), as suggested in Eq. 4-8 (Wildlife Dose Equations for Dietary Exposure [EPA, 1993]).

k = counter

m = Total number of foraging areas.

BW = Body weight (e.g., in kg).

TABLE 8-2
MARE ISLAND MEDIAN BIOACCUMULATION FACTORS FOR USE IN FOOD CHAIN MODEL

Analyte	Pickleweed	Plants	Earthworms	Aquatic Invertebrates	Mammals
Aluminum	0.0016	0.00066	NA	NA	0.0073
Antimony	1.72	0.19	NA	NA	1.27
Arsenic	0.07	0.064	1.52	1.36	NA
Barium	0.23	0.057	NA	NA	0.06
Cadmium	0.33	0.25	2.38	NA	NA
Chromium	NA	0.024	NA	NA	0.03
Copper	0.14	0.044	0.31	0.98	0.15
Lead	0.052	0.0055	0.14	0.37	0.14
Manganese	0.13	0.026	NA	5.12	NA
Mercury	0.59	0.61	NA	NA	NA
Molybdenum	4.14	NA	NA	NA	NA
Nickel	0.054	0.011	NA	NA	NA
Selenium	NA	NA	NA	NA	1.63
Vanadium	NA	0.021	NA	NA	NA
Zinc	0.12	0.066	0.6	1.43	0.89
Benzo(a)pyrene[1]	9.06	1.67	NA	NA	NA
Dieldrin	NA	1.23	NA	NA	3.35
Endrin ketone[2]	NA	NA	NA	NA	9.38
Endosulfan I	NA	6.56	NA	NA	NA

Notes:

Mare Island Median BAFs were calculated and presented in the Mare Island Onshore Ecological Risk Assessment in Table G-77 (Tetra Tech EM Inc 2002b).

1 The BAF for benzo(a)pyrene will be used as a surrogate for other HMW PAHs, and alternative PAH BAFs from Table 8-3 will be discussed in the SLERA Uncertainty Section.

2 The BAF for endrin ketone used as a surrogate for the total endrins BAF where available.

BAF Bioaccumulation factor
HMW High molecular weight
NA Not available
PAH Polynuclear aromatic hydrocarbons

References:

Tetra Tech EM Inc. 2002b. "Final Onshore Ecological Risk Assessment." Mare Island, Vallejo, California." July.

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TABLE 8-3
EXAMPLE OF BIOACCUMULATION MODELS FOR PLANTS

			Summary Statistics for BAFs				Parameters for Log-Linear Uptake Model					
Taxa	**Analyte**	**Transfer Type**	**N**	**Minimum**	**Median**	**Maximum**	**N**	**Slope**	**Intercept**	**R-square**	**p (model)**	**Reference**
Plants	Aluminum	soil-to-biota	28	0.00058	0.00287	0.0112	na	na	na	na	na	Efroymson, et al., 2001
Plants	Antimony	soil-to-biota	17	0.003	0.037	0.22	17	0.938	-3.233	0.79	0.0001	EPA 2007
Plants	Arsenic	soil-to-biota	122	0.00006	0.03752	9.0741	na	na	na	na	na	Bechtel-Jacobs 1998
Plants	Barium	soil-to-biota	28	0.036	0.156	0.92	na	na	na	na	na	Bechtel-Jacobs 1998
Plants	Beryllium	soil-to-biota	na	na	na	na	18	0.7345	-0.5361	0.7311	<0.0001	EPA 2007
Plants	Cadmium	soil-to-biota	17	0.003	0.037	0.22	na	0.546	-0.475	na	na	EPA 2007
Plants	Chromium	soil-to-biota	28	0.021	0.041	0.48	na	na	na	na	na	Bechtel-Jacobs 1998
Plants	Cobalt	soil-to-biota	28	0.0019	0.0075	0.045	na	na	na	na	na	Bechtel-Jacobs 1998
Plants	Copper	soil-to-biota	180	0.0011	0.12432	7.4	180	0.394	0.668	0.31	0.0001	Bechtel-Jacobs 1998
Plants	Lead	soil-to-biota	na	na	na	na	na	0.561	-1.328	na	na	EPA 2007
Plants	Manganese	soil-to-biota	28	0.0199	0.079	0.433	na	na	na	na	na	Bechtel-Jacobs 1998
Plants	Mercury	soil-to-biota	142	0.00145	0.663	12.23	na	na	na	na	na	Efroymson, et al., 2001
Plants	Nickel	soil-to-biota	111	0.00217	0.01786	22.2143	111	0.748	-2.223	0.37	0.0001	Bechtel-Jacobs 1998
Plants	Selenium	soil-to-biota	158	0.02	0.672	77	158	1.104	0.677	0.633	0.0001	Bechtel-Jacobs 1998
Plants	Silver	soil-to-biota	10	0.0029	0.014	0.04	na	na	na	na	na	Bechtel-Jacobs 1998
Plants	Vanadium	soil-to-biota	21	0.00173	0.00485	0.0097	na	na	na	na	na	Efroymson, et al., 2001
Plants	Zinc	soil-to-biota	na	na	na	na	na	0.554	1.575	na	na	EPA 2007
Plants	Pentachlorophenol	soil-to-biota	na	na	5.93	na	na	na	na	na	na	EPA 2007
Plants	Total HMW PAHs	soil-to-biota	na	na	na	na	na	0.9469	-1.7026	na	na	EPA 2007
Plants	Total LMW PAHs	soil-to-biota	na	na	na	na	na	0.4544	-1.3205	na	na	EPA 2007

Notes:

Highlighted data represent recommended selected bioaccumulation data.

Regression Formula: *ln* (tissue concentration) = *Y*- intercept + slope * (*ln* [soil concentration]).

BAFs reported in dry weight.

BAF	Bioaccumulation factor	HMW	High molecular weight	p	Probability
EPA	Environmental Protection Agency	*ln*	Natural log	PAH	Polycyclic aromatic hydrocarbons
ln	Natural log	LWM	Low molecular weight		
N	Number of studies or observations	na	Not available		

References:

Bechtel-Jacobs. 1998. Empirical Models for the Uptake of Inorganic Chemicals from Soil by Plants. Bechtel Jacobs Company LLC, Oak Ridge, TN. BJC/OR-133.

Efroymson, R.A., 2001, Uptake of Inorganic Chemicals from Soil by Plant Leaves: Regression of Field Data, Environ. Toxicol. Chem., 20:2561-2571.

EPA. 2007. "Attachment 4-1. Guidance for Developing Ecological Soil Screening Levels." Revised. April.

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TABLE 8-4
EXAMPLE OF BIOACCUMULATION MODELS FOR INVERTEBRATES

Taxa	Analyte	Transfer Type	Summary Statistics for BAFs				Parameters for Log-Linear Uptake Model					Eco-SSL Assumed BAF	Reference
			N	Minimum	Median	Maximum	N	Slope	Intercept	R-square	p (model)		
Earthworms	Aluminum	soil-to-biota	20	0.008	0.043	0.197	na	na	na	na	na	na	Sample and others 1998
Earthworms	Antimony	soil-to-biota	na	na	na	na	na	na	na	na	na	1	EPA 2007
Earthworms	Arsenic	soil-to-biota	53	0.006	0.224	0.925	na	0.706	-1.421	na	na	na	Sample and others 1999
Earthworms	Barium	soil-to-biota	20	0.005	0.091	0.31	na	na	na	na	na	na	Sample and others 1998
Earthworms	Beryllium	soil-to-biota	12	0	0.045	1.429	na	na	na	na	na	na	Sample and others 1999
Earthworms	Cadmium	soil-to-biota	na	na	na	na	na	0.795	2.114	na	na	na	EPA 2007
Earthworms	Chromium	soil-to-biota	67	0.021	0.306	11.416	67	0.067	2.481	0.0026	0.68	na	Sample and others 1999
Earthworms	Cobalt	soil-to-biota	17	0.031	0.122	0.321	na	na	na	na	na	na	Sample and others 1999
Earthworms	Copper	soil-to-biota	197	0.002	0.515	5.492	197	0.264	1.675	0.18	0.0001	na	Sample and others 1999
Earthworms	Lead	soil-to-biota	na	na	na	na	na	0.807	-0.218	na	na	na	EPA 2007
Earthworms	Manganese	soil-to-biota	36	0.012	0.054	0.228	36	0.682	-0.809	0.34	0.0002	na	Sample and others 1999
Earthworms	Mercury	soil-to-biota	30	0.03	1.693	33	29	-0.15	4.17	0.02	0.42	na	Sample and others 1999
Earthworms	Nickel	soil-to-biota	31	0.033	1.059	7.802	31	-0.26	3.677	0.06	0.19	na	Sample and others 1999
Earthworms	Selenium	soil-to-biota	14	na	na	na	13	0.733	-0.075	0.43	0.016	na	Sample and others 1999
Earthworms	Silver	soil-to-biota	10	0.001	2.045	19.5	na	na	na	na	na	na	Sample and others 1998
Earthworms	Vanadium	soil-to-biota	na	na	0.042	na	39	0.6049	-1.9224	0.2	na	na	EPA 2007
Earthworms	Zinc	soil-to-biota	244	0.025	3.201	49.51	244	0.328	4.449	0.45	0.0001	na	Sample and others 1999
Earthworms	Pentachlorophenol	soil-to-biota	na	na	14.63	na	na	na	na	na	na	na	EPA 2007
Earthworms	Total HMW PAHS	soil-to-biota	na	na	2.6	na	na	na	na	na	na	na	EPA 2007
Earthworms	Total LMW PAHS	soil-to-biota	na	na	3.04	na	na	na	na	na	na	na	EPA 2007

Notes:

Highlighted data represent recommended selected bioaccumulation data.

Regression Formula: *ln* (tissue concentration) = *Y*-intercept + slope * (*ln* [soil concentration])

BAF	Bioaccumulation factor	LWM	Low molecular weight
Eco-SSL	Ecological soil screening level	N	Number of studies or observations
EPA	U.S. Environmental Protection Agency	na	Not available
HMW	High molecular weight	p	Probability
ln	Natural log	PAH	Polycyclic aromatic hydrocarbons

References:

EPA. 2007. "Attachment 4-1. Guidance for Developing Ecological Soil Screening Levels." Revised. April.

Sample, B.E., J.J. Beauchamp, R.A. Efroymson, G.W. Suter,II, and T.L. Ashwood. 1998. Development and Validation of Bioaccumulation Models for Earthworms. Oak Ridge National Laboratory, Oak Ridge TN. 93 pp, ES/ER/TM-220.

Sample, B.E., J.J. Beauchamp, R.A. Efroymson, G.W. Suter,II. 1999. Literature-derived bioaccumulation models for earthworms: development and validation. Environ. Toxicol. Chem. 18:2110-2120.

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TABLE 8-5
EXAMPLE OF BIOACCUMULATION MODELS FOR SMALL MAMMALS AND SMALL BIRDS

Taxa	Analyte	Trophic Group	Transfer Type	Summary Statistics for BAFs				Parameters for Log-Linear Uptake Model					Eco-SSL BAF	Reference
				N	Minimum	Median	Maximum	N	Slope	Intercept	R-square	p (model)		
Small Mammals	Aluminum	General	soil-to-biota	7	0.0064	0.0171	0.031	na	na	na	na	na	NA	Sample and others 1998
Small Mammals	Antimony	na	diet-to-biota	na	na	na	na	na	na	na	na	na	C_m=0.001*50*C_d	Baes and others 1984
Small Mammals	Arsenic	General	soil-to-biota	72	0	0.0025	0.071	60	0.8188	-4.8471	0.52	0.0001	NA	Sample and others 1998
Small Mammals	Barium	na	diet-to-biota	14	0.0144	0.0566	0.25	na	na	na	na	na	C_m=0.00015*50*C_d	Baes and others 1984
Small Mammals	Beryllium	na	diet-to-biota	na	na	na	na	na	na	na	na	na	C_m=0.001*50*C_d	Baes and others 1984
Small Mammals	Cadmium	Herbivore	soil-to-biota	28	0.0153	0.1258	1	28	0.4723	-1.2571	0.64	0.0001	NA	Sample and others 1998
Small Mammals	Chromium	General	soil-to-biota	38	0.0314	0.0846	0.8	38	0.7338	-1.4599	0.42	0.0001	NA	Sample and others 1998
Small Mammals	Cobalt	General	soil-to-biota	15	0.0101	0.0205	0.18	15	1.307	-4.4669	0.41	0.01	NA	Sample and others 1998
Small Mammals	Copper	General	soil-to-biota	76	0.0044	0.1963	1.398	76	0.1444	2.042	0.26	0.0001	NA	Sample and others 1998
Small Mammals	Lead	General	diet-to-biota	138	0.0031	0.1054	2.659	138	0.4422	0.0761	0.37	0.0001	na	Sample and others 1998
Small Mammals	Manganese	General	soil-to-biota	12	0.0114	0.0205	0.079	na	na	na	na	na	NA	Sample and others 1998
Small Mammals	Mercury	General	soil-to-biota	18	0.0183	0.0543	1.046	na	na	na	na	na	NA	Sample and others 1998
Small Mammals	Nickel	General	soil-to-biota	43	0	0.2488	1.143	36	0.4658	-0.2462	0.55	0.0001	NA	Sample and others 1998
Small Mammals	Selenium	General	soil-to-biota	27	0	0.1619	1.754	27	0.3764	-0.4158	0.31	0.0026	NA	Sample and others 1998
Small Mammals	Silver	General	soil-to-biota	10	0	0.004	0.81	na	na	na	na	na	NA	Sample and others 1998
Small Mammals	Vanadium	Herbivore	soil-to-biota	7	0.0083	0.0123	0.019	na	na	na	na	na	NA	Sample and others 1998
Small Mammals	Zinc	Herbivore	soil-to-biota	30	0.00511	0.504	16.3636	30	0.0706	4.3632	0.31	0.0013	NA	Sample and others 1998
Small Mammals	Pentachlorophenol	General	diet-to-biota	na	na	na	na	na	na	na	na	na	C_m=0.00452*C_d+0.198	EPA 2007
Small Mammals	PAHs	General	diet-to-biota	See below [a]										Brandt et al. (2002)

Notes:

Highlighted data represent recommended selected bioaccumulation data.
Regression Formula: *ln* (tissue concentration) = *Y*-intercept + slope * (*ln* [soil concentration]).

BAF	Bioaccumulation factor	N	Number of studies or observations
Eco-SSL	Ecological Soil Screening Level	na	Not available
EPA	U.S. Environmental Protection Agency	p	Probability
ln	Natural log	PAH	Polycyclic aromatic hydrocarbons

References:

Baes, C.F., III, R.D. Sharp, A.L. Sjoreen, and R.W. Shor. 1984. A Review and Analysis of Parameters for Assessing Transport of Environmentally Released Radionuclides through Agriculture, ORNL-5786, Health and Safety Research Division, Oak Ridge National Laboratory, Oak Rid
EPA. 2007. "Attachment 4-1. Guidance for Developing Ecological Soil Screening Levels." Revised. April.
Sample, B.E., J.J. Beauchamp, R.A. Efroymson, G W. Suter II, and T.L. Ashwood. 1998. Development and Validation of Bioaccumulation Models for Small Mammals, ES/ER/TM-219, Oak Ridge National Laboratory, Oak Ridge, TN.

[a] PAH BAFs estimated using log Kows and number of alkyl groups, based on regression equation presented in Brandt et al. (2002), Distribution of polycyclic aromatic hydrocarbons in soils and terrestrial biota after a spill of crude oil in Trecate, Italy, Environmental Toxicology and Chemistry, Vol. 21 (8): 1638-1643. (See Table 8-6 for details).

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TABLE 8-6
EXAMPLE ESTIMATION OF BIOTA SOIL ACCUMULATION FACTORS (BSAFs)(UPTAKE FACTORS) FOR PAHs

PAH	Log K_{ow}	No. Alkyl Groups	Log Mouse BSAF	Mouse BSAF
1-Methylnaphthalene	3.72	1	0.32	1.38
2-Methylnaphthalene	3.72	1	0.32	1.38
Acenaphthene	3.98	0	-0.22	0.80
Acenaphthylene	4.07	0	-0.26	0.77
Anthracene	4.45	0	-0.45	0.64
Benz(a)anthracene	5.66	0	-1.04	0.35
Benzo(a)pyrene	6.16	0	-1.28	0.28
Benzo(b)fluoranthene	6.12	0	-1.26	0.28
Benzo(g,h,i)perylene	6.5	0	-1.45	0.24
Benzo(k)fluoranthene	6.06	0	-1.23	0.29
Chrysene	5.66	0	-1.04	0.35
Dibenz(a,h)anthracene	6.84	0	-1.61	0.20
Fluoranthene	4.95	0	-0.69	0.50
Fluorene	4.18	0	-0.32	0.73
Indeno(1,2,3-cd)pyrene	6.58	0	-1.48	0.23
Naphthalene	3.3	0	0.11	1.12
Phenanthrene	4.57	0	-0.51	0.60
Pyrene	4.88	0	-0.66	0.52

Notes:

Log Kow values from ATSDR, 1995, Toxicological Profile for PAHs; ATSDR, 1995, Toxicological Profile for Naphthalene.

Regression Equation: Log mouse BSAF = 1.72 - 0.487 * LogK_{ow} + 0.411 * No. of Alkyl Groups

BSAF	biota soil accumulation factor
K_{ow}	octanol-water partition coefficient
Log	Log base 10
PAH	Polycyclic aromatic hydrocarbons

References:

Brandt, C.A., J.M. Brecker, and A. Porta, 2002, *Distribution of PAHs in Soils and Terrestrial Biota* after a Spill of Crude Oil in Trecate, Italy, **Environmental Toxicology and Chemistry**, Vol. 21, No. 8: 163

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FIGURES

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Y:\Shared\GIS_CAD_GIN\T\Figures\Mare Island\ISSA\00 Mare Island Vicinity Map.mxd

LEGEND

Mare Island Base Boundary

N

0 2.5 5 10 Miles

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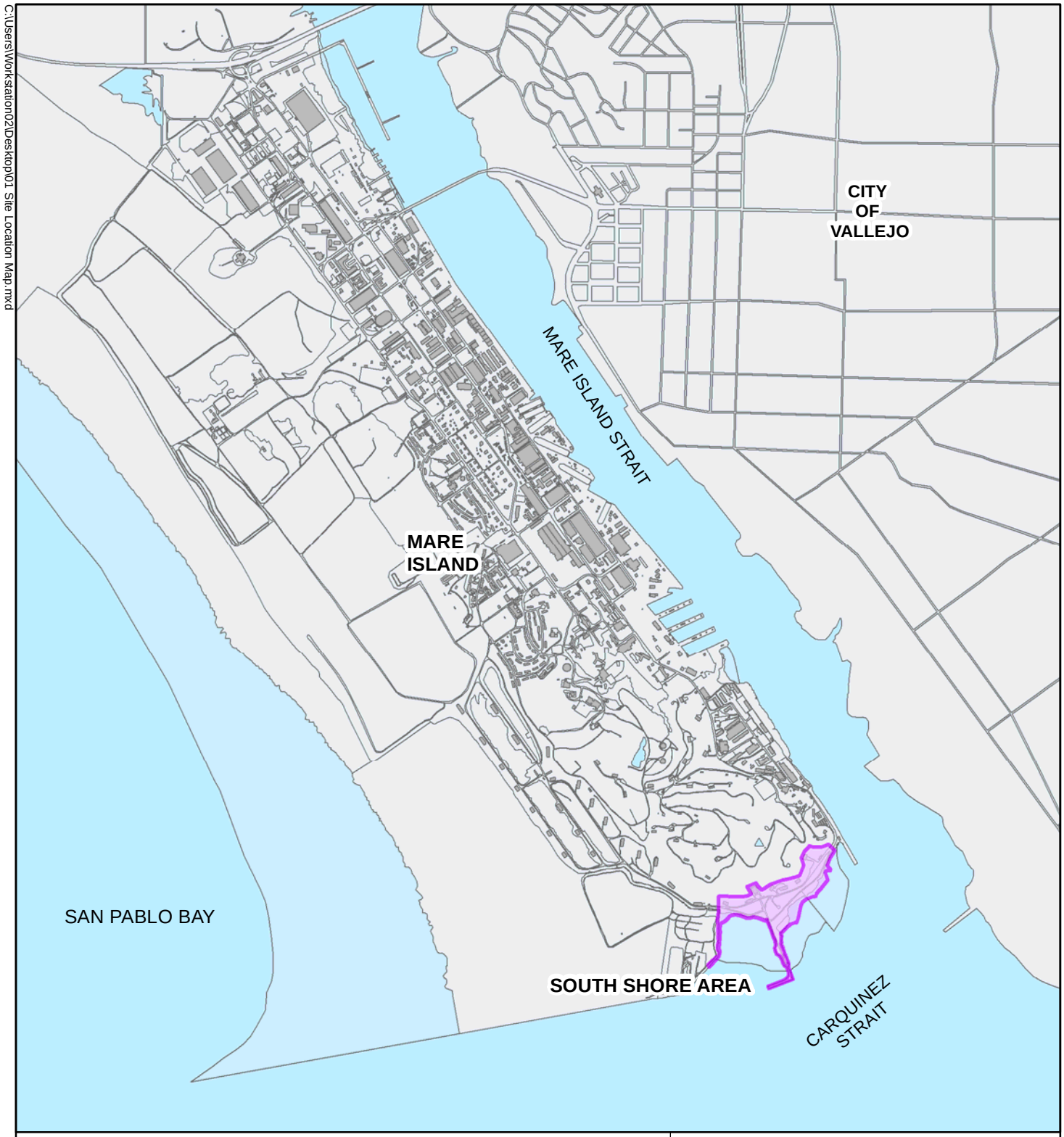
FIGURE 1-1
MARE ISLAND VICINITY MAP

NOREAS

DATE: MARCH 2014
CONTRACT NO.: N62473-12-C-4812
DCN: NRS-4812-0000-0001

C:\Users\Workstation02\Desktop\01 Site Location Map.mxd



LEGEND

SOUTH SHORE AREA BOUNDARY

N

0 0.25 0.5 1 Miles

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FIGURE 1-2
SITE LOCATION MAP

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PROJECT SCHEDULE
REMEDIAL INVESTIGATION SOUTH SHORE AREA
FORMER MARE ISLAND SHIPYARD
VALLEJO, CALIFORNIA
CONTRACT NO. 62473-12-C-4812

ID	Task Name	Duration	Start	Finish	Predecessors
1	**Award**	**0 days**	**Fri 9/28/12**	**Fri 9/28/12**	
9	Project Schedule	10 days	Fri 9/28/12	Thu 10/11/12	2
10	**Project Management (WE 1)**	630 days	Mon 5/5/14	Fri 9/30/16	2
11	**Project Meetings (WE 2)**	**299 days**	**Mon 5/5/14**	**Thu 6/25/15**	**2,10SS**
12	Project Kick-off Meeting	1 day	Mon 5/5/14	Mon 5/5/14	
13	Pre-Construction Meeting	1 day	Thu 6/25/15	Thu 6/25/15	
14	**RI Work Plan (WE 3)**	**717 days**	**Mon 10/1/12**	**Tue 6/30/15**	
26	**Field Activities (WE 5/Option 2)**	**60 days**	**Mon 7/20/15**	**Fri 10/9/15**	
27	Site Mark-out and Prep	2 days	Mon 7/13/15	Tue 7/14/15	
28	Mobilization	1 day	Mon 7/20/15	Mon 7/20/15	
29	Utility locate/Geophysical Survey	3 days	Mon 7/20/15	Wed 7/22/15	
30	Geophysical delineation of AF011 pit boundary	1 day	Thu 7/23/15	Thu 7/23/15	29
31	GW Monitoring Well Installation/Development	5 days	Wed 7/22/15	Tue 7/28/15	
32	GW Sampling	2 days	Mon 8/3/15	Tue 8/4/15	
33	Soil Boring and Sampling	10 days	Wed 7/29/15	Tue 8/11/15	31
34	Free Release/FSS - Deck Marker location	4 days	Wed 8/12/15	Mon 8/17/15	33
35	Additional Delineation (Potholing) of AF011 Grid - if necessary	2 days	Tue 8/18/15	Wed 8/19/15	34
36	Surveying	2 days	Mon 8/24/15	Tue 8/25/15	35
37	Biological Monitoring and Avoidance	23 days	Mon 7/20/15	Wed 8/19/15	
38	IDW Management & Disposal	2 days	Wed 8/26/15	Thu 8/27/15	36
39	Site Restoration & Demobilization	1 day	Wed 8/26/15	Wed 8/26/15	36
40	**RI Report (WE 4/Option 1)**	**280 days**	**Wed 8/26/15**	**Tue 9/20/16**	
41	Laboratory Analysis and Third-Party Data Validatation	30 days	Wed 8/26/15	Tue 10/6/15	36
42	Predraft RI Report	60 days	Wed 10/7/15	Tue 12/29/15	41
43	Navy Review	30 days	Wed 12/30/15	Tue 2/9/16	42
44	RTCs to Navy Comments	10 days	Wed 2/10/16	Tue 2/23/16	43

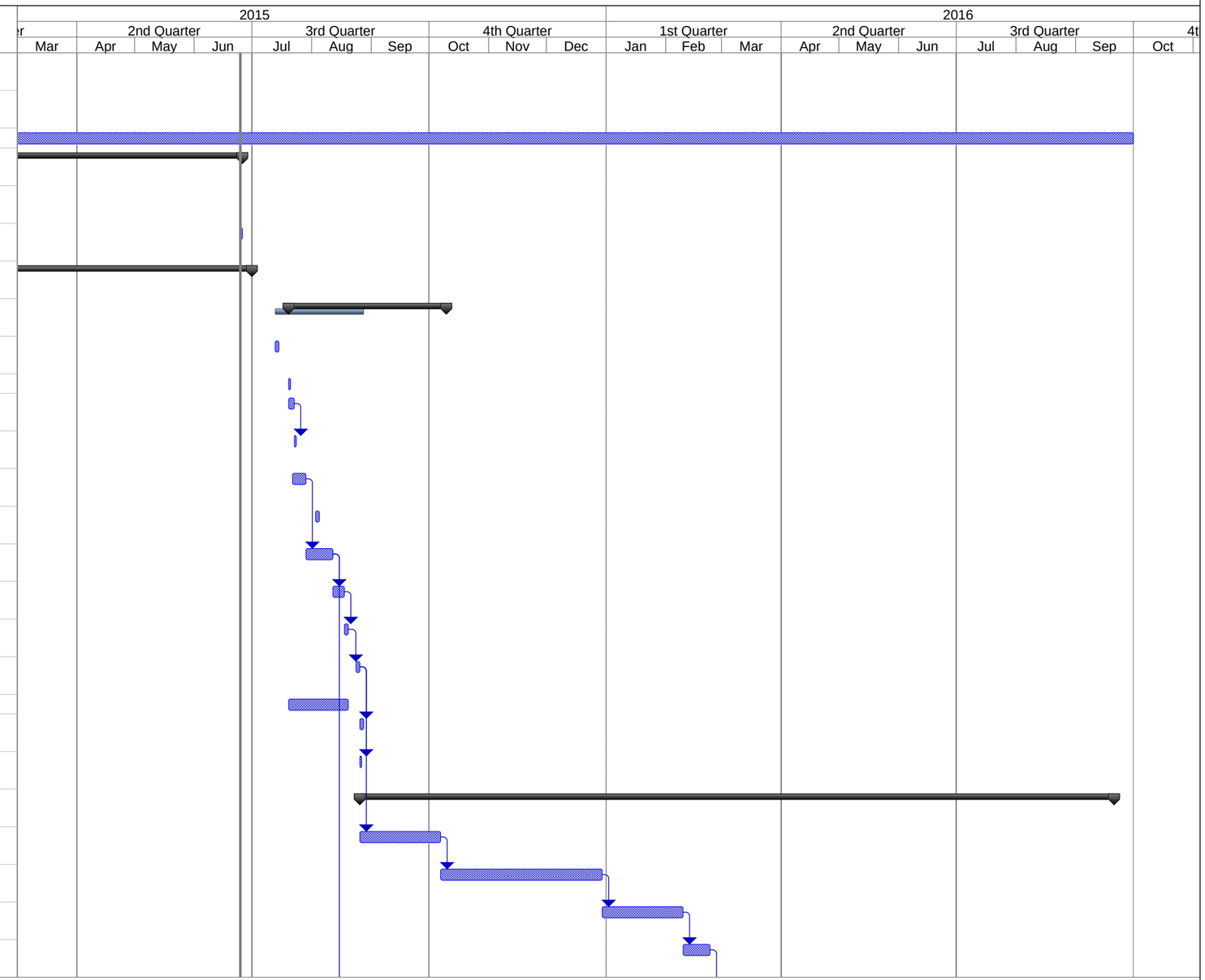


FIGURE 1-3

Task		Project Summary		Inactive Task		Duration-only		Finish-only	
Split		External Tasks		Inactive Milestone		Manual Summary Rollup		Progress	
Milestone		External Milestone		Inactive Summary		Manual Summary		Deadline	
Summary		Inactive Task		Manual Task		Start-only			

PROJECT SCHEDULE
REMEDIAL INVESTIGATION SOUTH SHORE AREA
FORMER MARE ISLAND SHIPYARD
VALLEJO, CALIFORNIA
CONTRACT NO. 62473-12-C-4812

ID	Task Name	Duration	Start	Finish	Predecessors
45	Draft RI Report	5 days	Wed 2/24/16	Tue 3/1/16	44
46	Agency Review	60 days	Wed 3/2/16	Tue 5/24/16	45
47	RTCs to Agency Comments	30 days	Wed 5/25/16	Tue 7/5/16	46
48	Draft Final RI Report	5 days	Wed 7/6/16	Tue 7/12/16	47
49	Agency Review	30 days	Wed 7/13/16	Tue 8/23/16	48
50	RTCs to Agency Comments	15 days	Wed 8/24/16	Tue 9/13/16	49
51	Final RI Report	5 days	Wed 9/14/16	Tue 9/20/16	50
52	**Additional RI - Rad Impacts (WE 6/Option 3)**	**621 days**	**Mon 4/1/13**	**Mon 8/17/15**	
53	RAD Screening Work Plan, includes RMMP and RPP	45 days	Mon 4/1/13	Fri 5/31/13	
54	Navy/RASO Review	60 days	Mon 6/3/13	Fri 8/23/13	53
55	Draft Work Plan/RMMP/RPP	1 day	Fri 11/8/13	Fri 11/8/13	
56	Agency Review	50 days	Mon 11/11/13	Fri 1/17/14	55
57	RTCs to Draft RAD Screening Work Plan/RMMP/RPP	50 days	Mon 1/20/14	Fri 3/28/14	56
58	Agency review	7 days	Mon 3/31/14	Tue 4/8/14	57
59	Final Work Plan/RMMP/RPP	3 days	Wed 4/9/14	Fri 4/11/14	58
60	Field Actvities - Free Release/FSS	4 days	Wed 8/12/15	Mon 8/17/15	33
61	**After Action Report (WE 7/Option 4)**	**85 days**	**Tue 8/18/15**	**Mon 12/14/15**	
66	**Update SCM (WE 8/Option 5)**	**110 days**	**Tue 9/8/15**	**Mon 2/8/16**	
73	**Groundwater Request for Exception to Drinking Water Policy (WE 9/Option 6)**	**135 days**	**Tue 8/14/12**	**Mon 2/18/13**	
74	Predraft Request	30 days	Tue 8/14/12	Mon 9/24/12	
75	Navy Review	30 days	Tue 9/25/12	Mon 11/5/12	74
76	RTCs to Navy Comments	5 days	Tue 11/6/12	Mon 11/12/12	75
77	Draft Request	5 days	Tue 11/13/12	Mon 11/19/12	76
78	Agency Review/Public Comment	60 days	Tue 11/20/12	Mon 2/11/13	77
79	Final Request	5 days	Tue 2/12/13	Mon 2/18/13	78

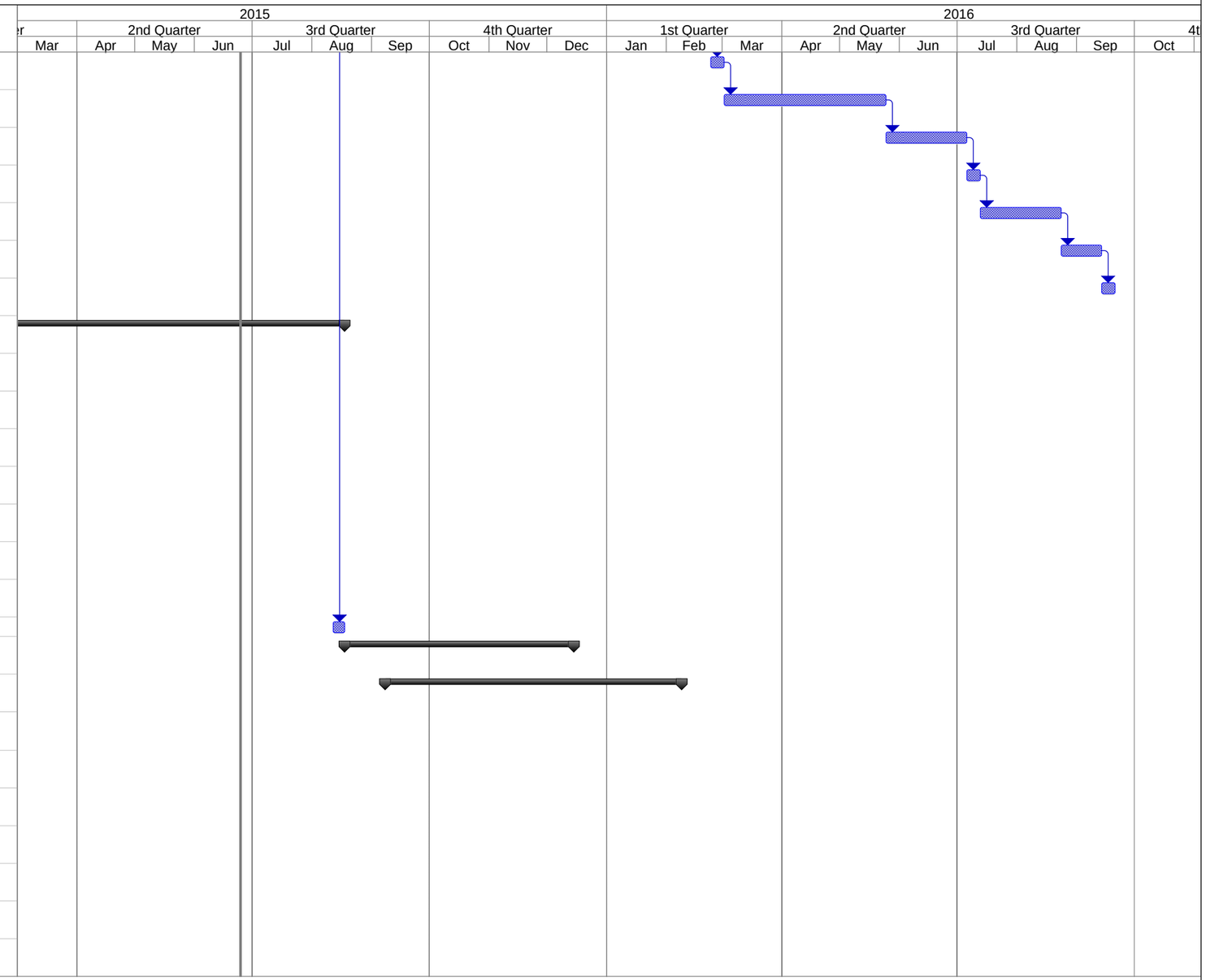
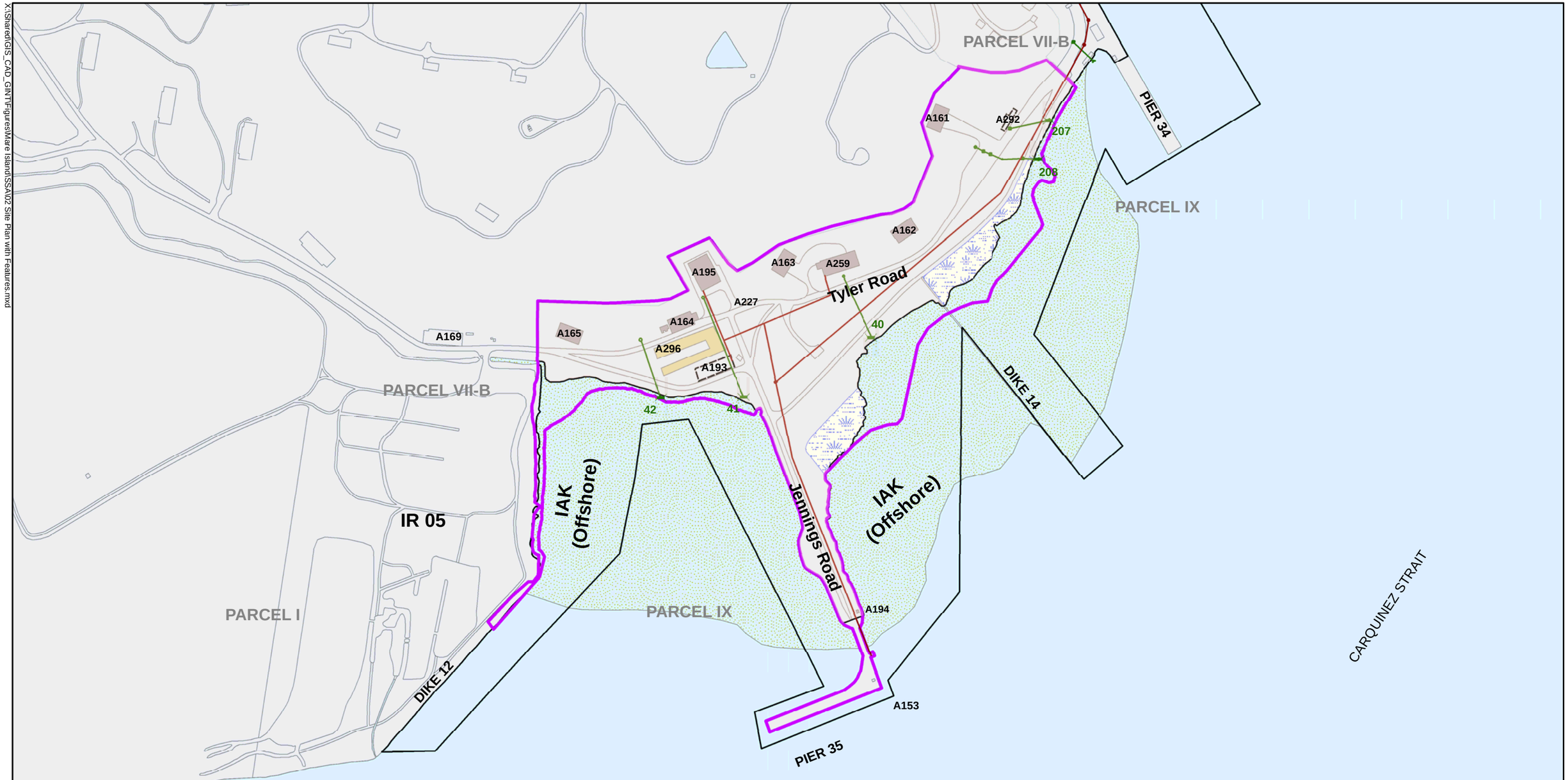


FIGURE 1-3

Task		Project Summary		Inactive Task		Duration-only		Finish-only	
Split		External Tasks		Inactive Milestone		Manual Summary Rollup		Progress	
Milestone		External Milestone		Inactive Summary		Manual Summary		Deadline	
Summary		Inactive Task		Manual Task		Start-only			

X:\Shared\GIS_CAD_GINT\Figures\Mare Island\SSA\02 Site Plan with Features.mxd



LEGEND

- INVESTIGATION AREA (IA)
- TRANSFER PARCEL BOUNDARY
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM SEWER DRAIN LINE (SWMU 93)
- INVESTIGATION AREA K (IAK)
- STORM SEWER OUTFALLS (SWMU 93)
- BUILDINGS
- REMOVED BUILDING
- SOUTH SHORE AREA BOUNDARY FOR RI
- WETLANDS
- TIDAL MUDFLATS
- EXPLOSIVES SAFE HAVEN

N

0 200 400 800 Feet

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FIGURE 2-1

SITE PLAN WITH FEATURES

NOREAS

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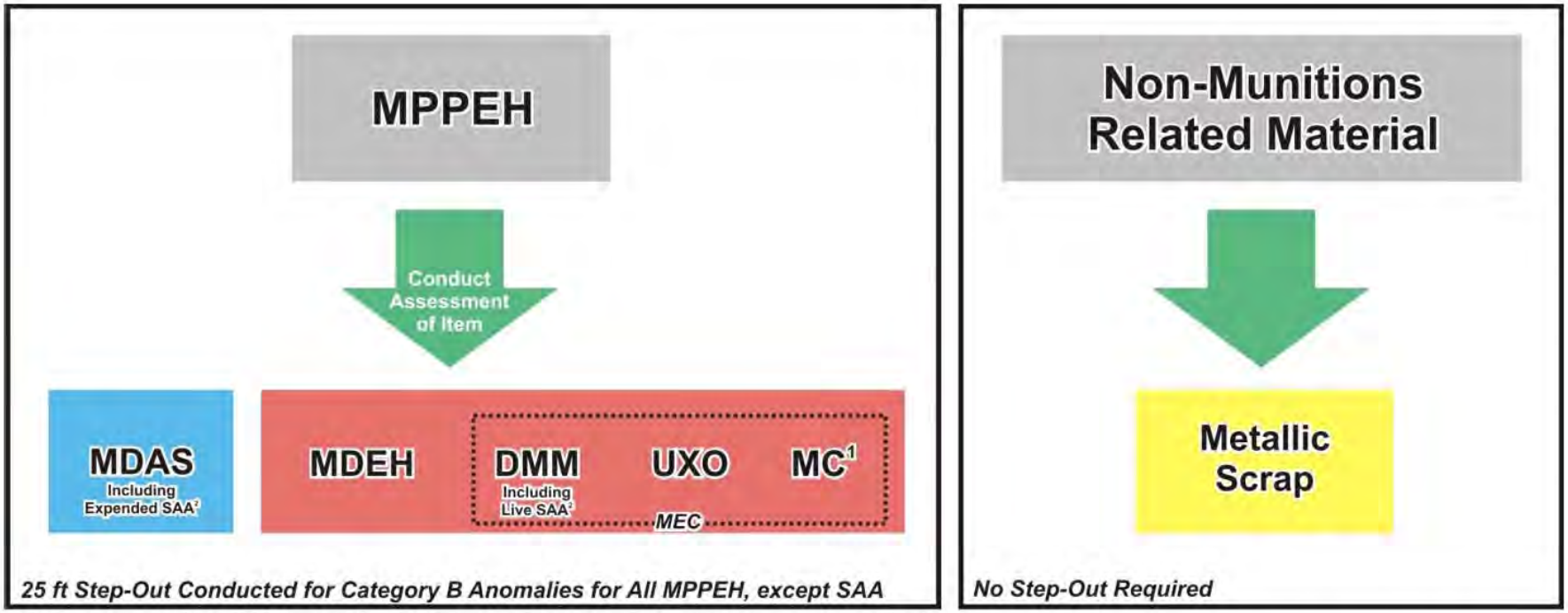
DCN: NRS-4812-0000-0009



(1) Corresponds to MC present in high enough concentrations to pose an explosive hazard.
(2) For the purposes of classifying and disposing of MPPEH, live SAA was handled as DMM and expended SAA was handled as MDAS. Step-out investigations were not conducted for SAA because it contains an insufficient quantity of filler to pose an explosive hazard and its presence in the environment was not considered indicative of larger caliber military munitions.

MPPEH - Material Potentially Presenting an Explosive Hazard
MDAS - Material Documented as Safe
MDEH - Material Documented as an Explosive Hazard
MC - Munitions Constituents
DMM - Discarded Military Munition
UXO - Unexploded Ordnance
MEC - Munitions and Explosives of Concern
SAA - Small Arms Ammunition

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FIGURE 2-2
SUMMARY OF MUNITIONS TERMINOLOGY

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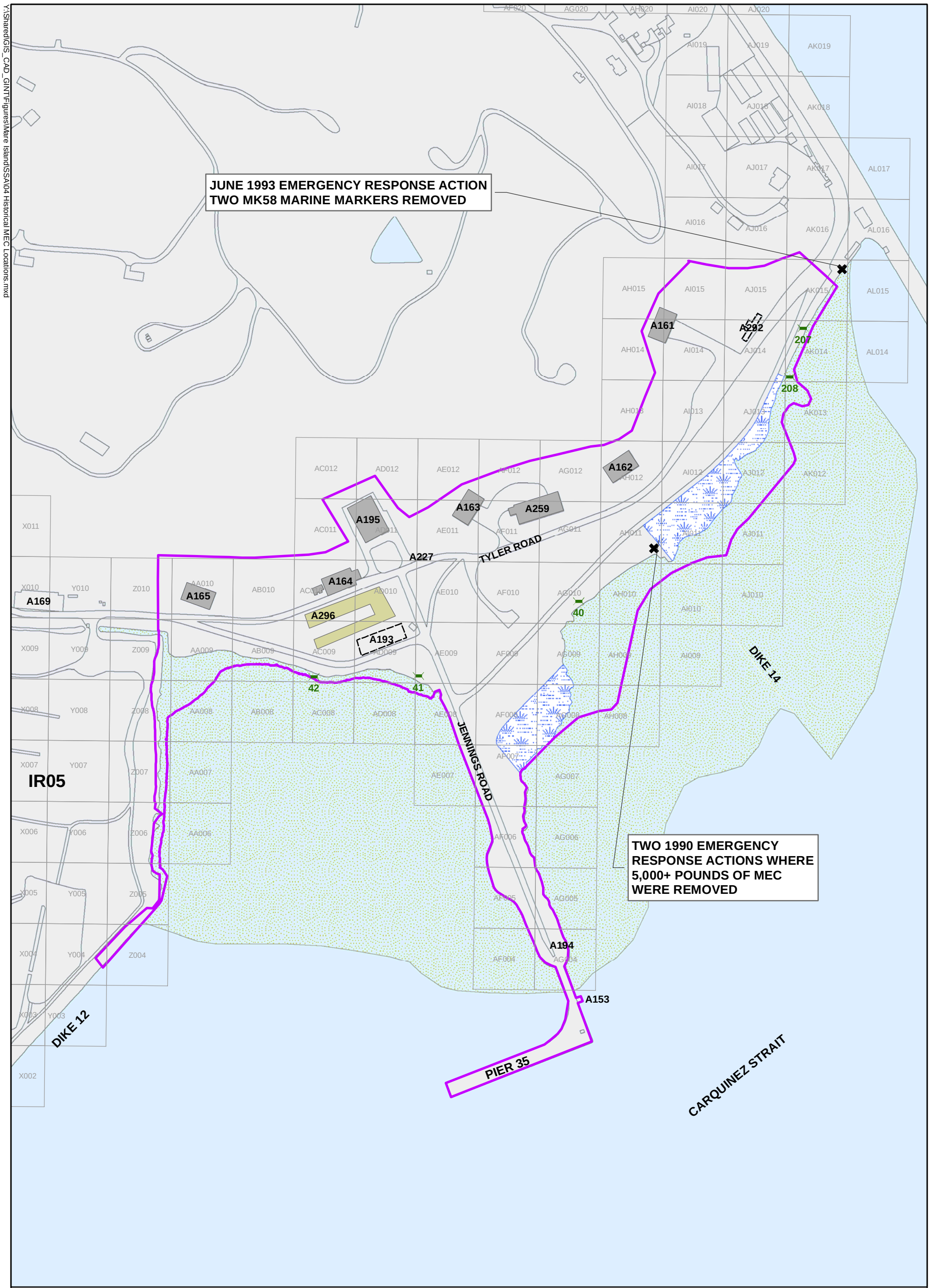

LEGEND

- ✖ RESPONSE ACTIONS (1990-1995)
- STORM/SEWER OUTFALLS (SWMU 93)
- SOUTH SHORE AREA BOUNDARY
- REMOVED BUILDING
- BUILDINGS
- WETLANDS
- TIDAL MUDFLATS
- EXPLOSIVES SAFE HAVEN

N

0 150 300 600 Feet

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FIGURE 2-3

MUNITIONS EMERGENCY RESPONSE ACTIONS (1990-1995)

NORESAS

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DCN: NRS-4812-0000-0001

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TORPEDO EXPLODER, GRENADES, FUZES, PRIMERS, 20 AND 40-MILLIMETER, 1.1-INCH, 3 AND 4-INCH PROJECTILES, 1,3,6,9, AND 12-POUNDERS, PROPELLANT, HE FILLER (1,545 TOTAL)

FUZES AND PRIMERS (26)

20-MILLIMETER (2)

20-MILLIMETER AND CARTRIDGE CASES (12)

FUZE (1)

20-MILLIMETER (1)

20-MILLIMETER (1)

FUZES, 4 AND 6-INCH PROJECTILES, PRIMERS (215)

APPROXIMATE LOCATION OF DECK MARKER FOUND DURING EMERGENCY REMOVAL ACTION IN 1999

FLARE BASE (1)

20-MILLIMETER AND CARTRIDGE CASES (2)

DRIFT FLARES (3)

20-MILLIMETER (1)

A161 A292 A162 A163 A259 A195 A227 A164 A165 A296 A193 A194

207 208 40 41 42

TYLER RD

JENNINGS RD

DIKE 14

DIKE 12

CARQUINEZ STRAIT

PIER 35

N

0 150 300 600 Feet

LEGEND

- MEC ITEMS RECOVERED DURING PREVIOUS INTRUSIVE INVESTIGATIONS AND REMOVAL ACTIONS (1997-2000)
- STORM/SEWER OUTFALLS (SWMU 93)
- SOUTH SHORE AREA BOUNDARY FOR RI
- REMOVED BUILDING
- PRIMER PIT
- OVEN PIT
- WETLANDS
- TIDAL MUDFLATS
- EXPLOSIVES SAFE HAVEN
- REMOVED BUILDING
- A195 BUILDINGS
- APPROXIMATE LOCATION WHERE DECK MARKER FOUND IN 1999
- (2) NUMBER INDICATES QUANTITY OF ITEMS RECOVERED

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FIGURE 2-4

RECOVERED MUNITIONS AND EXPLOSIVES OF CONCERN (1997-2000)

NORTHREAS

DATE: APRIL 2014
CONTRACT NO.: N62473-12-R-4812
DCN: NRS-4812-0000-0001

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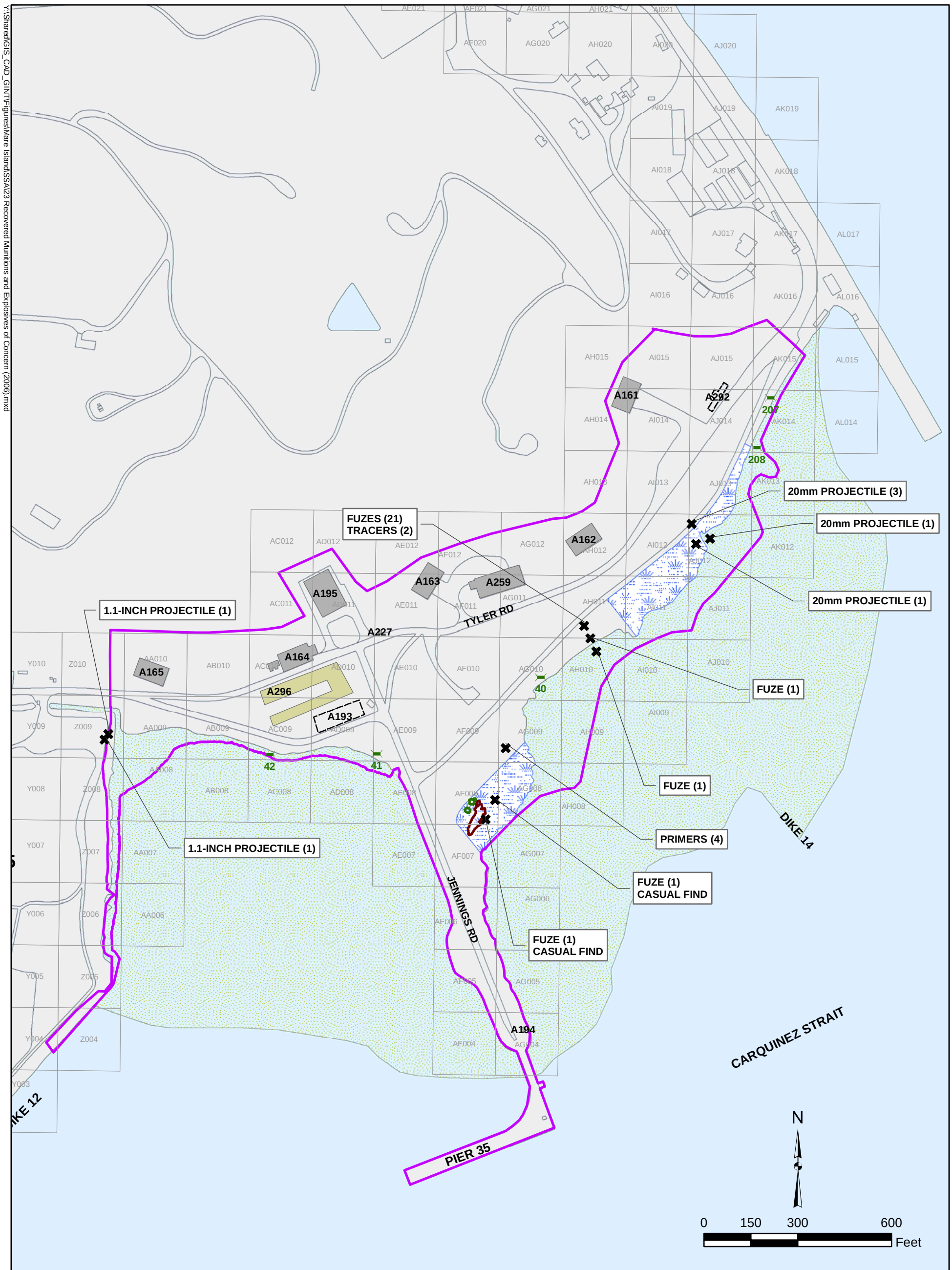

LEGEND

- ✖ MEC ITEMS RECOVERED DURING PREVIOUS INTRUSIVE INVESTIGATION AND REMOVAL ACTION (2006)
- STORM/SEWER OUTFALLS (SWMU 93)
- SOUTH SHORE AREA BOUNDARY FOR RI
- REMOVED BUILDING
- PRIMER PIT
- OVEN PIT
- WETLANDS
- TIDAL MUDFLATS
- EXPLOSIVES SAFE HAVEN

- REMOVED BUILDING
- BUILDINGS
- (2) NUMBER INDICATES QUANTITY OF ITEMS RECOVERED

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FIGURE 2-5

RECOVERED MUNITIONS AND EXPLOSIVES OF CONCERN (2006)

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DCN: NRS-4812-0000-0001

Legend

- PMA/SSA Upland Boundary
- Coastal Salt Marsh
- Grid
- Cat A Boundary
- non-picked Cat B anomalies

ISR-JV

- MEC (DMM)
- MDAS
- Live Small Arms
- Expended Small Arms
- Inaccessible
- Debris
- Blind QC Seed
- Blind QA Seed
- GPO Seed
- MK6 Depth Charge

Battelle

- MEC (DMM)
- MDAS
- MDEH
- Live Small Arms
- Expended Small Arms
- Debris
- No Contact
- Mag and Dig Area (Battelle)

FIGURE SOURCE
FIGURE 13 OF DRAFT REMOVAL ACTION COMPLETION REPORT FOR THE NON-TIME CRITICAL REMOVAL ACTION AT THE PRODUCTION MANUFACTURING AREA AND SOUTH SHORE AREA, FORMER MARE ISLAND NAVAL SHIPYARD, VALLEJO, CA (ISR-JV, 2013)

N

0 75 150 225
Feet

Service Layer Credits: Source: Esri, DigitalGlobe, GeoEye, i-cubed, USDA, USGS, AEX, Getmapping,

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FIGURE 2-6
EXCAVATION RESULTS MEC
NTCRA AT SSA (2012-2013)

NCREAS

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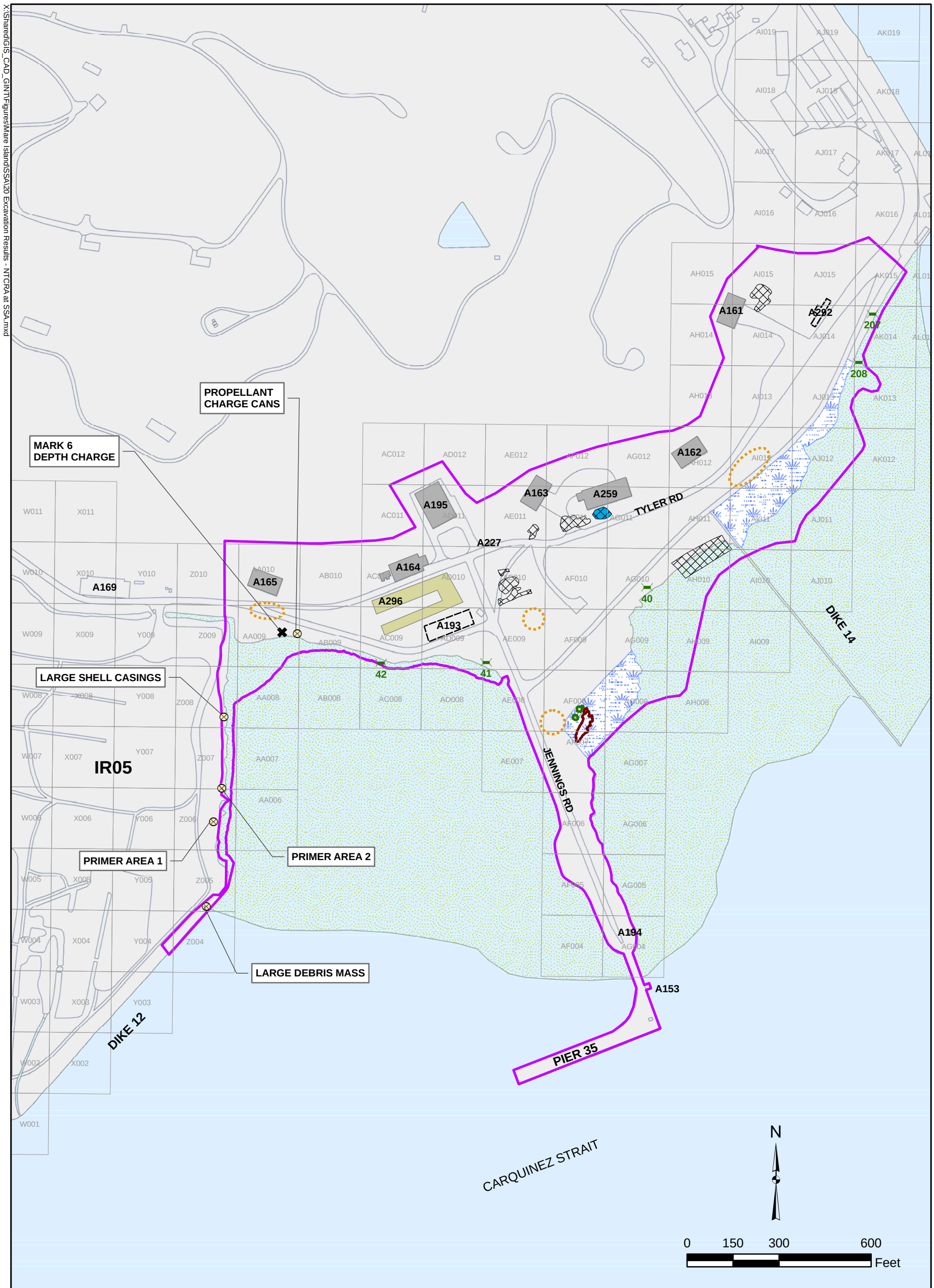
CONTRACT NO. N62473-12-R-4812
DCN: NRE-4812-0000-0001

X:\Shared\GIS_CAD_GIN\T\Figures\Mare Island\SSA\20 Excavation Results - NTCRA at SSA.mxd



LEGEND

- MUNITIONS ITEMS IDENTIFIED DURING VISUAL SURVEY (NOT REMOVED)
- STORM/SEWER OUTFALLS (SWMU 93)
- NON-PIT AREAS WHERE HIGH DENSITY OF MEC ITEMS REMOVED (2012-2013)
- SOUTH SHORE AREA BOUNDARY
- REMOVED BUILDING
- PRIMER PIT (REMOVED)
- OVEN PIT (REMOVED)
- DISPOSAL PIT AREA (REMOVED)
- AF011 PIT - UNRESOLVED
- A195 BUILDINGS
- WETLANDS
- TIDAL MUDFLATS
- EXPLOSIVES SAFE HAVEN
- REMOVED MEC ITEM (2012-2013)

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FIGURE 2-7

AREAS WHERE HIGH DENSITY OF MEC ITEMS FOUND - MEC NTCRA (2012-2013)

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DCN: NRS-4812-0000-0001

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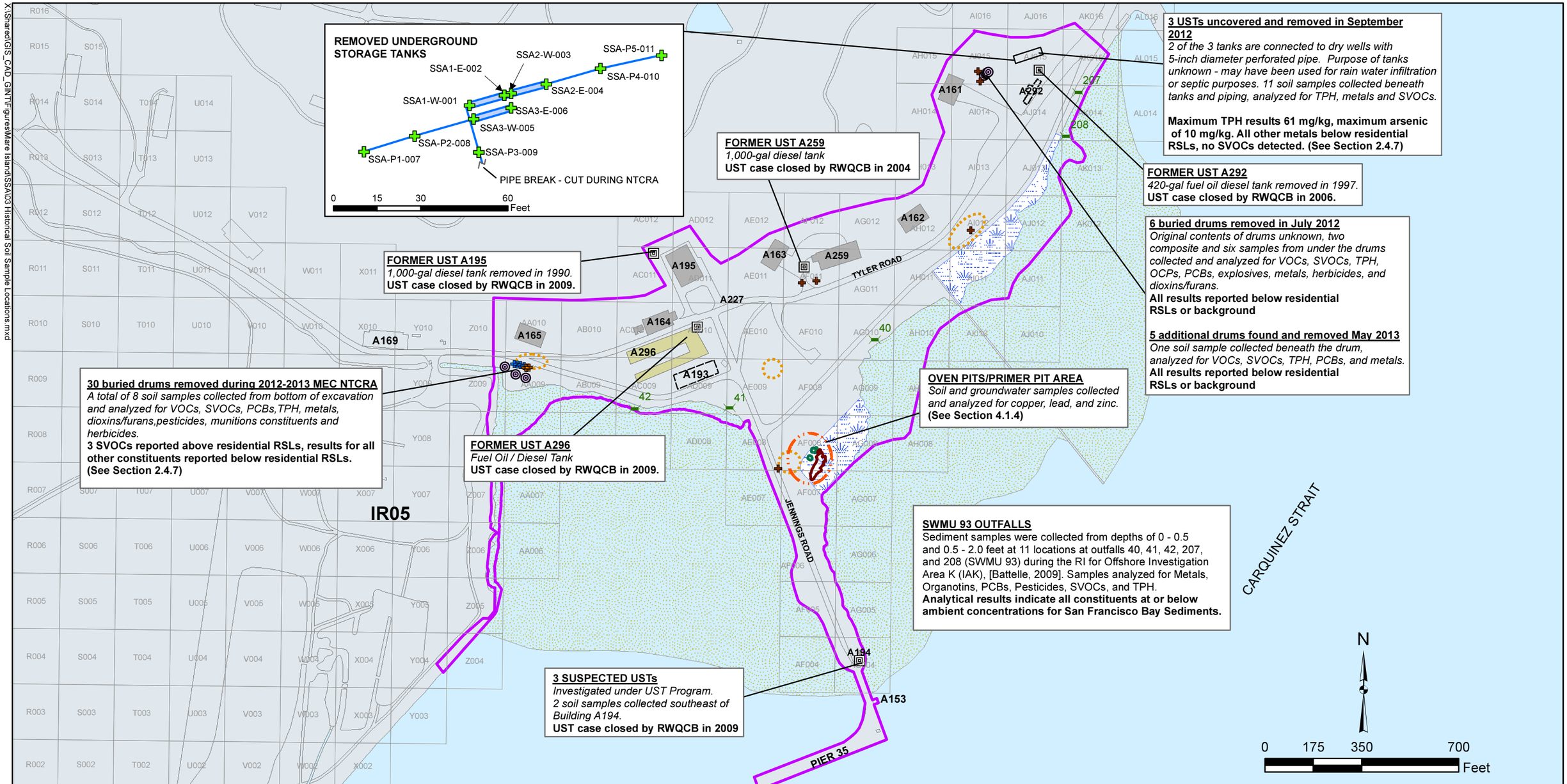

LEGEND

- PRIMER PIT
- OVEN PITS
- NON-PIT AREAS WHERE HIGH DENSITY OF MEC ITEMS REMOVED
- STORM/SEWER OUTFALLS (SWMU 93)
- BURIED DRUM LOCATION
- FORMER UNDERGROUND STORAGE TANK LOCATION
- SOUTH SHORE AREA BOUNDARY
- REMOVED BUILDING
- WETLANDS
- A196 BUILDINGS
- EXPLOSIVES SAFE HAVEN
- TIDAL MUDFLATS
- NTCRA Sample Location (Metals, SVOCs, TPH)
- NTCRA Sample Location (Metals, Explosives)
- NTCRA Sample Location (Metals, VOCs, SVOCs, PCBs, TPH)
- NTCRA Sample Location (Metals, VOCs, SVOCs, PCBs, Pesticides, Dioxins/Furans, Explosives, Herbicides, TPH)

ACRONYMS

BTEX - BENZENE, TOLUENE, ETHYLBENZENE, AND XYLENES

MEC - MUNITIONS AND EXPLOSIVES OF CONCERN

mg/kg - MILLIGRAM PER KILOGRAM

NTCRA - NON-TIME CRITICAL REMOVAL ACTION

RSL - REGIONAL SCREENING LEVEL (US EPA)

RWQCB - (CALIFORNIA) REGIONAL WATER QUALITY CONTROL BOARD - SAN FRANCISCO BAY REGION.

TEQ - TOXIC EQUIVALENT

TPH - TOTAL PETROLEUM HYDROCARBON

TPH-d - TOTAL PETROLEUM HYDROCARBON - DIESEL RANGE

UST - UNDERGROUND STORAGE TANK

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FIGURE 2-8

HISTORICAL SOIL SAMPLING LOCATIONS AT SSA

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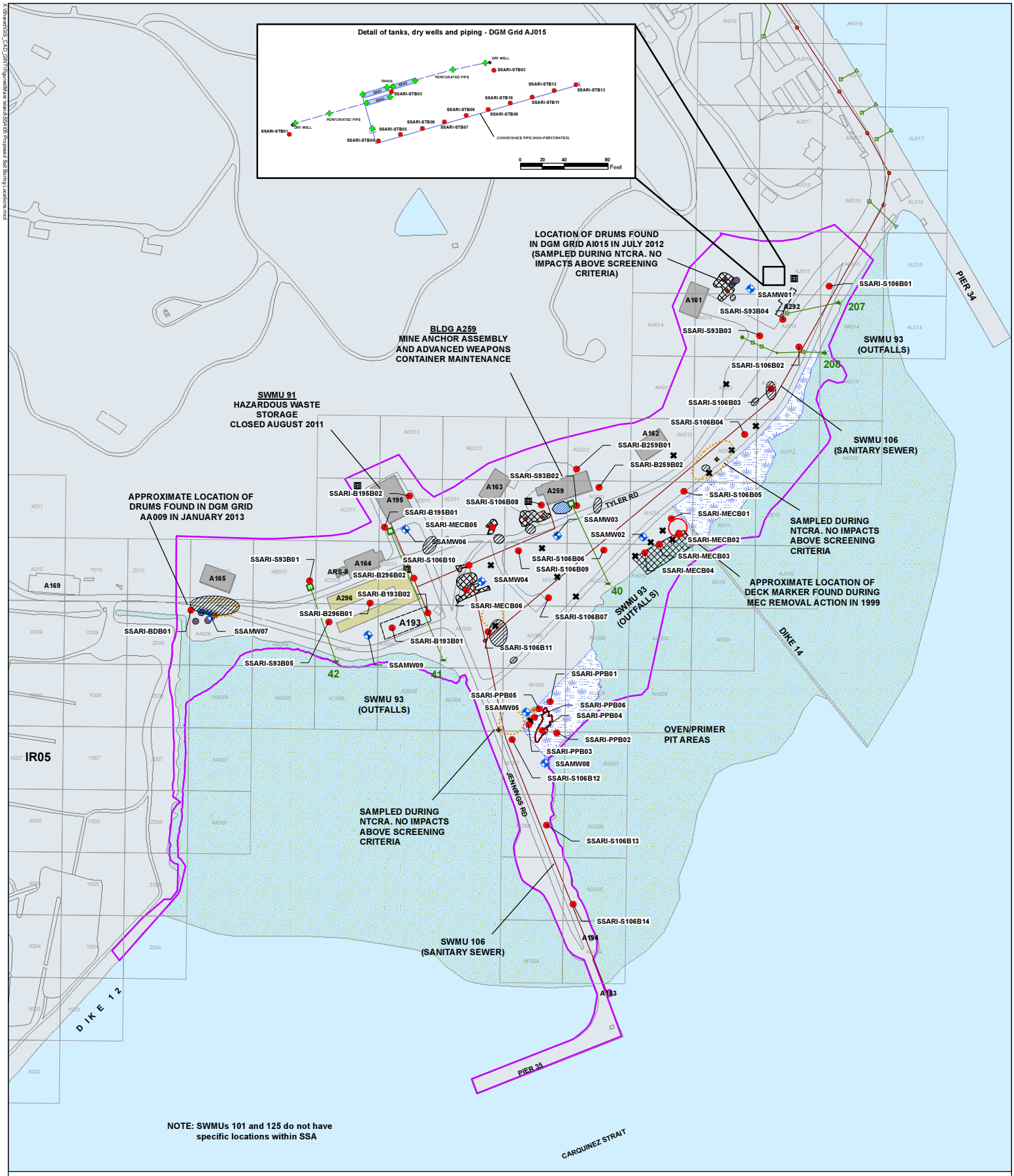
DATE: APRIL 2014
CONTRACT NO.: N62473-12-C-4812
DCN: NRS-4812-0000-0001



NOTE: SWMUs 101 and 125 do not have specific locations within SSA

LEGEND

- PROPOSED BORING LOCATIONS
- REMOVED MUNITIONS AND EXPLOSIVES OF CONCERN (MEC) LOCATION
- PROPOSED GROUNDWATER MONITORING WELL
- BURIED DRUMS (REMOVED)
- OVEN PIT
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM DRAIN LINE
- FORMER UNDERGROUND STORAGE TANK LOCATION
- SWMU — SOLID WASTE MANAGEMENT UNIT
- ABRASIVE BLAST MATERIAL
- STORM SEWER OUTFALLS (SWMU 93)
- DISPOSAL PIT AREA
- UNRESOLVED PIT AREA
- SOUTH SHORE AREA BOUNDARY FOR
- REMOVED BUILDING
- EXPLOSIVES SAFE HAVEN
- NON-PIT AREAS WHERE HIGH DENSITY OF MEC ITEMS REMOVED
- PRIMER PIT (REMOVED)
- BUILDINGS
- WETLANDS
- TIDAL MUDFLATS
- NTCRA Sample Location (Metals, SVOCs, TPH)
- NTCRA Sample Location (Metals, Explosives)
- NTCRA Sample Location (Metals, VOCs, SVOCs, PCBs, TPH)
- NTCRA Sample Location (Metals, VOCs, SVOCs, PCBs, Pesticides, Dioxins/Furans, Explosives, Herbicides, TPH)
- STORM DRAIN (SWMU 93)

N

0 150 300 600 Feet

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FIGURE 4-1
SUMMARY OF PROPOSED SOIL AND GROUNDWATER SAMPLING LOCATIONS

NOREAS Environmental Engineering and Science

DATE: JUNE 2015
CONTRACT NO.: N62473-12-C-4812
DCN: NRS-4812-0000-0009

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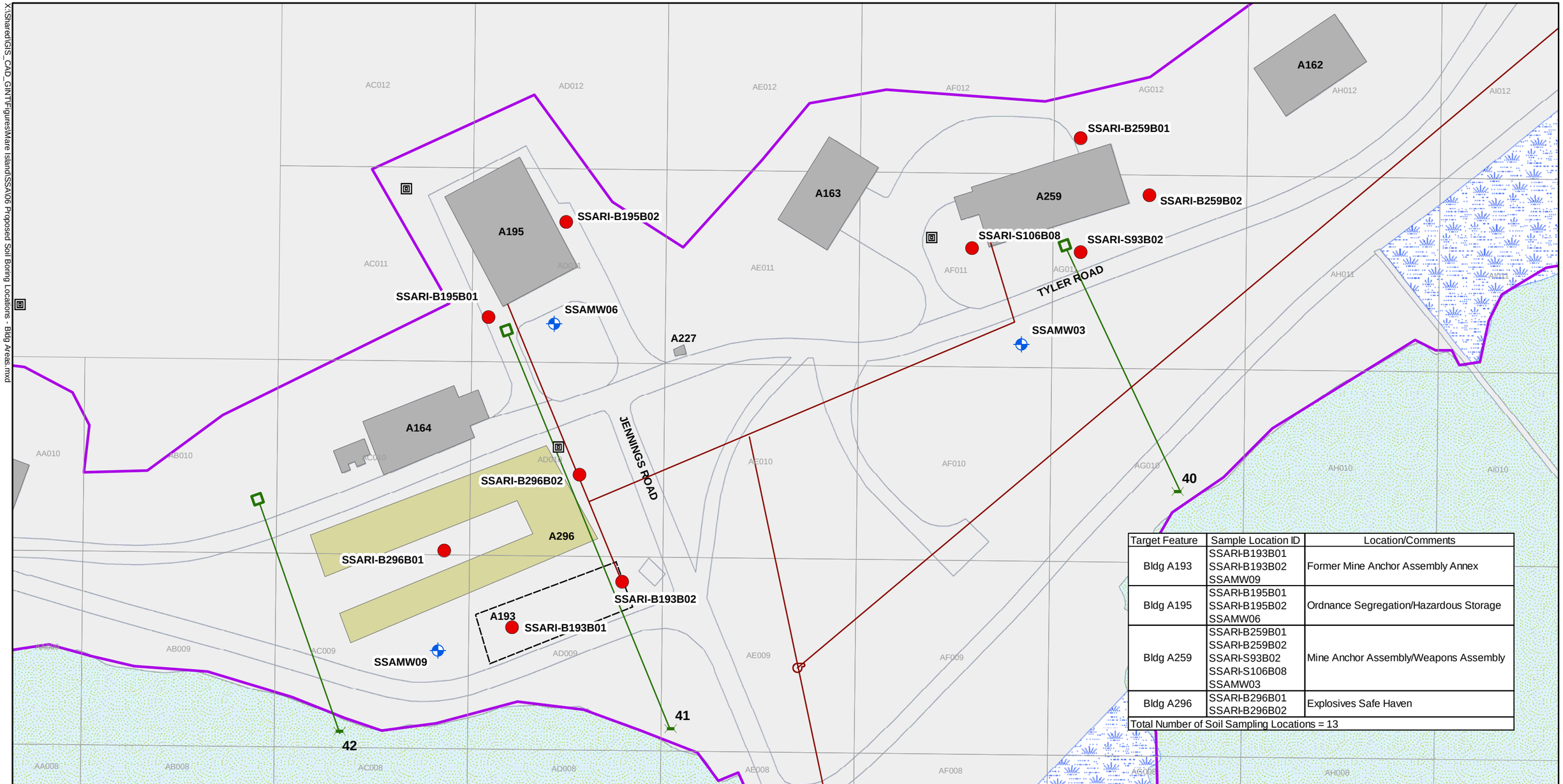

Target Feature	Sample Location ID	Location/Comments
Bldg A193	SSARI-B193B01 SSARI-B193B02 SSAMW09	Former Mine Anchor Assembly Annex
Bldg A195	SSARI-B195B01 SSARI-B195B02 SSAMW06	Ordnance Segregation/Hazardous Storage
Bldg A259	SSARI-B259B01 SSARI-B259B02 SSARI-S93B02 SSARI-S106B08 SSAMW03	Mine Anchor Assembly/Weapons Assembly
Bldg A296	SSARI-B296B01 SSARI-B296B02	Explosives Safe Haven
Total Number of Soil Sampling Locations = 13		

LEGEND

- PROPOSED BORING LOCATION
- PROPOSED GROUNDWATER MONITORING WELL
- STORM SEWER OUTFALLS (SWMU 93)
- FORMER UNDERGROUND STORAGE TANK LOCATION
- BUILDINGS
- SOUTH SHORE AREA BOUNDARY
- REMOVED BUILDING
- EXPLOSIVES SAFE HAVEN
- WETLANDS
- TIDAL MUDFLATS
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM SEWER DRAIN LINE (SWMU 93)
- STORM DRAIN (SWMU 93)

N

0 50 100 200 Feet

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FIGURE 4-2

PROPOSED SOIL SAMPLING LOCATIONS - BUILDING AREAS

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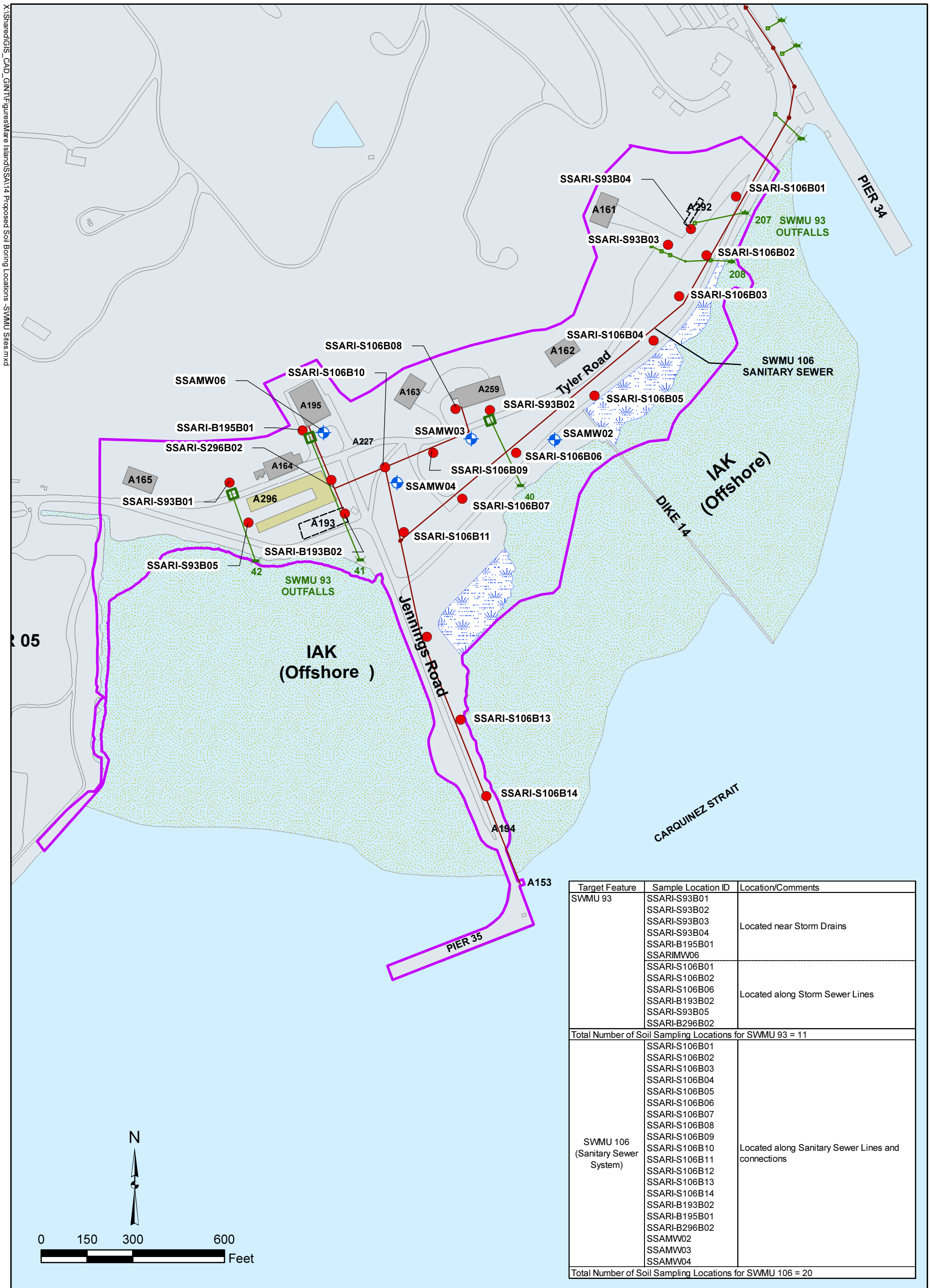

Target Feature	Sample Location ID	Location/Comments
SWMU 93	SSARI-S93B01 SSARI-S93B02 SSARI-S93B03 SSARI-S93B04 SSARI-B195B01 SSARIMW06	Located near Storm Drains
	SSARI-S106B01 SSARI-S106B02 SSARI-S106B06 SSARI-B193B02 SSARI-S93B05 SSARI-B296B02	Located along Storm Sewer Lines
Total Number of Soil Sampling Locations for SWMU 93 = 11		
SWMU 106 (Sanitary Sewer System)	SSARI-S106B01 SSARI-S106B02 SSARI-S106B03 SSARI-S106B04 SSARI-S106B05 SSARI-S106B06 SSARI-S106B07 SSARI-S106B08 SSARI-S106B09 SSARI-S106B10 SSARI-S106B11 SSARI-S106B12 SSARI-S106B13 SSARI-S106B14 SSARI-B193B02 SSARI-B195B01 SSARI-B296B02 SSAMW02 SSAMW03 SSAMW04	Located along Sanitary Sewer Lines and connections
Total Number of Soil Sampling Locations for SWMU 106 = 20		

LEGEND

- PROPOSED BORING LOCATION
- PROPOSED GROUNDWATER MONITORING WELL
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM SEWER DRAIN LINE (SWMU 93)
- IAK INVESTIGATION AREA K
- SWMU SOLID WASTE MANAGEMENT UNIT
- STORM DRAIN (SWMU 93)
- STORM SEWER OUTFALLS (SWMU 93)
- SOUTH SHORE AREA BOUNDARY
- REMOVED BUILDING
- BUILDINGS
- WETLANDS
- TIDAL MUDFLATS
- EXPLOSIVES SAFE HAVEN

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FIGURE 4-3

PROPOSED SOIL SAMPLING LOCATIONS
SWMU SITES

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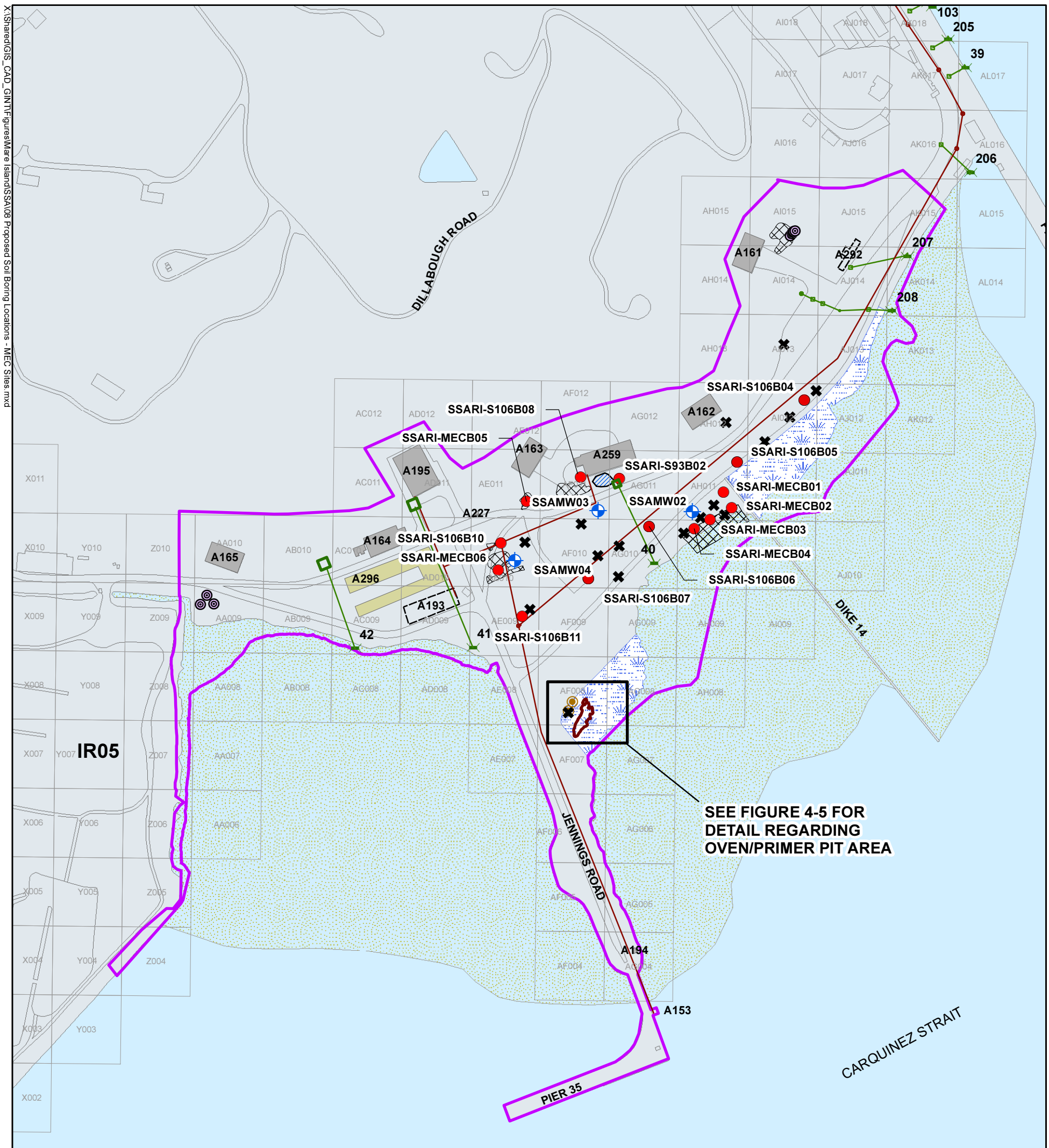

Target Feature	Sample Location ID	Location/Comments
Former MEC Sites	SSARI-MECB01	Disposal Pit in DGM Grids AH010/AH011 + deck marker recovered near Dike 14
	SSARI-MECB02	
	SSARI-MECB03	
	SSARI-MECB04	
	SSARI-MECB05	Disposal pit in DGM Grid AE011
	SSARI-MECB06	Disposal pit in DGM Grid AE010
	SSARI-S93B02	Disposal pit in DGM Grid AF011/AG011
	SSARI-S106B04	Disposal pit in DGM Grid AF011
	SSARI-S106B05	
	SSARI-S106B06	
	SSARI-S106B07	
	SSARI-S106B08	
	SSARI-S106B10	
	SSARI-S106B11	
	SSAMW02	
	SSAMW03	
	SSAMW04	
Total Number of Soil Sampling Locations = 17		
*See Figure 4-5 for soil sampling locations in the Oven/Primer Pit area		

N

0 150 300 600 Feet

LEGEND

- PROPOSED BORING LOCATION
- PROPOSED GROUNDWATER MONITORING WELL
- RECOVERED MUNITIONS AND EXPLOSIVE OF CONCERN (MEC)
- FORMER BURIED DRUM LOCATION
- OVEN PIT
- PRIMER PIT (REMOVED)
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM SEWER DRAIN LINE (SWMU 93)
- STORM DRAIN (SWMU 93)
- STORM SEWER OUTFALLS (SWMU 93)
- SOUTH SHORE AREA BOUNDARY
- BUILDINGS
- REMOVED BUILDING
- DISPOSAL PIT AREA
- UNRESOLVED PIT AREA (AF011)
- WETLANDS
- TIDAL MUDFLATS
- EXPLOSIVES SAFE HAVEN

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FIGURE 4-4
PROPOSED SOIL SAMPLING LOCATIONS - MEC SITES

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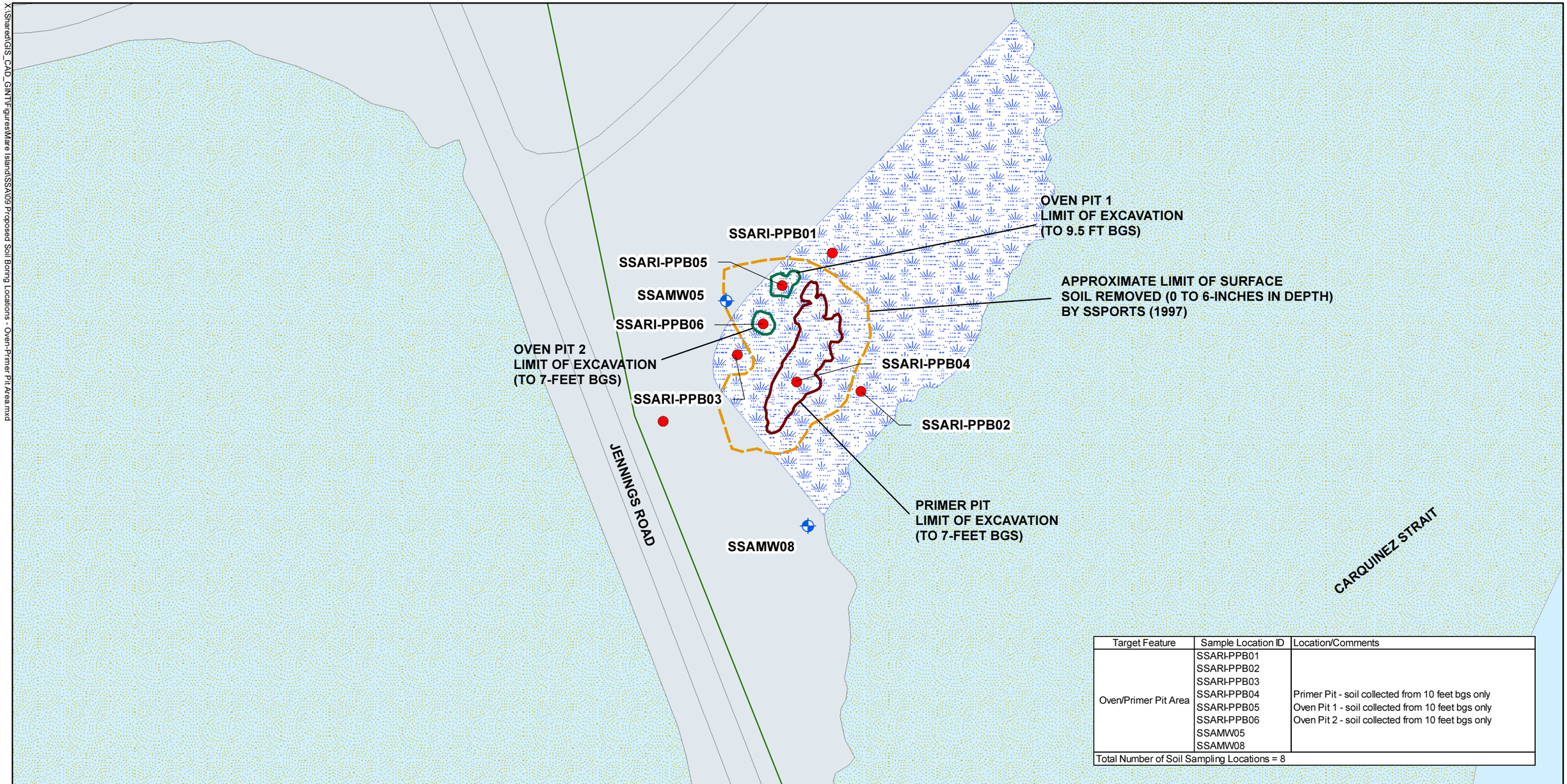

Target Feature	Sample Location ID	Location/Comments
Oven/Primer Pit Area	SSARI-PPB01	
	SSARI-PPB02	
	SSARI-PPB03	
	SSARI-PPB04	Primer Pit - soil collected from 10 feet bgs only
	SSARI-PPB05	Oven Pit 1 - soil collected from 10 feet bgs only
	SSARI-PPB06	Oven Pit 2 - soil collected from 10 feet bgs only
	SSAMW05	
	SSAMW08	
Total Number of Soil Sampling Locations = 8		

LEGEND

- PROPOSED BORING LOCATION
- PROPOSED GROUNDWATER MONITORING WELL
- SANITARY SEWER PIPELINE (SWMU 106)
- WETLANDS
- PRIMER PIT
- OVEN PITS
- BGS BELOW GROUND SURFACE
- LIMIT OF SURFACE SOIL EXCAVATION
- TIDAL MUDFLATS

N

0 35 70 140 Feet

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FIGURE 4-5

PROPOSED SOIL SAMPLING LOCATIONS - OVEN/PRIMER PIT AREAS

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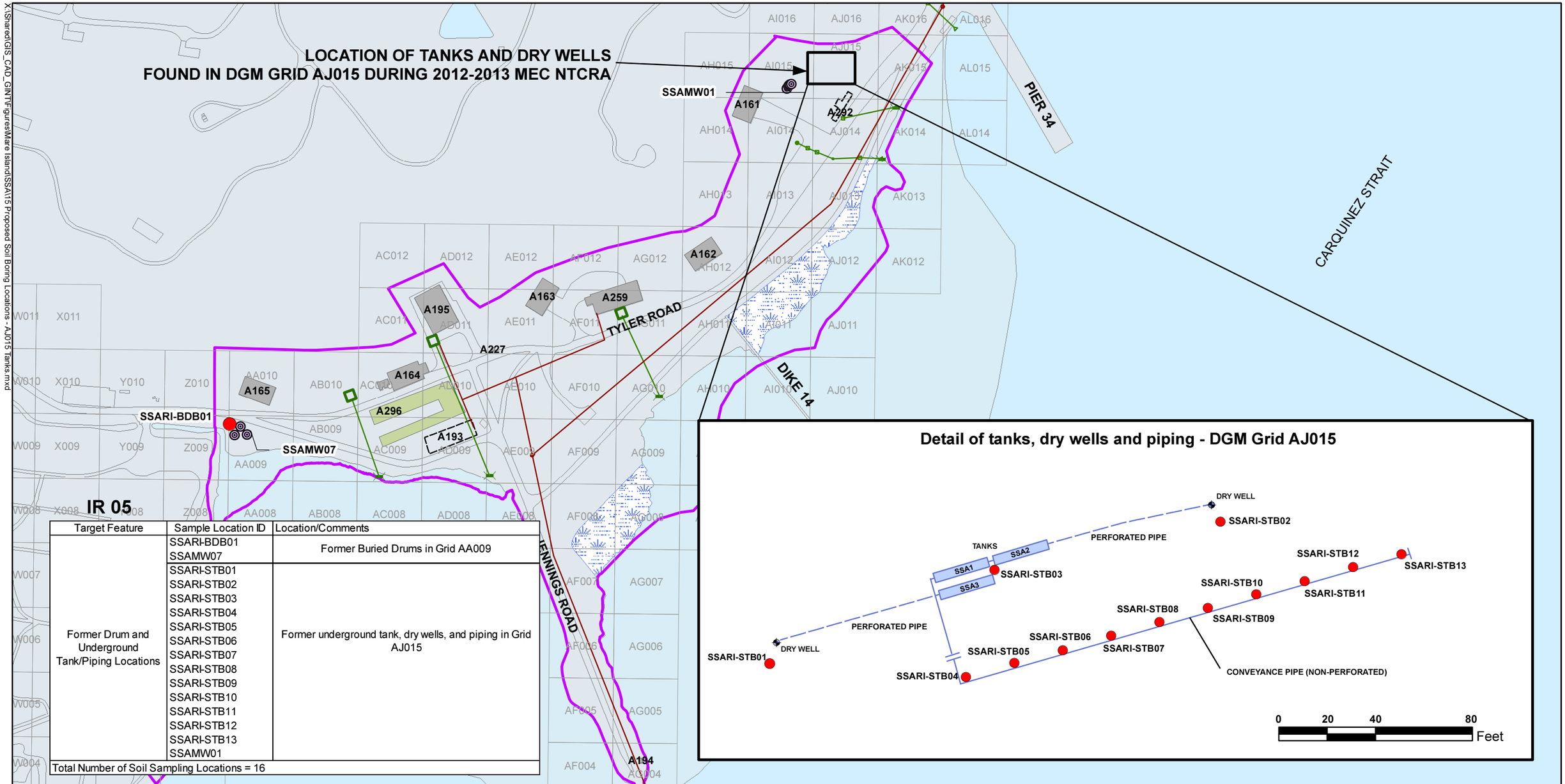

Target Feature	Sample Location ID	Location/Comments
Former Drum and Underground Tank/Piping Locations	SSARI-BDB01 SSAMW07	Former Buried Drums in Grid AA009
	SSARI-STB01 SSARI-STB02 SSARI-STB03 SSARI-STB04 SSARI-STB05 SSARI-STB06 SSARI-STB07 SSARI-STB08 SSARI-STB09 SSARI-STB10 SSARI-STB11 SSARI-STB12 SSARI-STB13 SSAMW01	Former underground tank, dry wells, and piping in Grid AJ015
Total Number of Soil Sampling Locations = 16		

LEGEND

- PROPOSED BORING LOCATION
- PROPOSED GROUNDWATER MONITORING WELL
- FORMER BURIED DRUM LOCATION (REMOVED)
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM SEWER DRAIN LINE
- STORM SEWER OUTFALLS (SWMU 93)
- SOUTH SHORE AREA BOUNDARY
- REMOVED BUILDING
- BUILDINGS
- WETLANDS
- EXPLOSIVES SAFE HAVEN
- FORMER DRY WELL
- STORM DRAIN (SWMU 93)

N

0 150 300 600 Feet

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FIGURE 4-6

PROPOSED SOIL SAMPLING LOCATIONS
TANKS (GRID AJ015) AND DRUMS (GRID AA009)

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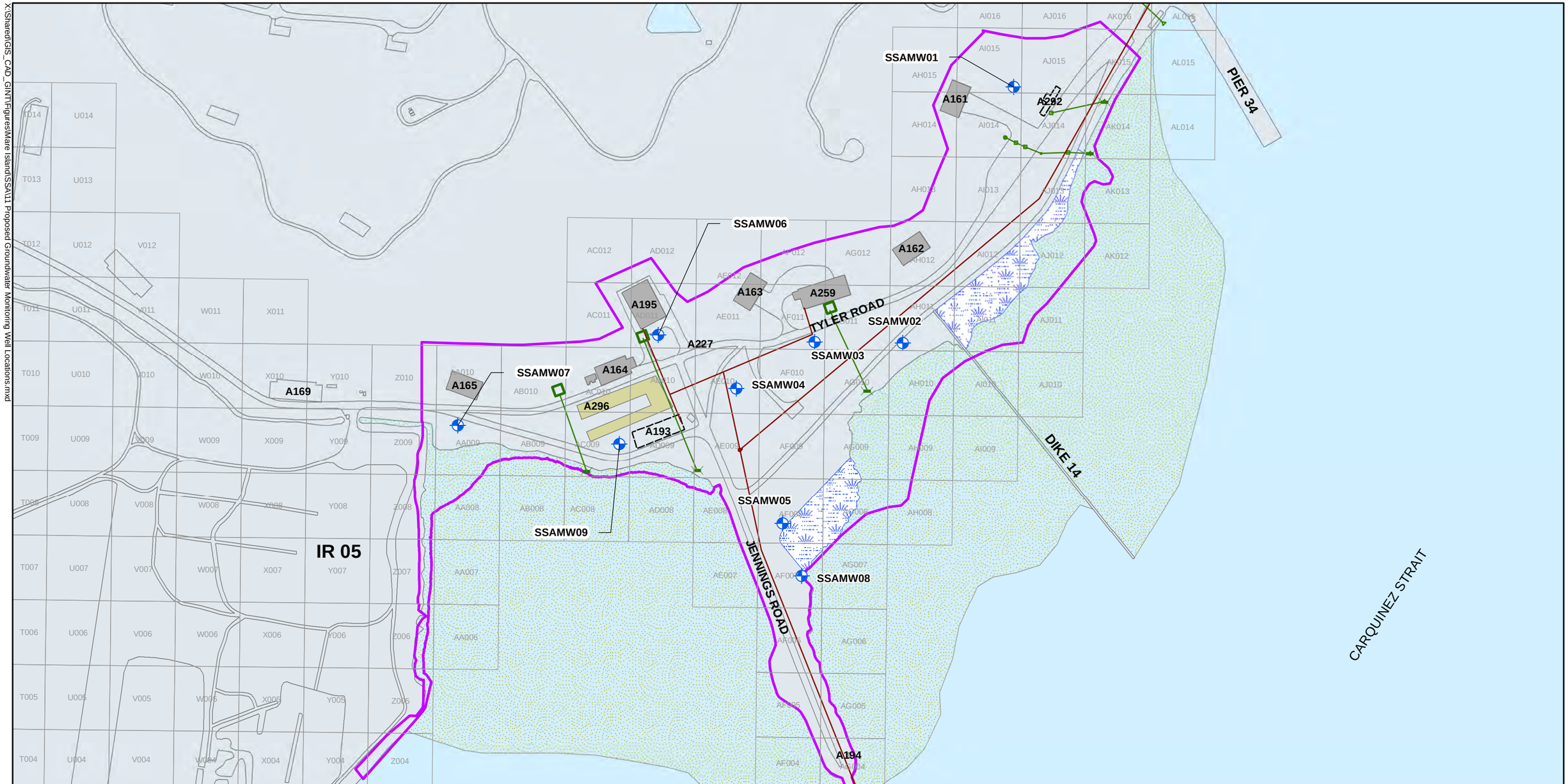

LEGEND

- PROPOSED GROUNDWATER MONITORING WELL
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM SEWER DRAIN LINE
- STORM SEWER OUTFALLS (SWMU 93)
- SOUTH SHORE AREA BOUNDARY
- REMOVED BUILDING
- BUILDINGS
- WETLANDS
- TIDAL MUDFLATS
- EXPLOSIVES SAFE HAVEN
- STORM DRAIN (SWMU 93)

N

0 150 300 600 Feet

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FIGURE 4-7

PROPOSED GROUNDWATER MONITORING WELL LOCATIONS

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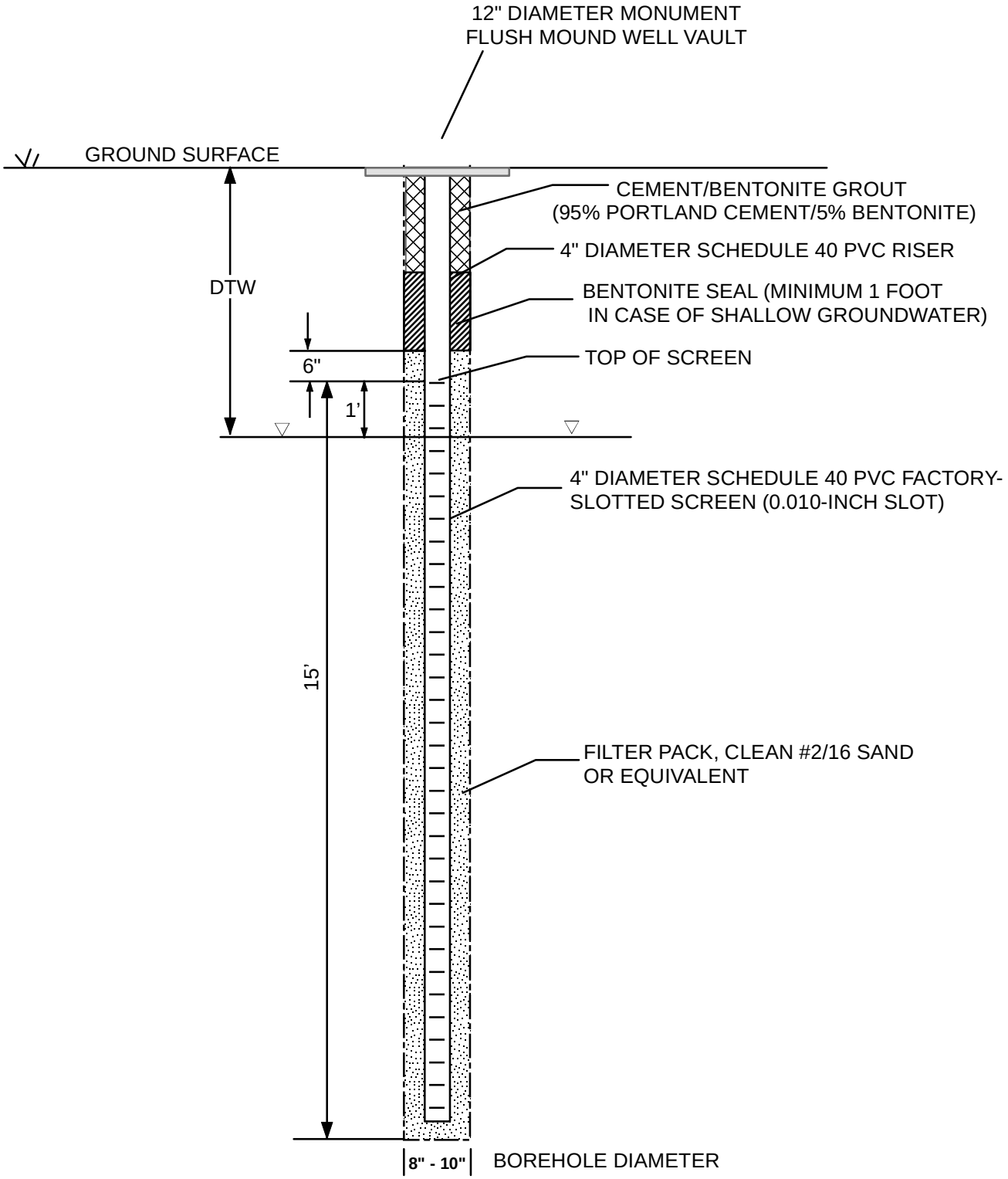
X:\Shared\GIS_CAD_GINT\Figures\Mare Island\SSA\12 MW Construction Diagram2.mxd



LEGEND

▽ GROUNDWATER

DTW APPROXIMATE DEPTH TO GROUNDWATER AS MEASURED FROM SURFACE AT APPROXIMATE HIGH TIDE

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FIGURE 5-1

PROPOSED GROUNDWATER MONITORING WELL CONSTRUCTION DETAILS

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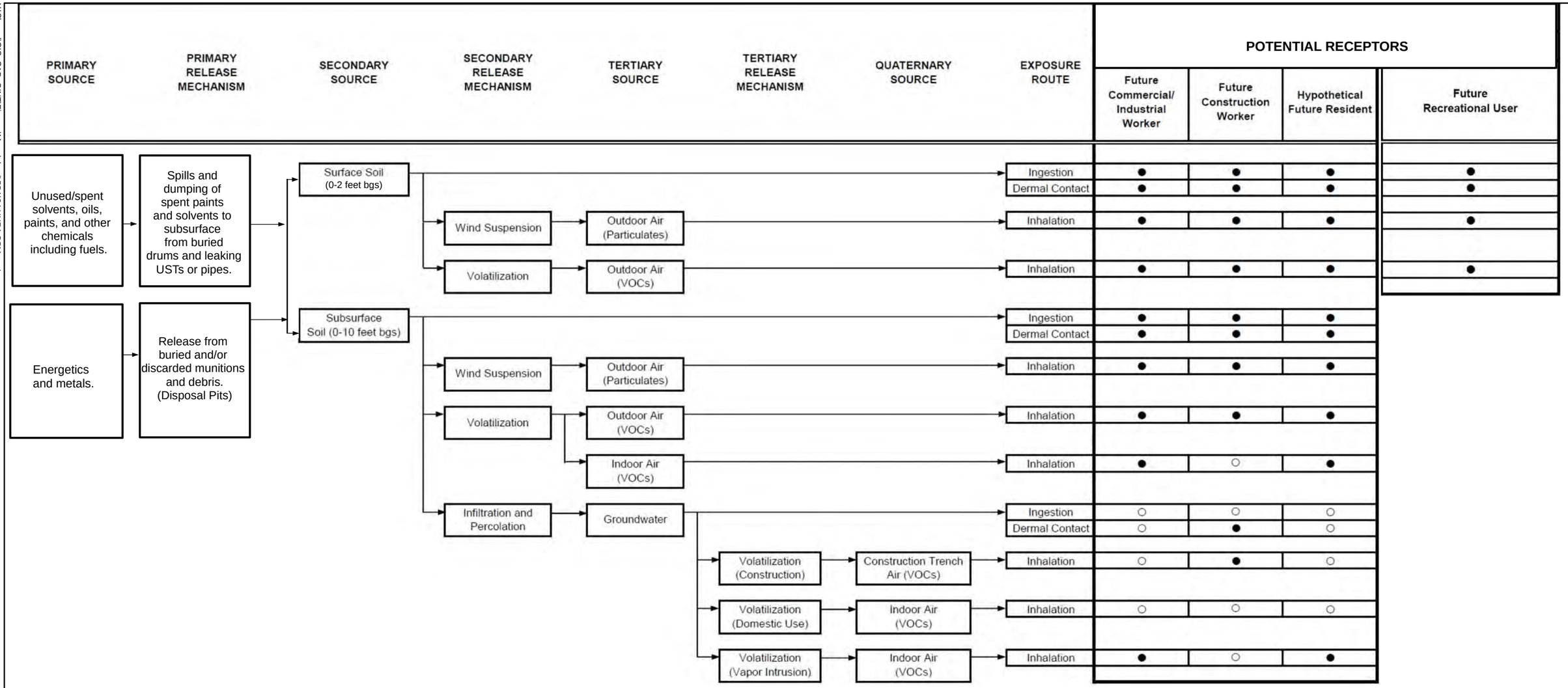

LEGEND

bgs	below ground surface
●	Potentially complete exposure pathway
○	Incomplete or negligible exposure pathway
HHRA	human health risk assessment
VOC	volatile organic compound

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FIGURE 7-1

PRELIMINARY HHRA
CONCEPTUAL SITE MODEL

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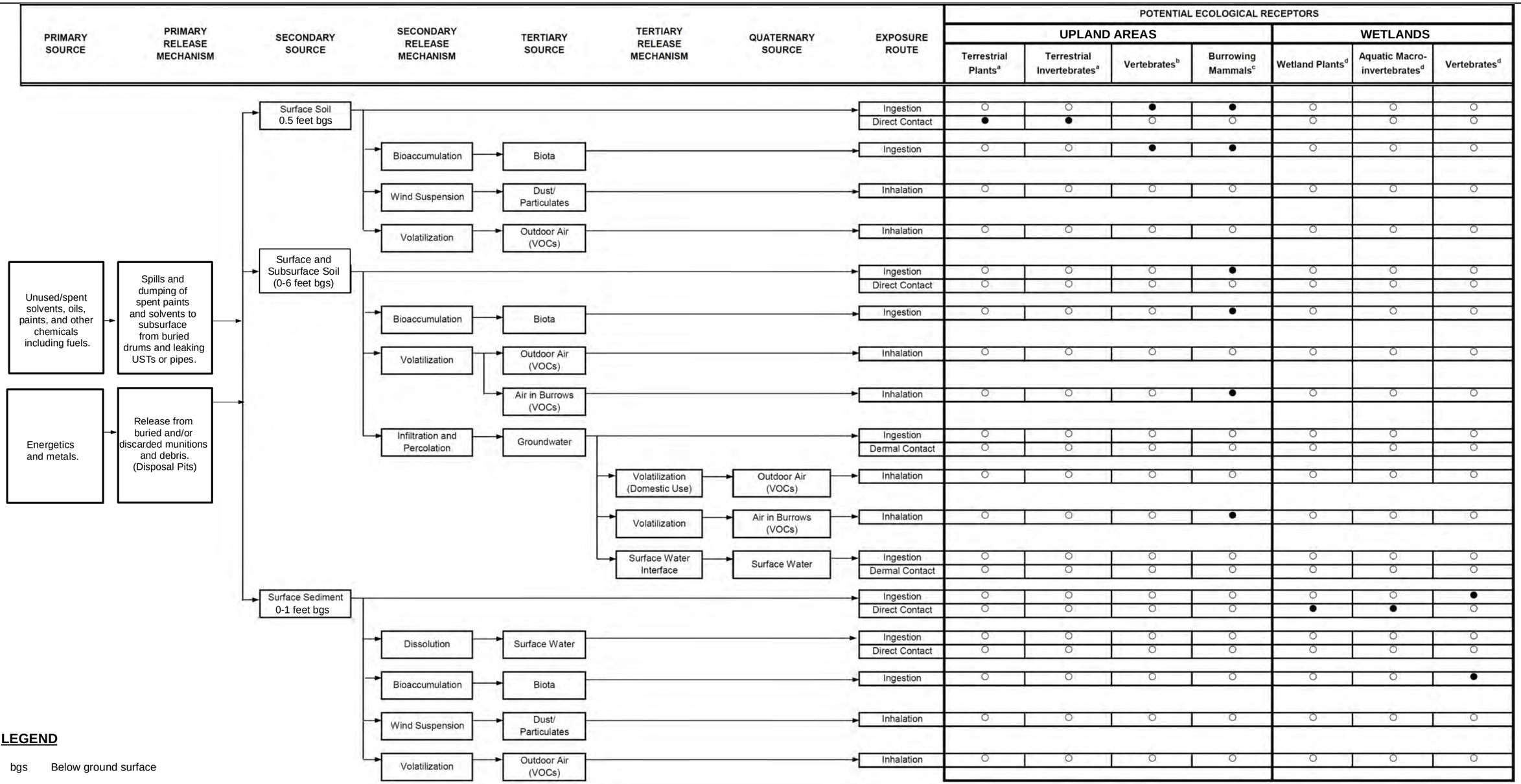

LEGEND

bgs	Below ground surface
●	Potentially complete exposure pathway
○	Incomplete or negligible exposure pathway
VOC	Volatile organic compound
a	Terrestrial plants and invertebrates are exposed to surface and subsurface soil (0 to 0.5 feet bgs)
b	Non-burrowing vertebrates (birds and mammals) are exposed to surface soil (0 - 0.5 feet bgs). Non-burrowing terrestrial vertebrates include omnivorous birds (Western meadowlark), mammals (ornate shrew), carnivorous birds (norther harrier), and carnivorous mammals (grey fox).
c	Burrowing receptors (California Ground Squirrel) are exposed to surface and subsurface soil (0 - 6 feet bgs)
d	Wetland plants, aquatic macroinvertebrates, and vertebrates are exposed to sediment (0 - 2 feet bgs). Vertebrates include herbivorous birds (mallard), herbivorous mammals (salt marsh harvest mouse), carnivorous birds (northern harrier and great blue heron), and carnivorous mammals (grey fox).

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FIGURE 8-1
EXAMPLE ECOLOGICAL CONCEPTUAL SITE MODEL

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APPENDIX A

SAMPLING AND ANALYSIS PLAN

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Prepared for:
Base Realignment and Closure
Program Management Office West
San Diego, California

NAVFAC Contract No.: N62473-12-C-4812
DCN: NRS-4812-0000-0010

Final

SAMPLING AND ANALYSIS PLAN

(Field Sampling Plan and Quality Assurance Project Plan)

July 2015

Remedial Investigation
South Shore Area
Former Mare Island Naval Shipyard
Vallejo, California

Prepared by:

NOREAS
Environmental Engineering and Science

16361 Scientific Way
Irvine, CA 92618

SAP Worksheet #1 – Title and Approval Page

FINAL

SAMPLING AND ANALYSIS PLAN
(Field Sampling Plan and Quality Assurance Project Plan)
July 2015

Remedial Investigation
South Shore Area
Former Mare Island Naval Shipyard
Vallejo, California

Prepared for:

Department of the Navy
Base Realignment and Closure Program Management Office West
San Diego, California

Prepared under:
NAVFAC Contract No. N62473-12-C-4812
DCN: NRS-4812-0000-0010

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Approval Signature:	Kenneth Bowers Kenneth Bowers NAVFAC LANT QA Officer/Navy Chemist	7/7/15 Date
Approval Signature:	Kenneth Bowers for Joseph Michalowski, Ph.D., CHMM NAVFAC SW QA Officer	7/7/15 Date

EXECUTIVE SUMMARY

This Sampling and Analysis Plan (SAP) has been prepared by NOREAS, Inc. to support the remedial investigation (RI) to be conducted at the South Shore Area (SSA) of the former Mare Island Naval Shipyard (MINS) in Vallejo, California. This document, which supplements the RI Work Plan, has been prepared on behalf of the U.S. Department of the Navy (DON), Base Realignment and Closure (BRAC) Program Management Office West under Contract No. N62473-12-C-4812.

The RI project involves groundwater and soil sampling, analysis, and reporting to investigate the nature and extent of potential contamination at the SSA. Project activities will be performed in accordance with Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) as discussed in the U.S. Environmental Protection Agency Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA (EPA 1988).

The former MINS occupies an area of approximately 3.5 square miles located on a peninsula in Solano County, California, northeast of San Francisco. It is bound by San Pablo Bay on the west, Carquinez Strait on the south, and Mare Island Strait (Napa River) to the east (Figure 1). MINS was established by the DON in 1854 and operated continuously until it was closed under the BRAC Program in 1996. The primary mission of the former MINS was to build, maintain, and repair Navy ships and submarines, though it also served as a munitions storage and production facility from approximately 1857 until 1975.

The SSA consists of approximately 38 acres of uplands, wetlands, and tidal mudflat areas located on the southern end of the former MINS. The location of the SSA within Mare Island is illustrated on Figure 2. A wide variety of buried munitions have been identified and removed from the subsurface soils at portions of the SSA, munitions filled with high explosives, propellants, primers, fuzes, small arms munitions, and small to medium caliber gun ammunition. Since 1990, seven separate emergency response actions have been conducted, along with an intrusive investigation to identify unexploded ordnance.

The purpose of this SAP is to provide the field sampling and analytical procedures, quality assurance and quality control requirements, and data collection methods that will be used to support the RI activities. This SAP will be used as a reference document by all field and laboratory personnel engaged in the sampling and analysis for this project. This SAP is prepared in accordance with the requirements of the Uniform Federal Policy for Quality Assurance Project Plans and supplements the RI Work Plan.

DON is the lead agency for implementing the RI activities at the former MINS. DON has entered into a Federal Facilities Site Remediation Agreement and is working in cooperation with the Regional Water Quality Control Board San Francisco Bay Region and California Department of Toxic Substances Control to implement the remedial actions at the former MINS. Both agencies are under the auspices of the California Environmental Protection Agency.

The objective of the RI is to characterize the extent of CERCLA contaminants, materials potentially presenting an explosive hazard, and munitions constituents in soil and groundwater at the MINS SSA to the extent that potential risks to human health and the environment can be assessed to ultimately support a feasibility study. In order to achieve the project objectives, the RI will focus on collecting soil and groundwater data from the following primary areas of interest at the SSA including:

- Former Buildings where hazardous materials were once stored and/or used;
- Solid Waste Management Units where hazardous materials were historically stored, managed, or potentially discharged;
- Oven/Primer Pit Area (including Oven Pits) where munitions were once discarded by burning;
- Historic munitions of explosive concern Sites as identified during past munitions of explosive concern removal actions at the SSA; and
- Other Areas as necessary; these may include those areas where evidence for chemical or munitions constituent contamination is encountered during the Non-Time Critical Removal Action recently completed in July 2013.

During the RI, soil samples will be collected from various depths at a total of approximately 52 soil boring locations throughout the SSA. The sample locations have been selected to correspond with those areas where potential impacts from chemical contaminants are most likely have occurred. In addition, nine groundwater monitoring wells will be installed and monitored to provide information relative to hydrogeologic conditions, potential contaminant impacts, and general water quality at the SSA. Proposed soil sampling boring and monitoring well locations are presented in Figures 3 through 9.

Data obtained during the RI will be used to: (1) evaluate and characterize the nature and extent of soil and groundwater contamination in terms of chemicals of potential concern at the SSA, and (2) assist in the preparation of a Feasibility Study that will evaluate remedial actions/approaches to mitigate potential threats or risks to human health and the environment and will ultimately support site closure efforts. As such, the RI is intended to address all environmental programs applicable to the SSA, including the Installation Restoration, Munitions Response, Resource Conservation and Recovery Act, underground storage tank, above ground storage tank, petroleum, and Toxic Substances Control Act (TSCA) programs.

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Figure 2 Site Plan with Features

Figure 3 Summary of Proposed Soil and Groundwater Sampling Locations

Figure 4 Proposed Soil Sampling Locations – Building Areas

Figure 5 Proposed Soil Sampling Locations – SWMU Sites

Figure 6 Proposed Soil Sampling Locations – MEC Sites

Figure 7 Proposed Soil Sampling Locations – Oven/Primer Pit Areas

Figure 8 Proposed Soil Sampling Locations – Tanks (Grid AJ015) and Drums (Grid AA009)

Figure 9 Proposed Groundwater Monitoring Well Locations

ATTACHMENTS

Attachment A-1 Example Chain-of-Custody Form, Low-Flow Purging and Sampling Sheet, Soil Boring Log, and Field Calibration Form

Attachment A-2 Laboratory Accreditation Letters

Attachment A-3 DoD Quality Systems Manual QC Limits

Attachment A-4 Laboratory Standard Operating Procedures

ABBREVIATIONS AND ACRONYMS

°C	degrees Celsius
µg/kg	microgram per kilogram
µg/L	microgram per liter
%D	percent difference
%R	percent recovery
%RSD	percent relative standard deviation
amu	atomic mass unit
BFB	bromofluorobenzene
bgs	below ground surface
BRAC	Base Realignment and Closure
CA	corrective action
CAS	Chemical Abstracts Service
CCC	calibration check compound
CCV	continuing calibration verification
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	chain-of-custody
COD	coefficient of determination
CSO	Caretaker Site Office
D	percent difference
DGM	digital geophysical mapping
DO	dissolved oxygen
DoD	Department of Defense
DON	U.S. Department of the Navy
DPT	direct-push technology
DQO	data quality objective
DTSC	California Department of Toxic Substances Control
EDD	electronic data deliverable
ELAP	Environmental Laboratory Accreditation Program
EPA	U.S. Environmental Protection Agency
ESL	environmental screening levels
EWI	Environmental Work Instruction

ABBREVIATIONS AND ACRONYMS
(Continued)

g	grams
GC	gas chromatograph
GC/MS	gas chromatograph/mass spectrometer
HCl	hydrochloric acid
HDPE	high density polyethylene
HSA	hollow-stem auger
ICAL	initial calibration
ICB	initial calibration blank
ICS	interference check solutions
ICSA	interference check solution A
ICV	initial calibration verification
J	estimated value
L	liter
LOQ	limit of quantitation
LCS	laboratory control sample
LLICV	low-level initial calibration verification
MB	method blank
MC	munitions constituents
MEC	munitions of explosive concern
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
MINS	Mare Island Naval Shipyard (former)
mL	milliliter
MPPEH	materials potentially presenting an explosive hazard
MS	matrix spike
MSA	method of standard addition
MSD	matrix spike duplicate
N/A	not applicable
NAD	North American Datum
NAVD	North American Vertical Datum
NAVFAC SW	Naval Facilities Engineering Command Southwest
NEDD	Naval Electronic Data Deliverable

ABBREVIATIONS AND ACRONYMS
(Continued)

NIRIS	Naval Installation Restoration Information Solution
NOREAS	NOREAS, Inc.
NTCRA	Non-Time Critical Removal Action
PARCC	precision, accuracy, representativeness, completeness, and comparability
PCB	polychlorinated biphenyl
PDS	post-digest spike
PDSD	post-digest spike duplicate
PMA	Production Manufacturing Area
PMO	Program Management Office
QA	quality assurance
QAO	Quality Assurance Officer
QAPP	Quality Assurance Project Plan
QC	quality control
QCM	Quality Control Manager
QL	quantitation limit
QSM	Quality Systems Manual
RDX	Research Department Explosive (cyclonite)
RI	remediation investigation
RPD	relative percent difference
RPM	Remedial Project Manager
RRF	relative response factor
RRT	relative retention time
RSD	relative standard deviation
RTC	response to comments
S&A	sampling and analytical
SAP	Sampling and Analysis Plan
SM	standard method
SOP	standard operating procedure
SPCC	system performance check compound
SSA	South Shore Area
SUXOS	Senior Unexploded Ordnance Supervisor
SVOC	semivolatile organic compound

ABBREVIATIONS AND ACRONYMS
(Continued)

SWDIV	Southwest Division
SWMU	solid waste management unit
TBD	to be determined
TDS	total dissolved solid
TSCA	Toxic Substances Control Act
TPH	total petroleum hydrocarbon
TPH-d	total petroleum hydrocarbons as diesel
TPH-g	total petroleum hydrocarbons as gasoline
TPH-mo	total petroleum hydrocarbons as motor oil
UFP-QAPP	Uniform Federal Policy-Quality Assurance Project Plans
UST	underground storage tank
UXO	unexploded ordnance
UXOQCS	Unexploded Ordnance Quality Control Specialist
UXOSO	Unexploded Ordnance Safety Officer
VOA	volatile organic analysis
VOC	volatile organic compound
WS	Worksheet

SAP Worksheet #2 – SAP Identifying Information

Site Name/Number: Former Mare Island Naval Shipyard (MINS), South Shore Area
Operable Unit: N/A
Contractor Name: NOREAS, Inc.
Contract Number: N62473-12-C-4812
Contract Title: Environmental Remediation Contract

1. This Sampling and Analysis Plan (SAP) was prepared in accordance with the requirements of the *Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP)* (U.S. Environmental Protection Agency [EPA] 2005) and *EPA Guidance for Quality Assurance Project Plans*, EPA QA/G-5, QAMS (EPA 2002).

2. Identify regulatory program: Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

3. This SAP is a project-specific SAP.

4. List dates of scoping sessions that were held:

Scoping Session	Date
Project kickoff meeting	October 12, 2012

A list of attendees and a summary of key decisions and action items identified during the project scoping meeting are provided in the Worksheet (WS) #9.

5. List dates and titles of any SAP documents written for previous site work that are relevant to the current investigation.

Battelle. 2012. Final Sampling and Analyses Plan (Field Sampling Plan and MEC Quality Assurance Project Plan) for the Non-Time Critical Removal Action at the Production Manufacturing Area and the South Shore Area, Former Mare Island Naval Shipyard, Vallejo, California. April.

Integrated Solutions for Remediation, JV. 2012. Final Addendum 1 to the Final Sampling and Analyses Plan for the Non-Time Critical Removal Action at the Production Manufacturing Area (PMA) and the South Shore Area (SSA), Former Mare Island Naval Shipyard, Vallejo, California. April.

6. List organizational partners (stakeholders) and connection with lead organization:
EPA Region 9, California EPA, California Regional Water Quality Control Board, San Francisco Bay Region, California Department of Toxic Substances Control (DTSC)

7. Lead organization:

U.S. Department of the Navy (DON), BRAC Program Management Office (PMO) West

SAP Worksheet #2 – SAP Identifying Information (Continued)

8. If any required SAP elements or required information are not applicable to the project or are provided elsewhere, then note the omitted SAP elements and provide an explanation for their exclusion below:

   Specialized training requirements for this project are described in WS #8.

SAP Worksheet #2 – SAP Identifying Information (Continued)

UFP-QAPP Worksheet #	Required Information	Crosswalk to Related Information
A. Project Management		
Documentation		
1	Title and Approval Page	
2	Table of Contents SAP Identifying Information	
3	Distribution List	
4	Project Personnel Sign-Off Sheet	
Project Organization		
5	Project Organizational Chart	
6	Communication Pathways	
7	Personnel Responsibilities and Qualifications Table	
8	Special Personnel Training Requirements Table	
Project Planning/ Problem Definition		
9	Project Planning Session Documentation (including Data Needs tables) Project Scoping Session Participants Sheet	
10	Problem Definition, Site History, and Background. Site Maps (historical and present)	
11	Site-Specific Project Quality Objectives	
12	Measurement Performance Criteria Table	
13	Sources of Secondary Data and Information Secondary Data Criteria and Limitations Table	
14	Summary of Project Tasks	
15	Reference Limits and Evaluation Table	
16	Project Schedule/Timeline Table	
B. Measurement Data Acquisition		
Sampling Tasks		
17	Sampling Design and Rationale	
18	Sampling Locations and Methods/Standard Operating Procedure (SOP) Requirements Table Sample Location Map(s)	
19	Analytical Methods/SOP Requirements Table	Attachment A-4
20	Field Quality Control Sample Summary Table	
21	Project Sampling SOP References Table Sampling SOPs	
22	Field Equipment Calibration, Maintenance, Testing, and Inspection Table	
Analytical Tasks		
23	Analytical SOPs Analytical SOP References Table	Attachment A-4
24	Analytical Instrument Calibration Table	
25	Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	
Sample Collection		
26	Sample Handling System, Documentation Collection, Tracking, Archiving and Disposal Sample Handling Flow Diagram	
27	Sample Custody Requirements, Procedures/SOPs Sample Container Identification Example Chain-of-Custody Form and Seal	Attachment A-1

SAP Worksheet #2 – SAP Identifying Information (Continued)

UFP-QAPP Worksheet #	Required Information	Crosswalk to Related Information
Quality Control Samples		
28	Quality Control (QC) Samples Table Screening/Confirmatory Analysis Decision Tree	Attachment A-3
Data Management Tasks		
29	Project Documents and Records Table	
30	Analytical Services Table Analytical and Data Management SOPs	
C. Assessment Oversight		
31	Planned Project Assessments Table Audit Checklists	
32	Assessment Findings and Corrective Action Responses Table	
33	Quality Assurance (QA) Management Reports Table	
D. Data Review		
34	Verification (Step I) Process Table	
35	Validation (Steps IIa and IIb) Process Table	
36	Validation (Steps IIa and IIb) Summary Table	
37	Usability Assessment	

SAP Worksheet #3 – Distribution List

Name of SAP Recipients	Title/Role	Organization	Telephone Number	E-mail Address or Mailing Address
U.S. Department of the Navy				
Heather Wochnick	Lead Navy RPM	BRAC PMO West	(619) 532-0763	heather.wochnick@navy.mil
Brooks Pauly	RPM	BRAC PMO West	(619) 532-0789	brooks.pauly@navy.mil
Janet Lear	BRAC Environmental Coordinator	BRAC PMO West	(619) 532-0976	janet.lear@navy.mil
Joseph Michalowski	QAO	NAVFAC SW	(619) 532-4125	joseph.michalowski@navy.mil
Patricia McFadden	BRAC PMO CSO Representative	BRAC CSO	(415) 743-4720	partricia.a.mcfadden@navy.mil
Izzat Amadea	Resident Officer in Charge of Construction	NAVFAC SW	(510) 755-5876	izzat.amadea@navy.mil
Fred Niehoff	BRAC Facilities Coordinator	BRAC CSO	(415) 743-4721	fred.neihoff@navy.mil
Diane Silva	Administrative Records Coordinator	NAVFAC SW	(619) 556-1280	diane.silva@navy.mil
NOREAS and Subcontractors				
Jeff Brenner	Project Manager	NOREAS	(949) 467-9106	jeff.brenner@noreasinc.com
Sevda Aleckson	Program QCM & Project Chemist	NOREAS	(949) 467-9117	sevda.aleckson@noreasinc.com
Wendy Bryant	Project QCM	NOREAS	(949) 351-3378	wendy.bryant@noreasinc.com
Scott Bailey	Project Manager (Anomaly Avoidance)	Bristol Environmental Services, LLC	(910) 545-6109	sbailey@bristol-companies.com
Terri Chang	Project Manager	Eurofins Calscience Inc.	(714) 895-5494	Terrichang@eurofinsUS.com
Ivana Vukovic	Project Manager	Maxxam Analytics (Dioxins)	(905) 17-5784 or (800) 668-0639	ivukovic@maxxam.ca
Linda Rauto	Project Manager	Laboratory Data Consultants, Inc.	(760) 634-0437	lrauto@lab-data.com

SAP Worksheet #3 – Distribution List (Continued)

Name of SAP Recipients	Title/Role	Organization	Telephone Number	E-mail Address or Mailing Address
Regulatory Agencies				
Patrick Hsieh	Project Manager	California Environmental Protection Agency – Department of Toxic Substances Control	(510) 540-3833	tphsieh@dtsc.ca.gov
Elizabeth Wells	Project Manager	Regional Water Quality Control Board, San Francisco Bay Region	(510) 622-2440	ewells@waterboards.ca.gov
Carolyn d'Almeida	Project Representative	EPA, Region IX	(415) 972-3150	Dalmeida.carolyn@epamail.epa.gov
Other Regulatory Entities				
Tami Nakahara	Project Representative	California Department of Fish and Wildlife	(916) 324-8452	tami.nakahara@wildlife.ca.gov

Notes:

BRAC – Base Realignment and Closure
CSO – Caretaker Site Office
EPA – U.S. Environmental Protection Agency
NAVFAC SW – Naval Facilities Engineering Command Southwest
NOREAS – NOREAS, Inc.
PMO – Program Management Office
QAO – Quality Assurance Officer (
QCM – Quality Control Manager
RPM – Remedial Project Manager
SAP – Sampling and Analysis Plan

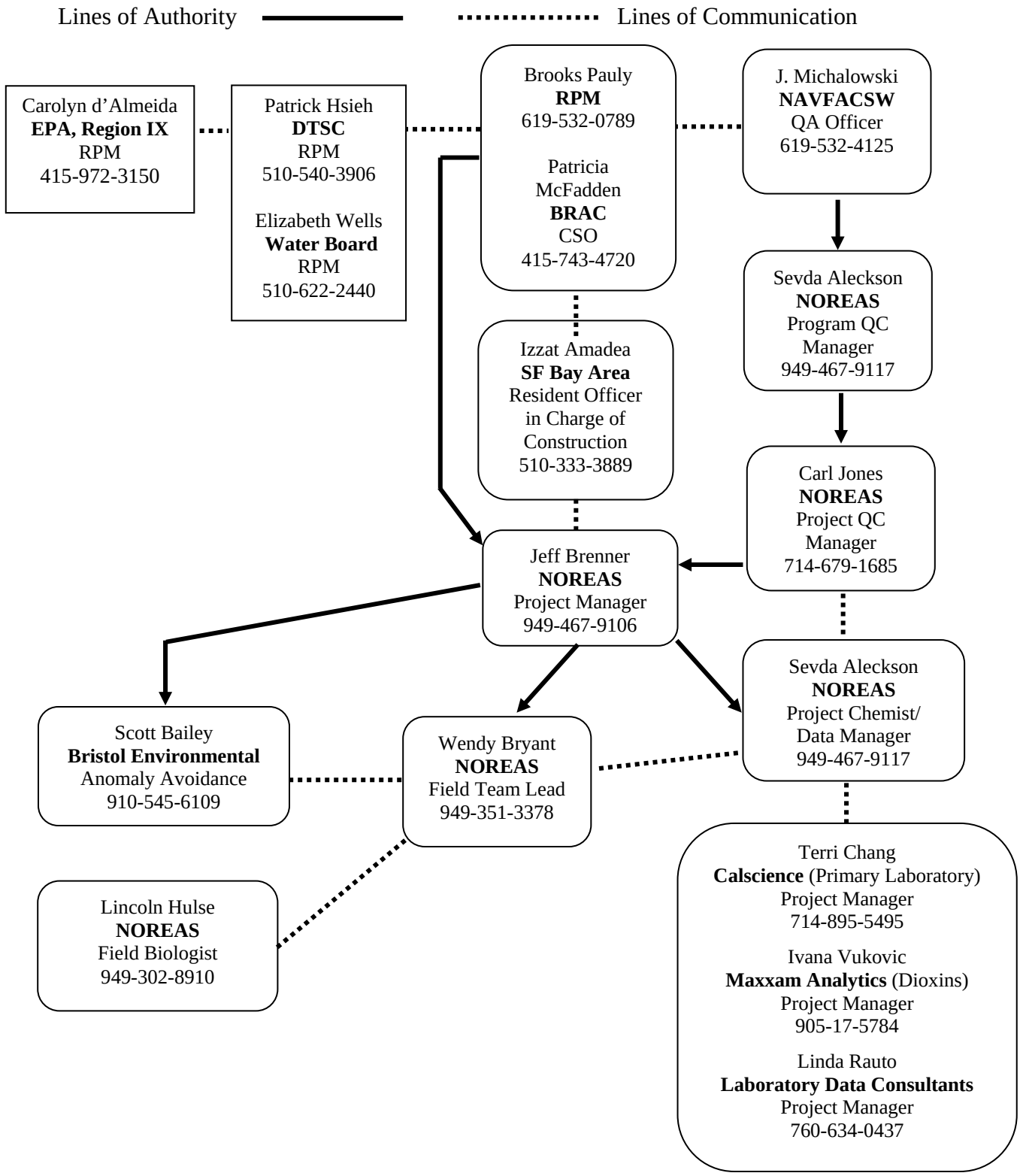
SAP Worksheet #4 – Project Personnel Sign-Off Sheet

Sampling personnel will be required to read and understand the SAP prior to any sample collection activities. Any on-site personnel conducting sampling will sign below to indicate that they have read the SAP and will perform the task as described. The signed worksheet will be maintained in the project file.

Name	Organization/Title/Role	Signature/ E-mail Receipt	SAP Section Reviewed	Date SAP Read
Jeff Brenner	NOREAS/Project Manager		Entire SAP	
Carl Jones	NOREAS/Project QCM		Entire SAP	
Sevda Aleckson	NOREAS/QCM/Project Chemist		Entire SAP	
Wendy Bryant	NOREAS/ Field Team Lead		Entire SAP	
Terri Chang	Eurofins Calscience Inc./Project Manager		Relevant sections for analytical methods to be performed	
Ivana Vukovic	Maxxam Analytics/Project Manager		Relevant sections for dioxins/furans testing	
Linda Rauto	Laboratory Data Consultants, Inc./Project Manager		Entire SAP	

NOREAS – NOREAS, Inc.
QCM – Quality Control Manager
SAP – Sampling and Analysis Plan

SAP Worksheet #5 – Project Organizational Chart



SAP Worksheet #6 – Communication Pathways

Communication Drivers	Responsible Affiliation	Name	Phone Number and/or E-mail	Procedure
Point of contact for DON quality issues	NAVFAC SW QAO	Joseph Michalowski	(619) 532-4125	Review and approve this SAP and all amendments to this SAP.
Stop work issues	NAVFAC SW QAO	Joseph Michalowski	(619) 532-4125	Issue stop work project execution at any point if quality-related issues are not adequately met.
Project management	Project Manager	Jeff Brenner	(949) 467-9106	Manage field and project personnel.
Project management for DON	Remedial Project Manager	Brooks Pauly	(619) 532-0789	Ensure that the project scope of work requirements are fulfilled.
Point of Contact for Mare Island Naval Shipyard	BRAC CSO	Patricia McFadden	(415) 743-4720	Review project documents and provide technical direction, as required.
Field QC oversight	Resident Officer in Charge of Construction	Izzat Amadea	(510) 755-5876	Verify that all fieldwork is completed in accordance with contract and project requirements.
SAP review	QCM	Sevda Aleckson	(949) 467-9117	Perform review of the project SAP prior to submittal to the NAVFACSW QAO.
Coordination and communication of fieldwork activities related to sampling	Task Manager/Field Supervisor	Wendy Bryant	(949) 351-3378	Communicate relevant field information to the Project QC Manager and Project Chemist.
Coordination of analytical laboratory and field sampling activities	Project Chemist	Sevda Aleckson	(949) 467-9117	Communicate project analytical requirements to the analytical laboratory and coordinate the delivery of all necessary sampling and shipping containers to the site prior to commencement of field sampling activities and throughout the course of the project.
Submittal of samples to the laboratory	Sampling Personnel	Wendy Bryant	(949) 351-3378	Package and ship samples in accordance with this SAP.
Daily COC reports and shipping documentation	Sampling Personnel	Wendy Bryant	(949) 351-3378	Submit COC and shipping records via fax or e-mail to the Project Chemist at the end of each day that samples are collected.
Reporting laboratory data quality issues	Laboratory Project Manager	Terri Chang	(714) 895-5494	Report all analytical QA/QC issues to the Project Chemist in writing within two business days.

SAP Worksheet #6 – Communication Pathways (Continued)

Communication Drivers	Responsible Affiliation	Name	Phone Number and/or E-mail	Procedure
Notification of data quality issues (rejected analytical data)	Program QCM	Sevda Aleckson	(949) 467-9117	Notify the NAVFACSW RPM and the NAVFACSW QAO within 24 hours or the next business day if significant problems are identified by the analytical laboratory or the project team that may potentially impact data usability for key constituents of interest or if project-specific data quality objectives are not met.
Field and analytical corrective actions	Project Chemist	Sevda Aleckson	(949) 467-9117	Immediately notify the QCM in writing of any nonconformances identified (or reported) during sampling and laboratory analyses. In coordination with the QCM, prepare a nonconformance form, document corrective actions to be taken, and verify that the corrective measures have been implemented adequately.
Release of analytical data	Project Chemist	Sevda Aleckson	(949) 467-9117	Review preliminary and final data to verify that data quality is met, as described in this SAP, prior to releasing the data to the technical team.
SAP procedure revision during field activities	Project Chemist	Sevda Aleckson	(949) 467-9117	Initiate a Field Change Request form in the event of any potential modifications required during sampling due to conditions in the field.
SAP amendments	Project Chemist	Sevda Aleckson	(949) 467-9117	Prepare an addendum to the SAP documenting any critical revisions for approval by the QCM and the NAVFACSW QAO prior to any field activities.

Notes:

BRAC – Base Realignment and Closure
COC – chain-of-custody
CSO – Caretaker Site Office
DON – Department of the Navy
NAVFAC SW – Naval Facilities Engineering Command Southwest
QA – quality assurance
QAO – Quality Assurance Officer
QC – quality control
QCM – Quality Control Manager
SAP – Sampling and Analysis Plan

SAP Worksheet #7 – Personnel Responsibilities and Qualifications Table

Name	Title/Role	Organizational Affiliation	Responsibilities
Joseph Michalowski	QAO	NAVFAC SW	Review and approve the SAP. Providing DON oversight of project QA Program. Provide technical and administrative oversight of project surveillance audit activities. Act as a liaison for matters concerning QA and the DON's Laboratory QA Program. Coordinate training on matters pertaining to production and maintenance of data quality. Issue stop work on project execution in the event QA requirements are not adequately followed.
Brooks Pauly	Remedial Project Manager	BRAC RPM	Perform project management for the DON. Ensure that the project scope of work requirements are fulfilled. Oversee the project cost and schedule. Provide formal technical direction to the NOREAS project team, as required. Act as a liaison with regulatory agencies.
Jeff Brenner	Project Manager	NOREAS	Manage work activities of subcontractors and NOREAS technical team and ensure that all personnel adhere to the administrative and technical requirements of the project. Monitor and report on work progress and ensure that project deliverables are completed on time and within budget. Monitor project budget and schedule, and notify the client and the RPM of any changes that may require administration actions. Ensure compliance with the contractual QA and QC requirements, project scope of work, and the project QC plans. Ensure that all work meets the requirements of the technical specifications and complies with applicable federal, state, and local regulations. Ensure that all work activities are conducted in accordance with the Site-Specific Health and Safety Plan, United States Army Corps of Engineers Safety *and Health Requirements* (EM-385-1-1) (USACE 2003), and all applicable Occupational Safety and Health Administration regulations. Serve as the primary liaison between the DON and NOREAS for actions and information related to the work, including appropriate NOREAS technical personnel in the decision-making. Coordinate satisfactory resolution and completion of evaluation and acceptance reporting for nonconformance reports.

SAP Worksheet #7 – Personnel Responsibilities and Qualifications Table (Continued)

Name	Title/Role	Organizational Affiliation	Responsibilities
Wendy Bryant	Field Sampling Lead	NOREAS	Ensure that all field operations are conducted in compliance with the Work Plan and the SAP. Provide oversight to field sampling staff and analytical laboratory. Submit field sampling and COC records to the Project Chemist.
Sevda Aleckson	QCM	NOREAS	Establish and maintain the QC Program. Oversee the project-specific QC Program, include construction and chemical data acquisition. Interact with the Project Manager and the DON to ensure implementation of the QC Program Plans. Lead the coordination of all project-related quality matters. Resolve any project-specific quality issues. Suspend project activities, if quality standards are not maintained. Interface with the DON, including the NAVFAC SW QAO, on quality-related items. Conduct field QC audits to ensure compliance with the RI Work Plan and project-specific SAP. Review audit and surveillance reports conducted by the regulatory entities. Implement DON technical direction letters related to quality topics. Evaluate and select a qualified subcontractor analytical laboratory. Evaluate and select a qualified data validation company. Monitor performance of the subcontract laboratory and data validator.

SAP Worksheet #7 – Personnel Responsibilities and Qualifications Table (Continued)

Name	Title/Role	Organizational Affiliation	Responsibilities
Sevda Aleckson	Project Chemist/ Data Manager	NOREAS	Oversee the implementation of project requirements for sampling and analysis. Provide technical support on chemistry-related issues. Ensure that sampling personnel have documented training on sampling procedures per the SAP. Evaluate and select a qualified subcontract analytical laboratory and data validation company Monitor performance of the analytical laboratory and data validator. Review analytical data, prior to use in decision making, and verify that data meet project requirements as documented in the SAP. Review third-party data validation reports for accuracy, completeness, and compliance with project requirements. Prepare a data quality assessment report to document data quality and an evaluation that data generated are of acceptable quality and meet project requirements. Submit NEDD-formatted data to the DON, in accordance with the requirements set forth in *Environmental Work Instruction (EWI) EVR.6, Environmental Data Management and Required Electronic Delivery Standards* (NFECSW 2005).
Terri Chang	Laboratory Project Manager	Eurofins Calscience Inc.	Ensure that analyses are performed in accordance with the SAP and COC procedures. Maintain and document accurate log-in records, internal COC records, and provide sample analysis progress. Report any discrepancies identified during sample receiving, sample analysis or data generation to the NOREAS Project Chemist immediately. Submit accurate and complete analytical data packages within the required turn-around-times. Immediately communicate with the NOREAS Project Chemist any nonconformance that may impact data quality.
Linda Rauto	Validation Project Manager	Laboratory Data Consultants, Inc.	Coordinate with NOREAS Project Chemist on data validation requirements. Perform analytical data validation in accordance with the DoD QSM and project-specific requirements documented in this SAP. Submit accurate and complete validation reports within the required timelines.

SAP Worksheet #7 – Personnel Responsibilities and Qualifications Table (Continued)

Name	Title/Role	Organizational Affiliation	Responsibilities
Bristol UXO Technician III (specific technician will be named later)	UXO Technician III/Anomaly avoidance and site escort	Bristol Environmental Remediation Services, LLC (subcontractor to NOREAS)	Oversees daily activities related to anomaly avoidance. Ensures all work is performed in compliance with the Work Plan. Qualified UXO Tech II that meets the standards of Department of Defense Explosive Safety Board Technical Paper 18. Will escort sampling personnel while they operate on site and will also check boreholes for anomalies that may represent MPPEH. Responsible for ensuring sample personnel are not exposed to explosive hazards.

Notes:

BRAC – Base Realignment and Closure
COC – chain-of-custody
DoD – Department of Defense
DON – U.S. Department of the Navy
MPPEH – materials presenting potential explosive hazard
NAVFAC SW – Naval Facilities Engineering Command Southwest
NEDD – Naval Electronic Data Deliverable
NOREAS – NOREAS, Inc.
QA – quality assurance
QAO – Quality Assurance Officer
QC – quality control
QCM – Quality Control Manager
QSM - Quality Systems Manual
SAP – Sampling and Analysis Plan
UXO – unexploded ordnance

SAP Worksheet #8 – Special Personnel Training Requirements Table

Project Function	Specialized Training By Title or Description of Course	Training Provider	Training Date	Personnel / Groups Receiving Training	Personnel Titles / Organizational Affiliation	Location of Training Records / Certificates
General Project Operations	Site orientation, general work rules, and administrative activities	Site Superintendent	Mobilization	All site personnel	NOREAS and subcontractor personnel	Project Office
	Accident Prevention Plan; Site Safety & Health Plan; Radiation Material Management Plan	SSHO & UXO Personnel				
	Field Sampling Plan and Munitions and Explosives of Concern QAPP/SOPs	Quality Control Manager				
	HAZWOPER	Vendor	Prior to mobilization			
	First Aid & cardiopulmonary resuscitation					
Intrusive Investigation: Soil Boring/Sampling/ Groundwater Well Installation	Munitions and Explosives of Concern Safety Training	UXO Personnel	Mobilization	All site personnel		
Radiation Monitoring, contamination control and materials management	Radiation Monitoring	Radiation Safety Officer	Mobilization	UXOSO, UXOQCS, RAD Team		

Notes:

HAZWOPER – Hazardous Waste Operations and Emergency Response
NOREAS – NOREAS, Inc.
QAPP – Quality Assurance Project Plan
RAD – Radiological
SOP – standard operating procedure
SSHO – Site Safety and Health Officer
UXO – Unexploded Ordnance
UXOQCS – Unexploded Ordnance Quality Control Specialist
UXOSO – Unexploded Ordnance Safety Officer

SAP Worksheet #8 – Special Personnel Training Requirements Table (Continued)

Routine Training Requirements

Routine training required for this project is described below.

Project personnel are required to meet the Occupational Safety and Health Administration training requirements defined in Title 29 Code of Federal Regulations Part 1910.120(e). These requirements are: 1) 40 hours of formal off-site instruction; 2) a minimum of 3 days of actual on-site field experience under the supervision of a trained and experienced field supervisor; and 3) 8 hours of annual refresher training.

Before work begins, project personnel will receive site-specific training that thoroughly covers the following areas:

- Names of personnel and alternates responsible for health and safety at the project site
- Health and safety hazards present on site
- Selection of the appropriate personal protection levels
- Correct use of personal protective equipment
- Work practices to minimize risks from hazards
- Safe use of engineering controls and equipment on site
- Medical surveillance requirements, including recognition of symptoms and signs that might indicate overexposure to hazardous substances

Copies of health and safety training records, including course completion certifications for the initial and refresher health and safety training, specialized supervisor training, and first aid and cardiopulmonary resuscitation training, are to be maintained in the project files.

In addition to the health and safety training, the samplers will be provided with the following training:

- Installation and sampling of monitoring wells
- Groundwater well development procedures
- Low-flow groundwater sampling procedures
- Soil sampling from hollow-stem augers (HSA) and direct-push technology

SAP Worksheet #8 – Special Personnel Training Requirements Table (Continued)

- Sample handling, packaging, and shipping procedures
- Use of related field and equipment
- Equipment decontamination procedures
- Radiation Monitoring, contamination control and materials management
- Biological training including the preparation and implementation of a Worker Environmental Awareness Program.

All training will be documented and training records will be maintained in the project file. Sampling personnel will be required to read and understand the SAP prior to any sample collection activities. The Project Personnel Sign-off Sheet (WS #4) will be signed by any on-site personnel conducting sampling to indicate that they have read the SAP and will perform the task as described. The sign-off sheet will be maintained in the project file.

SAP Worksheet #9 – Project Scoping Session Participants Sheet

Project Name: Remedial Investigation at South Shore Area **Projected Date(s) of Sampling:** Summer 2015 **Project Manager:** Jeff Brenner	**Site Name:** South Shore Area **Site Location:** Former Mare Island Naval Shipyard, Vallejo, California

Date of Session: 10/12/12
Scoping Session Purpose: Scope of Work for Remedial Investigation.

Name	Title	Affiliation	Phone #	E-mail Address	Project Role
Brooks Pauly	Remedial Project Manager	BRAC	619-532-0789	brooks.pauly@navy.mil	DON oversight
Jeff Brenner	Project Manager	NOREAS	949-467-9106	jeff.brenner@ noreasinc.com	Project Management
Vitthal Hosangadi	Senior Technical Lead/Consulting Engineer	NOREAS	949-467-9099	vitthal.hosangadi@ noreasinc.com	Technical engineering oversight
Jeff Oslick	QCM	NOREAS	626-823-4156	jeff.oslick@noreasinc.com	QC oversight

Notes:

BRAC – Base Realignment and Closure
DON – Department of the Navy
NOREAS – NOREAS, Inc.
QC – quality control
QCM – Quality Control Manager

Comments/Decisions:

The meeting was conducted as a mutual understanding meeting to review contractual issues and general scope items. General discussion focused on limited amount of soil and groundwater sample data available at the SSA and documentation of previous investigations at the SSA. Much of the previous soil and groundwater sampling projects were associated with unexploded ordnance (UXO) and munitions of explosive concern (MEC) removal actions and underground storage tank (UST) closures.

Specific discussion focused on the Munitions Non-Time Critical Removal Action (NTCRA) currently being conducted at the SSA and PMA by other contractors such as Battelle and Weston. As part of the NTCRA, areas identified as geophysical anomalies during a 2006 digital geophysical mapping (DGM) survey are being excavated and screened for MEC and materials presenting potential explosive hazard (MPPEH). During excavation and screening activities, a total of six buried 55-gallon drums and three USTs were unearthed near Building A161 in DGM Grids AI015 and AJ015, respectively.

The NTCRA contractors will collect soil samples at both locations; the Navy will provide the results of those sampling efforts to NOREAS for review and evaluation during preparation of the remedial investigation (RI) scope.

SAP Worksheet #9 – Project Scoping Session Participants Sheet (Continued)

Action Items:

- NOREAS to check the Administrative Record for MINS to determine if any additional documentation or reports related to site assessments or investigations at the SSA are available for review, apart the primary documents already provided by the Navy
- NOREAS will review sampling data associated with drums and USTs found in DGM Grids AI015 and AJ015. NOREAS will be prepared to conduct additional sampling at these locations under the RI, if additional characterization of the nature and extent of potential contaminants at those locations is deemed necessary.

SAP Worksheet #10 – Problem Definition

The former MINS is located on a peninsula in Solano County, California, northeast of San Francisco (Figure 1). The former MINS occupies approximately 3.5 square miles and is bordered by San Pablo Bay on the west, Carquinez Strait on the south, and the Napa River (Mare Island Strait) on the east (Figure 1). MINS was established by the DON in 1854 and served as a Naval Shipyard until it was closed under the BRAC program in April 1996. The primary mission of the former MINS was to build, maintain, and repair Navy ships and submarines; however, it also served a critical role as a munitions storage and production facility from 1857 until 1975.

The southern portion of former MINS, originally referred to as the ordnance facility, includes the Upland Magazine Area, the Western Magazine Area, as well as the PMA and the SSA. This area served a critical role as a munitions storage and production facility. Ordnance was received, maintained, refurbished, demilitarized, subjected to QA testing, and loaded on and off ships at the PMA and SSA. The SSA was used for the storage of general shipyard items as well as for the storage and handling of munitions. While the PMA and SSA have generally been grouped together for certain removal action purposes, this SAP only addresses the comprehensive RI for the SSA.

Seven separate emergency munitions response actions at the PMA and SSA were completed between August 1990 and May 1995. During the UXO intrusive investigation (Weston 2008) 1,824 MEC items 767,373 inert ordnance items (munitions-related debris), and 688,419 pounds of scrap metal were recovered from the SSA. None of the MEC items showed evidence of having been fired and all were classified as discarded military munitions. In addition to the MEC items, a radium button (deck marker) was found near the shoreline at the SSA during the MEC removal activities in 1989. A summary of MEC related investigations and response actions performed at the SSA is provided in the *Final Engineering Evaluation and Cost Analysis/Interim Remedial Action Plan* (Weston 2011).

Historical activities at several buildings at the SSA also included the presence of USTs (up to 1,000-gallon capacity) for storage of fuel oils and diesel, hazardous waste storage areas for halogenated and non-halogenated solvents, storage of mine batteries, and maintenance of advanced weapons containers that may have involved the use of metal preparation compounds (solvents/degreasers) and paints.

Information derived from previous site assessments also indicates that the storm drain and domestic sanitary sewer systems were completely connected until 1959, and remained partly connected through 1972. Industrial wastes from sheet metal operations, boiler shop acid tanks, plating shop sump, and other facilities at MINS were also known to have been discharged to the storm sewer system. Hazardous wastes discharged through the storm sewer before 1972 likely included solvents, coolants, oils, mercury, lead acids, and paint strippers (PRC 1995b). Rinse waters from sheet metal operations discharged to the storm system likely contained metal cleaning solutions, etching solutions, chromic acid, caustic soda, metal brightening compounds, and rust inhibitors. A total of five storm sewer outfalls are located in the SSA. Impacts to the soil

SAP Worksheet #10 – Problem Definition (Continued)

and groundwater at the SSA may have resulted from discharges of hazardous materials at these outfalls.

Three burn pits located near the shoreline were identified as locations were disposal of ordnance by burning was suspected based on the discoloration of the soil and disposition of debris during UXO removal activities. Based on these observations, confirmation soil sampling was conducted for copper, lead, and zinc at the locations subsequently identified as the Oven/Primer pit areas. Though sampled specifically for copper, lead, and zinc, no other compounds were analyzed at that time. However, impacts from other compounds at these locations may have occurred in the past in the event that other hazardous materials were disposed in the burn pits.

In addition, several disposal pits were identified in five areas during the completion of the recent MEC NTCRA activities at the SSA. Although all identified munitions-related items and debris was removed during the excavation and screening activities, the presence of buried munitions items in such quantity may have contributed to environmental impacts of munitions constituents (MC), metals, and other possible contaminants.

Accordingly, the data obtained in the proposed RI at the SSA will be used to: (1) evaluate and characterize the nature and extent of potential soil and groundwater contamination with respect to potential chemical contaminants, and (2) assist in the preparation of a feasibility study that will evaluate remedial actions/approaches to mitigate potential threats or risks to human health and the environment and will ultimately support site closure efforts. As such, the RI is intended to address all environmental programs applicable to the SSA, including the Installation Restoration, Munitions Response, Resource Conservation and Recovery Act, UST, above ground storage tank, petroleum, and Toxic Substances Control Act programs.

SAP Worksheet #11 – Project Quality Objectives/Systematic Planning Process Statements

Project quality objectives define the type, quantity, and quality of data that are needed to answer specific environmental questions and support environmental decisions. Project quality objectives are developed using a systematic planning process described in the *Guidance for the Data Quality Objectives Process* (DQOs) (EPA QA/G4 2006). The DQOs consists of seven iterative steps, which are:

1. State the problem (see WS #10)
2. Identify the goals of the study
3. Identify information inputs
4. Define the boundaries of the study
5. Develop the analytic approach
6. Specify performance or acceptance criteria
7. Develop the plan for obtaining data

The project-specific DQOs are described below.

1. State the Problem

Although a number of response actions have been conducted and a significant amount of UXO and MEC materials have been removed during previous removal actions, only a limited amount of sampling for chemical contaminants has been completed at the SSA to date. Information obtained from the review of previous site assessments and investigations indicates that past activities at the site included the possible use and storage of solvents, paints, fuel oils, mine batteries, and other hazardous materials. Historical information regarding the storm drain system for the base indicates that hazardous industrial wastes were discharged through the storm drains prior to 1972. Furthermore, hazardous wastes may have been disposed on near the shoreline in the three burn pits identified as the Oven/Primer pits.

However, past soil sampling events have been limited to specific UST removal locations and confirmation sampling for copper, lead and zinc in the burn pit areas. As a result, contaminants in soil beneath areas of interest in SSA have not been adequately investigated or characterized in terms of the lateral and vertical extent of potential chemical contaminants [e.g., volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), metals, total petroleum hydrocarbons (TPH), and dioxins in select locations. In addition, the lateral and vertical extent of potential chemical contaminants in groundwater at SSA has not been adequately delineated. If present at significant concentrations, contaminants could pose risk to future human receptors or ecological receptors. Assessment of chemical contaminants in soil and groundwater is therefore needed to determine contaminant distributions and support decision-making as to whether or not remediation is warranted.

SAP Worksheet #11 – Project Quality Objectives/Systematic Planning Process Statements (Continued)

2. Identify the Goals of the Study

The principal study questions that must be addressed by the analytical data for each major area to be investigated are as follows:

BUILDING AREAS

Former Buildings A193, A195, and A259

1. What is the current lateral and vertical extent of chemical contaminants (VOCs, SVOCs, total petroleum hydrocarbons as gasoline [TPH-g], total petroleum hydrocarbons as diesel [TPH-d], total petroleum hydrocarbons as motor oil [TPH-mo], metals, pesticides, and organotins, [if abrasive blast material, ABM, encountered]) in soil?

2. Is the contamination at Former Buildings A193, A195, and A259 such that additional step out sampling will be required to adequately delineate its extent?

Former Building A296

1. What is the current lateral and vertical extent of chemical contaminants (TPH-g, TPH-d, TPH-mo, and metals) in soil?

2. Is the contamination at Former Building A296 such that additional step out sampling will be required to adequately delineate its extent?

SOLID WASTE MANAGEMENT UNITS (SWMUs)

SWMU 93 – Storm Drains near A161, A195, and A292

1. What is the current lateral and vertical extent of chemical contaminants (VOCs, SVOCs, TPH-g, TPH-d, TPH-mo, polychlorinated biphenyls [PCBs], and metals) in soil?

2. Is the contamination at these locations (storm drains near A161, A195, and A292) such that additional step out sampling will be required to adequately delineate its extent?

SWMU 93 – Storm Drain near A259 + nearby MEC disposal pit in AF011

1. What is the current lateral and vertical extent of chemical contaminants (VOCs, SVOCs, TPH-g, TPH-d, TPH-mo, PCBs, and metals) in soil?

2. Is the contamination at the storm drain near A259 such that additional step out sampling will be required to adequately delineate its extent?

SAP Worksheet #11 – Project Quality Objectives/Systematic Planning Process Statements (Continued)

SWMU 106 – Locations adjacent to the lines

1. What is the current lateral and vertical extent of chemical contaminants (VOCs, SVOCs, TPH-g, TPH-d, TPH-mo, PCBs, and metals) in soil?

2. Is the contamination at these locations adjacent to the line such that additional step out sampling will be required to adequately delineate its extent?

SWMU 106 – Locations adjacent to the lines + former MEC sites

1. What is the current lateral and vertical extent of chemical contaminants (VOCs, SVOCs, TPH-g, TPH-d, TPH-mo, PCBs, and metals) in soil?

2. Is the contamination at these locations adjacent to the line and near former MEC Sites such that additional step out sampling will be required to adequately delineate its extent?

<u>FORMER MEC SITES</u>

Disposal Pits AE010, AE011, AF011, and AH010/011 (+ former deck marker location)

1. What is the current lateral and vertical extent of chemical contaminants (metals) in soil?

2. Is the contamination at these former MEC Sites such that additional step out sampling will be required to adequately delineate its extent?

<u>FORMER OVEN/PRIMER PITS</u>

1. What is the current lateral and vertical extent of chemical contaminants (VOCs, SVOCs, TPH-g, TPH-d, TPH-mo, metals, dioxins/furans) in soil?

2. Is the contamination at the former Oven/Primer Pit area such that additional step out sampling will be required to adequately delineate its extent?

<u>OTHER AREAS – TANKS (AJ015) AND DRUMS (AA009)</u>

Former Tanks/Dry Wells (DGM Grid AJ015)

1. What is the current lateral and vertical extent of chemical contaminants (VOCs and PCBs) in soil?

2. Is the contamination at the area where the former tanks and dry wells were located such that additional step out sampling will be required to adequately delineate its extent?

SAP Worksheet #11 – Project Quality Objectives/Systematic Planning Process Statements (Continued)

Tank Conveyance Pipeline (DGM Grid AJ015)

1. What is the current lateral and vertical extent of chemical contaminants (VOCs, SVOCs, TPH-g, TPH-d, TPH-mo, PCBs, and metals) in soil?

2. Is the contamination in the location of the conveyance pipeline such that additional step out sampling will be required to adequately delineate its extent?

Former Buried Drums (DGM Grid AA009)

1. What is the current lateral and vertical extent of chemical contaminants (SVOCs, TPH-d, and TPH-mo) in soil?

2. Is the contamination in the location of the former buried drums such that additional step out sampling will be required to adequately delineate its extent?

<u>SOIL SAMPLES FROM MONITORING WELL BORINGS</u>

SSA-MW01 through SSSA-MW09

1. What is the current lateral and vertical extent of chemical contaminants (VOCs, SVOCs, TPH-g, TPH-d, TPH-mo, and metals) in soil?

2. Is the contamination in the areas around each of these wells (SSA-MW02, SSA-MW03, SSA-MW-04, and SSA-MW05) such that additional step out sampling will be required to adequately delineate its extent?

<u>GROUNDWATER SAMPLE LOCATIONS</u>

SSA-MW01 through SSSA-MW09

1. What is the current lateral and vertical extent of chemical contaminants (VOCs, SVOCs, TPH-g, TPH-d, TPH-mo, PCBs, metals, dioxins/furans, and total dissolved solid [TDS]) in groundwater?

2. Is the contamination in the areas around each of these wells (SSA-MW01, SSA-MW02, SSA-MW-03, SSA-MW04, SSA-MW05, SSA-MW06, and SSA-MW07) such that additional step out sampling will be required to adequately delineate its extent?

3. What is the general water quality of groundwater at the SSA with respect to use for drinking water purposes?

SAP Worksheet #11 – Project Quality Objectives/Systematic Planning Process Statements (Continued)

Sampling locations and analytical parameters are presented in WS #18. Additional remedial investigation approach and the results of previous investigations are provided in Section 4.0 of the Remedial Investigation Work Plan.

3. Identify Information Inputs

- Concentrations of potential contaminants, including VOCs, SVOCs, TPH, pesticides, PCBs, metals, organotins (if ABM encountered/identified), and dioxins/furans will be selectively measured in soil samples collected from three discrete depth intervals from a total of 52 soil borings located in areas of interest (not all analytes will be measured in all borings).
- Concentrations of potential contaminants, including VOCs, SVOCs, TPH, and metals, and TDS, as well as water quality parameters, will be measured in groundwater samples collected from a total of nine groundwater monitoring wells to be installed in areas of interest (not all analytes will be measured in all wells).

4. Define the Boundaries of the Study

The proposed lateral boundaries of the RI include areas associated with prior use, storage, or disposal of chemicals. This essentially encompasses all of the SSA.

The proposed lateral boundaries of the study are depicted on Figures 3 through 9. Soil samples will be collected from soil borings at depths planned in each area as depicted below:

Location/ Feature	Number of Soil Borings/ Sampling Locations	Proposed Depths (feet)
Building Areas	8	0.5 to 10
SWMUs	18	0.5 to 10
MEC Sites	6	0.5 to 10
Oven/Primer Pit Areas	6	0.5 to 10
Other Areas	14	0.5 to 10
Pilot Borings for Wells	9	0.5 to 10
Total	61	

Field activity is expected to begin in February to April 2015. There are no seasonal restrictions on the work with respect to known biological activities at the SSA, although some areas of interest are located in wetland areas within the tidal influence of Carquinez Strait and San Pablo Bay. As such, field activities in these locations will be restricted to periods of low tide.

5. Develop the Analytical Approach

1. If chemical contaminants are detected in soil samples at concentrations exceeding project screening goals (refer to WS #15), then the extent of the contaminants in the soil may not be delineated and additional sampling will be required. If chemical contaminants are detected in soil at concentrations below project screening goals (refer to WS #15), then

SAP Worksheet #11 – Project Quality Objectives/Systematic Planning Process Statements (Continued)

the results will be used to evaluate the nature and extent of contamination for the purpose of conducting Feasibility Studies and Risk Assessments.

2. If chemical contaminants are detected in groundwater samples at concentrations exceeding project screening goals (refer to WS #15), then the extent of the contaminants in the groundwater may not be delineated and additional sampling will be required. If chemical contaminants are detected in groundwater at concentrations below project screening goals (refer to WS #15), then the results will be used to evaluate the nature and extent of contamination for the purpose of conducting Feasibility Studies and Risk Assessments.

In addition, as part of the overall efforts in determining the nature and extent of all potential environmental impacts and potential risks to human health from historic activities at MINS, a Final Status Survey for potential radiological impacts will also be conducted in conjunction with the soil and groundwater investigations described in this SAP (RSRS and NOREAS 2014). In September 1999, one discrete radiological item, a deck marker (radium button), was found during the previous site investigations and removal actions at the SSA. The item was removed and not additional radiological items have since been found at the SSA.

For the purposes of worker health and safety, soil samples collected from 4 locations in the area where the deck marker was found will be scanned in the field for gamma emissions using a portable sodium iodide scintillation detector. The scan results will be compared to background levels as established for the SSA as part of the screening for the Final Status Survey that will be conducted in conjunction with and concurrent to the RI activities described under this work plan. Details regarding the radiological screening, sampling, waste handling procedures are provided in the Final Work Plan for the Radiological Screening and Survey Activities that has been prepared under separate cover (RSRS and NOREAS 2014).

Screening goals presented in WS #15 are intended as advisory only and will be used to guide the RI process. For groundwater samples, this SAP proposes to follow the environmental screening levels (ESLs) listed in the Table B: *ESLs Shallow Soils (≤ 3 m below ground surface [bgs]), Groundwater is not a Current or Potential Source of Drinking Water* in the document entitled *Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater* (*California Regional Water Quality Control Board, San Francisco Bay Region [Water Board]* 2008). The EPA Industrial Regional Screening Limits are proposed for evaluating soil chemical data (EPA 2012). A detailed description of the screening goals as well as the use of shallow versus deep soil ESLs will be further discussed in the RI report.

6. Specify Performance or Acceptance Criteria

The proposed soil and groundwater sampling areas are based on evaluation of previous investigations and historical site data and are presented in Figures 3 through 8. Professional judgment was used in conjunction with existing site data to develop the sampling plan.

SAP Worksheet #11 – Project Quality Objectives/Systematic Planning Process Statements (Continued)

To minimize sampling error, samples will be collected by NOREAS personnel who are trained in the collection of soil and groundwater samples following procedures described in the UFP-QAPP, including sampling procedures, sample handling, and documentation. NOREAS personnel will collect samples following the procedures described in WS #14 of this SAP.

Samples will be analyzed for chemical parameters by a Department of Health Services Environmental Laboratory Accreditation Program (ELAP), and Department of Defense (DoD) ELAP-approved laboratory facility. The primary analytical laboratory supporting the RI will be Eurofins Calscience Inc. located in Garden Grove, California. Analyses for dioxins and furans will be subcontracted to Maxxam Analytics in Ontario, Canada through Eurofins Calscience Inc.. Sampling and analytical performance or acceptance criteria are specified in WSs #12, #15 and #28. Third-party data validation will be performed on project analytical data as described in WSs #29 and #36.

7. Develop the Plan for Obtaining Data

Groundwater and soil samples will be collected in accordance with the sampling approach discussed above and at the approximate locations depicted on Figures 3 through 8. Details of the sampling and analysis strategy are provided in WSs #17 and #18. Should field conditions require adjustment of the proposed sampling locations; changes will be made and documented in consideration of achieving the project goals described above.

SAP Worksheet #12.1 – Measurement Performance Criteria Table – Field QC Samples for Groundwater Samples

QC Sample	Analytical Group	Frequency	Data Quality Indicators	Measurement Performance Criteria	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
Field duplicate	VOCs, SVOCs, TPH, PCBs, dioxins/furans and metals	1 per 10 field samples	Field Precision	RPD less than 30 percent for sample/duplicate concentrations greater than 10X reporting limit	S
Equipment Rinsate	VOCs, SVOCs, metals, and TPH	1 per sampling day, per non-dedicated sampling equipment	Presence of potential contaminants/accuracy	No target analyte greater than LOQ	S & A
Source Blank	VOCs, SVOCs, metals, and TPH	1 per lot	Accuracy	No target analyte greater than LOQ	S & A
Trip Blank	VOCs	One per shipping cooler containing VOAs	Presence of potential contaminants/accuracy	No target analyte greater than LOQ	S & A
MS/MSD[1]	VOCs, SVOCs, TPH, PCBs, dioxins/furans, and metals	1 per 20 field samples 1 per project for dioxins/furans	Laboratory Precision and Accuracy	Refer to QC Limits in WS #28	S & A

Notes:

[1] Analyzed by the analytical laboratory, but additional sample volume collected at designated sampling location as specified in the field.

º C – degrees Celsius
LOQ – limit of quantitation
MS/MSD – matrix spike/matrix spike duplicate
PCBs – polychlorinated biphenyls
QC – quality control
RPD– relative percent difference
SVOC – semivolatile organic compound
TPH – total petroleum hydrocarbons
VOA – volatile organic analysis
VOC – volatile organic compound

SAP Worksheet #12.2 – Measurement Performance Criteria Table – Field QC Samples for Soil Samples

QC Sample	Analytical Group	Frequency	Data Quality Indicators	Measurement Performance Criteria	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
Field duplicate [1]	N/A	N/A	N/A	N/A	N/A
Equipment Rinsate	VOCs, SVOCs, TPH, and metals	1 per sampling day, per non-dedicated sampling equipment	Presence of potential contaminants/accuracy	No target analyte greater than LOQ	S & A
MS/MSD[2]	VOCs, SVOCs, TPH, pesticides, PCBs, metals, organotins, and dioxins/furans	1 per 20 field samples; 1 per project for dioxins/furans	Precision and accuracy	Refer to QC Limits in WS #28	S & A

Notes:

[1] Field duplicate samples will not be collected for soil matrix due to anticipated nonhomogeneous nature of the soil.
[2] Analyzed by the analytical laboratory, but additional sample volume collected at designated sampling location as specified in the field.

MS/MSD – matrix spike/matrix spike duplicate
N/A – not applicable
PCBs – polychlorinated biphenyls
QC – quality control
SVOC – semivolatile organic compound
TPH – total petroleum hydrocarbons
VOC – volatile organic compound
WS – Worksheet

SAP Worksheet #13 – Secondary Data Criteria and Limitations Table

Secondary Data	Data Source (originating organization, report title and date)	Data Generator(s) (Originating organization, data types, data generation/collection dates)	How Data Will Be Used	Limitations on Data Use
Primarily historical use information with respect to buildings, very little soil or groundwater data for the SSA.	PRC. 1995a. *Preliminary Assessment Final Summary Report, Ordnance Sites, Mare Island Naval Shipyard, Vallejo California.* September.	*PRC*. Preliminary site assessment of sites at entire MINS installation that potentially contain UXO and related contaminants. PAs covered active and historical dredge ponds, 500 acres of filled areas, 5 small arms ranges, and 118 ordnance facilities at MINS. Report provided results of ordnance PAs and recommendations for further action, where warranted. Only very limited amount of soil sampling data for SSA sites as summarized from UST removal documents.	Historical data were used to determine proposed soil and groundwater sampling locations as well as the potential contaminants at the SSA during the RI.	None known
Primarily historical use information with respect to SWMUs at MINS, no soil or groundwater data for the SSA.	PRC. 1995b. *Preliminary Assessment/Site Inspection Final Summary Report for Non-Radiological Sites, Mare Island Naval Shipyard, Vallejo California.* May.	*PRC*. Included an evaluation of 129 SWMUs, potential SWMUs, and other areas of concern at MINS. The PA/SI provided recommendations with respect to the need for further action or investigation at each of the SMWU sites evaluated.	Information and recommendations in the report were used to evaluate soil and groundwater sampling locations at the SSA for the RI, as well as the potential contaminants for the proposed sample locations.	None known
UXO/MEC data from intrusive investigations at the SSA.	Roy F. Weston, Inc. 2003. *Unexploded Ordnance Intrusive Investigation Summary Report, South Shore Area, Mare Island, Vallejo, California, Draft Final.* January.	*Weston.* Provides a summary of results from previous UXO/MEC removal actions and site investigations at the SSA. Primarily includes descriptions of MEC items found and removed from various locations in the SSA. Also includes results of confirmation soil and groundwater samples collected from three ordnance disposal areas identified and the Primer Pit and Oven Pit Areas. Sample data limited to copper, lead, and zinc.	Data were used to evaluate soil sampling locations for MC (i.e., explosives) based on MEC removal actions. Data from Primer/Oven Pit Areas used to evaluate the need for additional soil sampling at that location, along with potential contaminants.	None known

SAP Worksheet #13 – Secondary Data Criteria and Limitations Table (Continued)

Secondary Data	Data Source (originating organization, report title and date)	Data Generator(s) (Originating organization, data types, data generation/collection dates)	How Data Will Be Used	Limitations on Data Use
UXO/ MEC data from MEC NTCRA completed in 2012-2013 at the SSA	ISR-JV, 2013. *Removal Action Completion Report for the Non-Time Critical Removal Action at the Production Manufacturing Area and South Shore Area, Former Mare Island, Vallejo, California Draft.* December. and Battelle, 2013. *Removal Action Completion Report for the Non-Time Critical Removal Action at the Production Manufacturing Area and South Shore Area, Former Mare Island, Vallejo, California Draft.* December.	*ISR-JV and Battelle.* Provides a summary of the MEC NTCRA removal activities at the SSA including locations where highest density of munitions items were recovered, along with descriptions of items found. During the removal activities, several disposal pits were identified and cleared of munitions and debris. In addition, buried 55-gallon steel drums and USTs were recovered during the excavation and clearing of anomalies at several locations at the SSA. The reports provide analytical data for confirmation soil sampling that was conducted following the removal of these items during the NTCRA.	Data were used to evaluate soil sampling locations for MC (i.e., explosives) based on MEC removal actions. In addition, soil sampling results from areas where drums and UST were recovered were also used in the evaluation of potential soil and groundwater sampling locations and potential contaminants for the RI.	None known

Notes:

MC – munitions constituents
MEC – munitions of explosive concern
MINS – Former Mare Island Naval Shipyard
PA/SI – Preliminary Assessment/Site Inspection
PRC – Environmental Management, Inc.
RI – Remedial Investigation
SSA – South Shore Area
SWMU – Solid Waste Management Unit
UST – underground storage tank
UXO – unexploded ordnance

SAP Worksheet #14 – Summary of Project Tasks

Major Tasks:

This worksheet summarizes the major tasks planned for this project. Figures 3 through 9 depict the proposed soil boring and new monitoring well locations during the RI.

Biological Monitoring and Avoidance Procedures

Due to the potential for sensitive wildlife species, including the Salt Marsh Harvest Mouse and California Clapper Rail, to be present in the SSA, NOREAS will provide biological education training, biological monitoring, and appropriate avoidance and minimization measures. Biological training will include the preparation and implementation of an Environmental Protection Plan. As the majority of the planned investigation locations are located off-road, a biological monitor will be onsite prior to mobilization activities to establish ingress and egress routes to the proposed sampling locations. The path to and from each sampling location will be cleared by a biologist before vehicles or heavy equipment drive off-road to ensure that there are no special status species in the path of ingress or egress.

Underground Utility Survey

Buried utilities or other underground infrastructure could be present within the project boundaries. Prior to initiating field work, the Base Utility Locator Service and Underground Service Alert will be contacted to assist in locating underground utilities in the project area. The ground surface over areas of suspected underground utilities will be marked with appropriately colored paints. NOREAS will also retain a geophysical utility locating company to map the area before field activities can begin. Proposed boring and well locations will be repositioned as necessary to avoid underground utilities.

Prior to drilling and sampling, the nearest shut-off valves for all utilities that may be encountered will be identified, and access to those shut-off valves will be ensured during all field activities.

MPPEH Avoidance

Detector-aided surface sweeps will be performed at the SSA prior to any intrusive activities and will be in accordance with all local, state, and federal regulations including all applicable DoD requirements. The objective of the detector-aided surface survey is to determine if an anomaly which may represent suspect munitions or explosives of concern (MEC), MPPEH, or munitions debris (MD) exist on the ground surface at the proposed direct-push technology (DPT) boring, and/or groundwater monitoring well locations. If a surface anomaly is discovered on the site while employing anomaly avoidance techniques, the location and description of the item will be reported to the Navy RPM. The specific boring location will then be moved to an area that is free of metal anomalies. The anomaly will not be excavated or handled.

Due to the prevalence of MPPEH items previously recovered at the SSA, MPPEH avoidance procedures will also be conducted during all intrusive phases of the RI. During borehole installation (hollow stem augers for monitoring wells and DPT for soil samples), the boring will be checked at one-foot intervals for anomalies using a down hole detector. If an anomaly is

SAP Worksheet #14 – Summary of Project Tasks (Continued)

detected prior to the completion of the boring, the boring will be terminated and the depth of detection and location of the boring will be recorded. The anomaly will not be excavated for identification. The boring will then be relocated, and anomaly avoidance measures will resume.

Additional details regarding the MPPEH avoidance measures are provided in Section 5.5 of the RI Work Plan.

Land Survey

All soil boring/sampling and well locations will be surveyed for elevation and location coordinates by a California-licensed Professional Surveyor. The survey will be accurate to 0.01 foot (monitoring wells) or 0.1 foot (soil borings) vertically above mean sea level and will be surveyed to the State Plane Coordinate System based on the North American Vertical Datum 88; horizontal coordinates (0.1 foot accuracy) will be surveyed to the California State Plane Coordinate System North American Datum (NAD) 83. The surveyor will also report the horizontal data as feet in California State Plane NAD 1927 (feet); vertical data as feet msl in National Geodetic Vertical Datum 1929. The final survey data will be provided in Naval Electronic Data Deliverable (NEDD) format and uploaded into Naval Installation Restoration Information Solution.

Soil Sampling Procedures

For the RI, a total of up to 52 soil borings will be advanced to depths of up to 10 feet bgs at the SSA (see Figures 3 through 8). At all of the sampling locations except for those associated with the underground storage tanks and piping (see Figures 3 and 8), soil samples will be collected from depths of 0.5, 5, and 10 feet bgs. For those borings located near the tanks and piping (Figure 8), soil samples will be collected from depths of 2 and 5 feet bgs. In addition, to the soil boring locations, soil samples will also be collected from 0.5, 5, and 10 feet bgs during the advancement of the pilot boring for the monitoring wells. Soil samples from the 0.5 feet bgs depth interval will not be analyzed for VOCs due to the potential for the results to be biased low.

At each of the soil boring locations, soil samples will collected by advancing a 3-inch diameter borehole using a DPT drilling rig. The DPT rig will be capable of providing a continuous sample of soil for visual observations and sampling. All DPT drilling operations will be conducted by a California C-57 licensed drilling subcontractor.

Continuous soil cores will be logged by the field geologist. Soil cores will be: (1) visually inspected for potential chemical impacts, (2) field screened for organic vapors using a photoionization detector, and (3) used to generate lithologic soil boring logs. Lithologic soil boring logs generated during field work will be signed by a State of California Professional Geologist.

The DPT procedure utilizes a hydraulic driven soil sampling system consisting of a 3-inch diameter, 4-foot long stainless steel macro-core sampler with an inner core acetate liner sample

SAP Worksheet #14 – Summary of Project Tasks (Continued)

tube. Once the sample depth has been reached, the soil core will be brought to the surface. The sample liner (new, acetate material) will be removed from the sampler with as little disturbance as possible. At the pilot boring locations for the groundwater monitoring wells, samples will be collected using a split-spoon sampler or equivalent method to provide driven samples.

Soil samples will then be collected into method-required clean glass jars with minimal headspace for all analytical parameters other than VOC analysis. For VOC preparation and analysis, TerraCore® samplers will be used to collect and preserve soil samples in accordance with the EPA methods 5035/8260B. All samples will be labeled, placed in self-sealing plastic bags, and placed on ice in a cooler for transport to the analytical laboratory. Method-required sample containers are provided in WS #19. The samples will be maintained and transported under strict chain-of-custody protocols at all times as specified in WS #27.

As a contingency measure, all soil samples collected during the RI will be temporarily archived by the analytical laboratory for a minimum of 60 days, pending need for additional analyses.

Disposable nitrile gloves will be worn during sampling. Gloves will be disposed of after each sample is collected, and a new pair will be worn before the next sample is collected to avoid possible cross-contamination.

Groundwater Monitoring Well Drilling and Installation

A total of 9 groundwater monitoring wells will be installed to anticipated depths of up to 20 feet bgs as part of this RI (see Figure 3 and Figure 9). The wells will be drilled and installed by a C-57 licensed drilling subcontractor using a HSA drilling rig. The HSA rig will be used to advance a 6 to 8 inch diameter pilot borehole to the target depth at each location. The augers will consist of carbon steel and will be free of paint or other materials that could impact water sample results. The target depth for each well location will be determined based on the approximate depth of groundwater encountered at the time of drilling. Where possible, the wells will be installed such that the top of the screen interval will be located approximately one foot above the water table. Upon reaching target depth at a given location, the well casing will be constructed and hung in the borehole. Well construction details and a conceptual design of the wells are provided in Section 5.3 of the Work Plan.

Well Development

The monitoring wells will be developed to settle and establish the filter pack materials and clear fine-grained materials from the well casing, sand pack, and formation adjacent to the well. The purpose of well development is to ensure the well is in hydraulic connection with the formation and that it produces groundwater samples representative of the aquifer.

Well development will begin no sooner than 48 hours after final grout placement. A surge block and submersible pump will be used to surge and pump the well. Well development will continue until the purge water turbidity is 50 Nephelometric turbidity units or less and a minimum of 5

SAP Worksheet #14 – Summary of Project Tasks (Continued)

casing volumes have been removed. If the well does not properly develop within 4 hours, the well development data will be reviewed with the supervising Hydrogeologist who will determine if development should continue and for how long or if alternative development methods should be employed.

Well development will be performed by the drilling or well sampling subcontractor under supervision of the field geologist.

Groundwater Sampling and Analysis (Low-Flow Groundwater Sampling Procedure)

Groundwater samples will be collected from the nine newly installed monitoring wells, SSA-MW01 through SSA-MW07, to establish baseline concentrations during the RI as shown on Figure 9. All groundwater samples will be analyzed for analytical constituents and frequency detailed in WS #18. All purging and sampling activities will be recorded on the *Low-Flow Purging and Sampling Data Sheet* (Attachment 1). All non-disposable sampling equipment and materials used during the field operations will be decontaminated in accordance with the procedures outlined in this WS.

Groundwater level measurements will be collected from all monitoring wells before groundwater sampling is initiated. At each well, the depth to groundwater will be measured from a reference point of known elevation using a Solinst® (or equivalent) electronic water-level indicator with an accuracy of ±0.01-foot. The elevation of the reference point at each well is already available or will be provided (if not available) by a California-licensed surveyor, and the exact location of the reference point will be clearly marked on the well casing and/or monument. The water quality meter will be calibrated to the manufacturer's specifications using current (unexpired) standards. Calibration results will be documented on the *Field Calibration Form* (Attachment 1). A flow-through cell will be used to monitor the water quality indicator parameters. Disposable nitrile gloves will be worn during sampling. Nitrile gloves will be disposed of after each sample is collected, and a new pair will be worn before the next sample is collected to avoid possible cross-contamination. Groundwater samples will be collected using the low-flow purging and sampling method as follows:

1. Calibrate a water quality meter to the manufacturer's specifications using current (unexpired) standards.
2. Document calibration results on the field calibration form.
3. Use a flow-through cell to monitor the water quality indicator parameters.
4. Wear disposable nitrile gloves during all purging and sampling.
5. Arrive at the monitoring well, and confirm the well identification number.
6. Open the traffic box.
7. Remove any standing water that may have accumulated.
8. Unlock the well.

SAP Worksheet #14 – Summary of Project Tasks (Continued)

9. Install the water level indicator probe through a hole in the sampling cap.
10. Measure the groundwater from sampling cap to the nearest 0.01-foot.
11. Record the measurement on the well sampling log to the nearest 0.01-foot.
12. To avoid possible cross-contamination, place the flow-through cell and purge water container in a plastic tub or equivalent.
13. Attach the flow-through cell tubing and pressure hose to the sampling cap.
14. Begin pumping the well with a bladder.
15. Pump at 0.1 to 0.5 liter (L) per minute (100 milliliters [mL] to 500 mL). Check the water level in the well, and measure the discharge rate of the pump by using a graduated cylinder every minute for the first 5 minutes. Ideally, the pumping rate should equal the well recharge rate with little or no water level drawdown in the well (drawdown shall be less than 0.3-foot.)
16. Measure and record the water level, discharge rate, and water quality indicator parameters on the well sampling log every 5 minutes during purging.
17. Check the discharge tubing for air bubbles during the purging process. If bubbles are visible, pluck the tubing where the bubble is located to enable the bubble to pass through the tubing and into the flow-through cell.
18. During purging, monitor pH, temperature, turbidity, specific conductance, oxidation reduction potential, and dissolved oxygen approximately every 5 minutes with a calibrated water quality meter.
19. Purge the groundwater until indicator parameters have stabilized. The well is stable and ready for sample collection when the indicator parameters have stabilized for three consecutive readings as follows:
    - Consecutive readings within plus or minus (±) 0.1 standard units for pH
    - Consecutive readings within ± 1 degree Celsius (ºC) for temperature
    - Consecutive readings within ± 10% for turbidity (<u>when turbidity is greater than 10 Nephelometric turbidity units</u>)
    - Consecutive readings within ± 3% micromhos per centimeter for specific conductance
    - Consecutive readings within ± 10 millivolts for oxidation reduction potential
    - Consecutive readings within ± 0.3 for dissolved oxygen (milligrams per liter [mg/L])

    If stabilization is not occurring and the procedure has been strictly followed, <u>then sample collection can take place once, at a minimum, three to six casing volumes have been removed</u>. Record the specific information on purging in the field logbook or on the groundwater sampling log.
20. Once the indicator parameters have stabilized, disconnect the flow-through cell from the pump discharge tubing.

SAP Worksheet #14 – Summary of Project Tasks (Continued)

21. Collect samples for analysis of VOCs first, then collect samples for analysis of organic compounds, inorganic parameters, and general chemistry parameters (as applicable).
22. Fill three 40-mL volatile organic analysis (VOA) vials by initially tilting the vials, allowing the pump discharge to flow gently down the inside of the vial with minimal turbulence. Decrease the flow rate, if necessary, to reduce sample agitation. Fill each vial until a meniscus is formed at the top of the VOA vial. After the vial is full, cap immediately, invert the vial, tap the side lightly, and check for the presence of air bubbles. If air bubbles are present, discard the sample, and resample using a new vial.
23. Do not allow containers with preservative to be overfilled to the point where overflow occurs because overfilling may result in loss of preservative.
24. Containers should be kept capped, except when they are being filled.
25. Affix a completed sample label to the sample container and cover with clear packaging tape.
26. Wrap glass bottles in bubble-wrap packaging material, place into resealable bags, and place sample containers into a cooler containing ice.
27. Record sample number, time and date, and requested analysis on the COC form.

Equipment Decontamination

Non-disposable equipment used to drill, and sample groundwater will be decontaminated between boreholes and prior to leaving the site. All downhole equipment will be thoroughly decontaminated using steam cleaner/pressure washing equipment supplied by potable water. If required, brushes will be used to aid in the removal of gross contamination prior to steam/pressure washing. A decontamination trailer will be used to facilitate collection of the wastewater. In the event any small downhole equipment is used that is not practical to steam/pressure wash, such equipment shall be decontaminated using the following steps: (1) thoroughly wash using a non-phosphate detergent in potable water in a bucket, brushing/agitating as necessary; (2) thoroughly rinse in potable water; (3) thoroughly rinse in a second water rinse bucket containing distilled/deionoized water. The source containers for the distilled/deionized water shall be used for equipment rinsate samples.

Waste Management

The soil cuttings, development water, purge water, and rinsate from equipment decontamination will be collected and placed into Department of Transportation-approved 55-gallon drums. The wastewater will be transported to an appropriate off-site permitted facility for treatment and/or disposal. Investigation-derived waste will be characterized based upon sampling results.

Soil cuttings will be contained in 55-gallon Department of Transportation-approved drums and/or roll-off containers and stored at a designated staging area at the site pending waste classification. Soil cuttings and other investigation-derived wastes will be transported by appropriately licensed carrier and disposed of at an appropriately licensed Treatment, Storage,

SAP Worksheet #14 – Summary of Project Tasks (Continued)

Disposal Facility. Soil samples for waste classification will be collected from the drums and analyzed in accordance with the waste receiving facility requirements.

Quality Control Task

Groundwater samples will be collected using procedures presented above. Field QC samples to be collected are presented in WS #12. Sample collection activities will be documented in accordance with procedures described in WS #27. In addition, sample handling, packaging and shipping procedures are also presented in WS # 27.

Data Management

Field data will be recorded in the field logbook as described in WS #27.

The laboratory will verify the sample receipt and document it in a sample receipt form after samples are received at the laboratory. In addition, samples will be assigned a unique number and recorded in the laboratory internal COC.

The laboratory will report data by submitting data packages. For this project, 80 percent of the data will be submitted in an EPA Level III-equivalent data package, and 20 percent submitted in an EPA Level IV-equivalent data package.

Level III data quality is assessed by comparing the parameters listed below to the appropriate criteria (or limits) as specified in the project SAP, by Contract Laboratory Program requirements, or by method-specific requirements.

Level IV data validation will follow the EPA protocols and Contract Laboratory Program criteria set forth in the *EPA National Functional Guidelines for Superfund Organic Methods Data Review* (EPA 2008). These guidelines apply to analytical data packages that include the raw data (e.g., spectra and chromatograms) and backup documentation for calibration standards, analysis run logs, laboratory control samples (LCSs), dilution factors, and other types of information. This additional information is utilized in the Level IV data validation process for checking calculations of quantified analytical data. Calculations are checked for QC samples (e.g., MS/MSD and LCS data) and routine field samples (including field duplicates, field and equipment rinsate blanks, and trip blanks for VOCs). To ensure that RLs and data are appropriate, an evaluation is made of instrument performance, method of calibration, and the original data for calibration standards.

All data reported by the analyst must be reviewed by a peer analyst qualified to perform the method, and a supervisor, prior to reporting the data. In addition, the laboratory QA manager must annually review 10 percent of the data reported for each section. The laboratory QA manager review may be conducted after the data have been reported.

Review of laboratory data by an independent, third-party is also required, as detailed in WS #34, WS #35, and WS #36.

SAP Worksheet #14 – Summary of Project Tasks (Continued)

All data will be reported on or before the designated turnaround time by fax/e-mail. The Project Chemist will review the data upon receipt prior to releasing it to project personnel to verify that the sampling procedures and analytical results were obtained following the protocols in this SAP and are of sufficient quality to satisfy DQOs provided in WS #11.

Initial laboratory reports (Level III) will be due within 5 business days following sample receipt, unless otherwise specified in writing by NOREAS. On or before 21 calendar days from sample receipt, the laboratory will submit hard-copy data or a CD-ROM with associated QC information, along with an electronic data deliverable (EDD) compatible with NEDD.

Electronic Data

Survey data will be recorded by a field surveyor and also entered into the database. All sample locations, except for waste characterization samples, will be surveyed in accordance with Environmental Work Instruction (EWI) EVR.6, Environmental Data Management and Required Electronic Delivery Standards (SWDIV 2005). For NEDD deliverables, horizontal control information will be captured in the State Plane Coordinate System (NAD 83) in feet, and vertical control standards will be in mean sea level (NAD 88) in feet. Validated analytical data will be tabulated and all manual entries into the data tables will be verified by the Project Chemist or designee by checking the manual entry against the hard-copy information.

The EDD from the laboratory that will be compatible with NEDD requirements will be uploaded to the Naval Installation Restoration Information Solution (NIRIS) as specified in EWI #6. The data will be checked for required values and project-specific requirements by the database. Any discrepancies in the EDD will either be corrected by NOREAS, or the laboratory will be notified to make corrections. The electronic data in NEDD format will be submitted to the DON within 30 calendar days after the final validation report is received.

SAP Worksheet #15.1 – Reference Limits and Evaluation Table (Water)

Matrix: Water
Analytical Group: Volatile Organic Compounds by EPA 8260B

Analyte	CAS Number	Screening Criteria (µg/L)	Screening Criteria Reference	Project QL Goal (µg/L)	Laboratory-Specific Limits		
					LOQ (µg/L)	LOD (µg/L)	DL (µg/L)
1,1,1-Trichloroethane	71-55-6	8,000	RSL[1]	5.0	5.0	0.50	0.30
1,1,2,2-Tetrachloroethane	79-34-5	0.076	RSL[1]	1.0	1.0	0.50	0.41
1,1,2-Trichloroethane	79-00-5	0.28	RSL[1]	1.0	1.0	0.50	0.38
1,1-Dichloroethane	75-34-3	2.7	RSL[1]	5.0	5.0	0.50	0.28
1,1-Dichloroethene	75-35-4	280	RSL[1]	1.0	1.0	0.50	0.43
1,2,4-Trichlorobenzene	120-82-1	1.1	RSL[1]	5.0	5.0	1.0	0.50
1,2-Dibromo-3-chloropropane	96-12-8	0.00033[2]	RSL[1]	10	10	5.0	1.2
1,2-Dibromoethane	106-93-4	0.0075[2]	RSL[1]	1.0	1.0	0.50	0.36
1,2-Dichlorobenzene	95-50-1	300	RSL[1]	1.0	1.0	0.50	0.46
1,2-Dichloroethane	107-06-2	0.17[2]	RSL[1]	1.0	1.0	0.50	0.24
1,2-Dichloropropane	78-87-5	0.44[2]	RSL[1]	1.0	1.0	0.50	0.42
1,3-Dichlorobenzene	541-73-1	65	RSL[1]	1.0	1.0	0.50	0.40
1,4-Dichlorobenzene	106-46-7	0.48[2]	RSL[1]	1.0	1.0	0.50	0.43
2-Butanone	78-93-3	5,600	RSL[1]	10	10	5.0	2.2
4-Methyl-2-pentanone	108-10-1	1,200	RSL[1]	10	10	5.0	4.4
Acetone	67-64-1	14,000	RSL[1]	20	20	10	6.0
Benzene	71-43-2	0.45[2]	RSL[1]	1.0	1.0	0.50	0.14
Bromodichloromethane	75-27-4	0.13[2]	RSL[1]	5.0	5.0	0.50	0.21
Bromoform	75-25-2	9.2	RSL[1]	10	10	1.0	0.50
Bromomethane	74-83-9	7.5	RSL[1]	20	20	5.0	3.9
Carbon Tetrachloride	56-23-5	0.45[2]	RSL[1]	1.0	1.0	0.50	0.23
Chlorobenzene	108-90-7	78	RSL[1]	5.0	5.0	0.50	0.17
Chloroethane	75-00-3	21,000	RSL[1]	10	10	5.0	2.3

SAP Worksheet #15.1 – Reference Limits and Evaluation Table (Water) (Continued)

Analyte	CAS Number	Screening Criteria (µg/L)	Screening Criteria Reference	Project QL Goal (µg/L)	Laboratory-Specific Limits		
					LOQ (µg/L)	LOD (µg/L)	DL (µg/L)
Chloroform	67-66-3	0.22[2]	RSL[1]	5.0	5.0	0.50	0.46
Chloromethane	74-87-3	190	RSL[1]	10	10	5.0	1.8
cis-1,2-Dichloroethene	156-59-2	36	RSL[1]	1.0	1.0	0.50	0.48
cis-1,3-Dichloropropene	542-75-6	0.47[2]	RSL[1]	1.0	1.0	0.50	0.25
Dibromochloromethane	124-48-1	0.17[2]	RSL[1]	1.0	1.0	0.50	0.25
Ethylbenzene	100-41-4	1.5	RSL[1]	1.0	1.0	0.50	0.14
Hexachlorobutadiene	87-68-3	0.30[2]	RSL[1]	1.0	1.0	0.50	0.32
m,p-Xylenes	1330-20-7	190	RSL[1]	10	10	1.0	0.24
Methylene Chloride	75-09-2	11	RSL[1]	5.0	5.0	1.0	0.64
Methyl-tert-butyl-ether	1634-04-4	14	RSL[1]	1.0	1.0	0.50	0.31
Naphthalene	91-20-3	0.17[2]	RSL[1]	10	10	5.0	2.5
o-Xylene	95-47-6	190	RSL[1]	1.0	1.0	0.50	0.23
Styrene	100-42-5	1,200	RSL[1]	1.0	1.0	0.50	0.17
trans-1,2-Dichloroethene	156-60-5	360	RSL[1]	1.0	1.0	0.50	0.37
Tetrachloroethene	127-18-4	11	RSL[1]	5.0	5.0	0.50	0.39
Toluene	108-88-3	1,100	RSL[1]	1.0	1.0	0.50	0.24
Trichloroethene	79-01-6	0.49[2]	RSL[1]	1.0	1.0	0.50	0.37
Vinyl Chloride	75-01-4	0.019[2]	RSL[1]	1.0	1.0	0.50	0.30

Notes:

1 EPA Residential Regional Screening Levels (RSLs), January 2015. http://www.epa.gov/region9/superfund/prg/index.html. In the event that groundwater is determined to be a current or potential source of drinking water, the screening levels will be updated accordingly.

2 The LOQ exceeds the screening goal. The laboratory detection limit is the lowest possible limit achievable following the EPA analytical method and will be used as the project screening goal. Data will be reported down to the DL; trace values detected between the DL and LOQ will be reported with a "J" qualifier. Any uncertainty associated with the analyte will be discussed in the risk assessment section of the Remedial Investigation report that will be prepared following field activities.

µg/L – micrograms per liter
CAS – Chemical Abstracts Service
DL – detection limit
EPA – U.S. Environmental Protection Agency
LOD – limit of detection
LOQ – limit of quantitation
QL – quantitation limit

SAP Worksheet #15.1 – Reference Limits and Evaluation Table (Water) (Continued)

Matrix: Water
Analytical Group: Semivolatile Organic Compounds by EPA 8270C

Analyte	CAS Number	Screening Criteria (µg/L)	Screening Criteria Reference	Project QL Goal (µg/L)	Laboratory-Specific Limits		
					LOQ (µg/L)	LOD (µg/L)	DL (µg/L)
Acenaphthene	83-32-9	530	RSL[1]	10	10	6.0	2.8
Acenaphthylene	208-96-8	30	RSL[1]	10	10	6.0	2.9
Anthracene	120-12-7	1,800	RSL[1]	10	10	6.0	3.0
Benzo(a)anthracene	56-55-3	0.034[2]	RSL[1]	10	10	6.0	4.7
Benzo(a)pyrene	50-32-8	0.034[2]	RSL[1]	10	10	6.0	2.4
Benzo(b)fluoranthene	205-99-2	0.034[2]	RSL[1]	10	10	6.0	2.3
Benzo(g,h,i)perylene	191-24-2	0.1[2]	RSL[1]	10	10	6.0	2.5
Benzo(k)fluoranthene	207-08-9	0.034[2]	RSL[1]	10	10	6.0	3.2
Bis(2-Chloroethyl)ether	111-44-4	0.014[2]	RSL[1]	10	10	6.0	2.5
Bis(2-Chloroisopropyl)ether	39638-32-9	0.36[2]	RSL[1]	10	10	6.0	3.2
Bis(2-Ethylhexyl)phthalate	117-81-7	5.6[2]	RSL[1]	10	10	6.0	3.2
4-Chloroaniline	106-47-8	0.36[2]	RSL[1]	10	10	6.0	2.0
2-Chlorophenol	95-57-8	91	RSL[1]	10	10	6.0	2.3
Chrysene	218-01-9	3.4[2]	RSL[1]	10	10	6.0	2.8
Dibenzo(a,h)anthracene	53-70-3	0.0034[2]	RSL[1]	10	10	6.0	2.5
1,2-Dichlorobenzene	95-50-1	300	RSL[1]	10	10	6.0	3.0
1,3-Dichlorobenzene	541-73-1	65	RSL[1]	10	10	6.0	3.1
1,4-Dichlorobenzene	106-46-7	0.48[2]	RSL[1]	10	10	6.0	2.9
3,3'-Dichlorobenzidine	91-94-1	0.12[2]	RSL[1]	40	40	6.0	2.6
2,4-Dichlorophenol	87-65-0	3.0[2]	RSL[1]	10	10	6.0	1.6
Diethyl Phthalate	84-66-2	1,500	RSL[1]	10	10	6.0	2.8
Dimethyl Phthalate	131-11-3	1.5[2]	RSL[1]	40	40	6.0	2.6

SAP Worksheet #15.1 – Reference Limits and Evaluation Table (Water) (Continued)

Analyte	CAS Number	Screening Criteria (µg/L)	Screening Criteria Reference	Project QL Goal (µg/L)	Laboratory-Specific Limits		
					LOQ (µg/L)	LOD (µg/L)	DL (µg/L)
2,4-Dimethylphenol	105-67-9	360	RSL[1]	10	10	6.0	2.4
2,4-Dinitrophenol	51-28-5	39	RSL[1]	40	40	16	13
2,4-Dinitrotoluene	121-14-2	0.24[2]	RSL[1]	10	10	6.0	2.3
Fluoranthene	206-44-0	80	RSL[1]	10	10	6.0	3.1
Fluorene	86-73-7	290	RSL[1]	10	10	6.0	2.7
Hexachloro-1,3-Butadiene	87-68-3	0.30[2]	RSL[1]	10	10	6.0	2.9
Hexachlorobenzene	118-74-1	0.049[2]	RSL[1]	10	10	6.0	3.1
Hexachloroethane	67-72-1	0.90[2]	RSL[1]	40	40	6.0	3.0
Indeno(1,2,3-c,d)pyrene	193-39-5	0.034[2]	RSL[1]	10	10	6.0	2.1
2-Methylnaphthalene	91-57-6	36	RSL[1]	10	10	6.0	2.8
Naphthalene	91-20-3	0.17[2]	RSL[1]	100	100	6.0	2.9
Pentachlorophenol	87-86-5	0.040[2]	RSL[1]	40	40	6.0	4.6
Phenanthrene	85-01-8	4.6[2]	RSL[1]	10	10	6.0	2.9
Phenol	108-95-2	5,800	RSL[1]	10	10	6.0	2.1
Pyrene	129-00-0	120	RSL[1]	10	10	6.0	3.0
1,2,4-Trichlorobenzene	120-82-1	1.1[2]	RSL[1]	10	10	6.0	2.8
2,4,6-Trichlorophenol	88-06-2	4.0[2]	RSL[1]	10	10	6.0	2.5
2,4,5-Trichlorophenol	95-95-4	1,200	RSL[1]	10	10	6.0	2.5

Notes:

1 EPA Residential Regional Screening Levels (RSLs), January 2015. http://www.epa.gov/region9/superfund/prg/index.html. In the event that groundwater is determined to be a current or potential source of drinking water, the screening levels will be updated accordingly.

2 The LOQ exceeds the screening goal. The laboratory detection limit is the lowest possible limit achievable following the EPA analytical method and will be used as the project screening goal. Data will be reported down to the DL; trace values detected between the DL and LOQ will be reported with a "J" qualifier. Any uncertainty associated with the analyte will be discussed in the risk assessment section of the Remedial Investigation report that will be prepared following field activities.

SAP Worksheet #15.1 – Reference Limits and Evaluation Table (Water) (Continued)

µg/L – micrograms per liter
CAS – Chemical Abstracts Service
DL – detection limits
EPA – U.S. Environmental Protection Agency
LOD – limit of detection
LOQ – limit of quantitation
QL – quantitation limit
RSL – EPA Regional Screening Level

SAP Worksheet #15.1 – Reference Limits and Evaluation Table (Water) (Continued)

Matrix: Water
Analytical Group: Metals by EPA 6020A/7470A (Mercury)

Analyte	CAS Number	Screening Criteria (µg/L)	Screening Criteria Reference	Project QL Goal (µg/L)	Laboratory-Specific Limits		
					LOQ (µg/L)	LOD (µg/L)	DL (µg/L)
Aluminum	7429-90-5	480	Ambient[1]	50	50	10	3.25
Antimony	7440-36-0	5.6	Ambient[1]	1.0	1.0	0.2	0.13
Arsenic	7440-38-2	78	Ambient[1]	1.0	1.0	0.5	0.39
Barium	7440-39-3	1,200	Ambient[1]	1.0	1.0	0.2	0.11
Beryllium	7440-41-7	1.6[2]	Ambient[1]	1.0	1.0	0.5	0.20
Cadmium	7440-43-9	16[2]	Ambient[1]	1.0	1.0	0.5	0.12
Chromium	7440-47-3	22	Ambient[1]	1.0	1.0	0.5	0.12
Cobalt	7440-48-4	100	Ambient[1]	1.0	1.0	0.2	0.13
Copper	7440-50-8	33	Ambient[1]	1.0	1.0	0.5	0.12
Lead	7439-92-1	10	Ambient[1]	1.0	1.0	0.2	0.14
Manganese	7439-96-5	5,400	Ambient[1]	1.0	1.0	0.5	0.13
Mercury	7439-97-6	0.22[2]	Ambient[1]	0.5	0.5	0.1	0.45
Molybdenum	7439-98-7	8.8	Ambient[1]	1.0	1.0	0.5	0.15
Nickel	7440-02-0	7.5	Ambient[1]	1.0	1.0	0.5	0.13
Selenium	7782-49-2	12	Ambient[1]	1.0	1.0	0.5	0.26
Silver	7440-22-4	15	Ambient[1]	1.0	1.0	0.2	0.14
Thallium	7440-28-0	2.0	RSL[3]	1.0	1.0	0.2	0.10
Vanadium	7440-62-2	140	Ambient[1]	1.0	1.0	0.5	0.14
Zinc	7440-66-6	260	Ambient[1]	5.0	5.0	1.0	0.79

Notes:

1 Ambient metals concentrations in groundwater at Mare Island as established in *Final Compilation of Technical Memorandum on Ambient Analyses of Metals in Soils and Groundwater, Mare Island, Vallejo, California (Tetra Tech, 2002)*. Where ambient concentrations are not established, value for EPA Regional Screening Levels used, January 2015. http://www.epa.gov/region9/superfund/prg/index.html.

SAP Worksheet #15.1 – Reference Limits and Evaluation Table (Water) (Continued)

2 The LOQ exceeds the screening goal. The laboratory detection limit is the lowest possible limit achievable following the EPA analytical method and will be used as the project screening goal. Data will be reported down to the DL; trace values detected between the DL and LOQ will be reported with a "J" qualifier. Any uncertainty associated with the analyte will be discussed in the risk assessment section of the Remedial Investigation report that will be prepared following field activities.

3 Screening level from EPA Residential Regional Screening Levels (RSLs), January 2015. http://www.epa.gov/region9/superfund/prg/index.html. In the event that groundwater is determined to be a current or potential source of drinking water, the screening levels will be updated accordingly.

mg/L – milligrams per liter
CAS – Chemical Abstracts Service
DL – detection limit
LOD – limit of detection
LOQ – limit of quantitation
QL – quantitation limit
RSL – EPA Regional Screening Level

SAP Worksheet #15.1 – Reference Limits and Evaluation Table (Water) (Continued)

Matrix: Water
Analytical Group: Polychlorinated biphenyls by EPA 8082

Analyte	CAS Number	Screening Criteria (µg/L)	Screening Criteria Reference	Project QL Goal (µg/L)	Laboratory-Specific Limits		
					LOQ (µg/L)	LOD (µg/L)	DL (µg/L)
Aroclor-1016	12674-11-2	1.1	RSL[1]	1.0	1.0	0.50	0.29
Aroclor-1221	11104-28-2	0.0046[2]	RSL[1]	1.0	1.0	0.50	0.28
Aroclor-1232	11141-16-5	0.0046[2]	RSL[1]	1.0	1.0	0.50	0.25
Aroclor-1242	53469-21-9	0.0039[2]	RSL[1]	1.0	1.0	0.50	0.18
Aroclor-1248	12672-29-6	0.0039[2]	RSL[1]	1.0	1.0	0.50	0.20
Aroclor-1254	11097-69-1	0.0039[2]	RSL[1]	1.0	1.0	0.50	0.23
Aroclor-1260	11096-82-5	0.0039[2]	RSL[1]	1.0	1.0	0.50	0.26

Notes:

1 EPA Residential Regional Screening Levels (RSLs), January 2015. http://www.epa.gov/region9/superfund/prg/index.html. In the event that groundwater is determined to be a current or potential source of drinking water, the screening levels will be updated accordingly.

2 The LOQ exceeds the screening goal. The laboratory detection limit is the lowest possible limit achievable following the EPA analytical method and will be used as the project screening goal. Data will be reported down to the D; trace values detected between the DL and LOQ will be reported with a "J" qualifier. Any uncertainty associated with the analyte will be discussed in the risk assessment section of the Remedial Investigation report that will be prepared following field activities.

µg/L – micrograms per liter
CAS – Chemical Abstracts Service
DL – detection limit
EPA – U.S. Environmental Protection Agency
LOD – limit of detection
LOQ – limit of quantitation
QL – quantitation limit
RSL – EPA Regional Screening Level

SAP Worksheet #15.1 – Reference Limits and Evaluation Table (Water) (Continued)

Matrix: Water
Analytical Group: Total Petroleum Hydrocarbons (TPH) by EPA 8015B Modified

Analyte	CAS Number	Screening Criteria (µg/L)		Screening Criteria Reference	Project QL Goal (µg/L)	Laboratory-specific Limits		
		Within 300 foot buffer zone[2]	Outside buffer zone			LOQ (µg/L)	LOD (µg/L)	DL (µg/L)
TPH-g	8006-61-9	443	5,000	Site-Specific Tier 2 Screening Levels[1]	200	200	100	44
TPH-d	68334-30-5	640	5,000		50	50	20	15
TPH-mo	NE	640	5,000		250	250	80	25

Notes:

1 Screening levels are site-specific Tier 2 screening levels established at the Investigation Area F1 (IA F1) of former Mare Island Naval Shipyard as described in the *Final Addendum to Technical Memorandum: Evaluation of Extent of Contamination Where Total Petroleum Hydrocarbon Sample Results Exceed Tier 2 Screening Levels at Investigation Area F1, Former Mare Island Naval Shipyard* (Tetra Tech, 2012).

2 Aquatic protection buffer zone value for shallow groundwater within 300 feet of Mare Island Strait/value for shallow groundwater inland of the 300 feet buffer zone.

µg/L – micrograms per liter
CAS – Chemical Abstracts Service
DL – detection limit
LOD – limit of detection
LOQ – limit of quantitation or reporting limit
NE – not established
QL – quantitation limit
TPH – total petroleum hydrocarbon
TPH-d – total petroleum hydrocarbons as diesel
TPH-g – total petroleum hydrocarbons as gasoline
TPH-mo – total petroleum hydrocarbons as motor oil

SAP Worksheet #15.1 – Reference Limits and Evaluation Table (Water) (Continued)

Matrix: Water
Analytical Group: Dioxins/Furans by EPA 8290A (Low Concentration)

Analyte	CAS Number	Screening Criteria (pg/L)	Screening Criteria Reference	Project QL Goal (pg/L)	Laboratory-Specific Limits		
					LOQ (pg/L)	LOD (pg/L)	DL (pg/L)
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	1746-01-6	0.6[2]	RSL[1]	20	20	4.0	1.457
Hexachlorodibenzo-p-dioxin, mixture	34465-46-8	11	RSL[1]	50[3]	50[3]	4.0	2.116

Notes:

1 EPA Residential Regional Screening Levels (RSLs), January 2015. http://www.epa.gov/region9/superfund/prg/index.html. In the event that groundwater is determined to be a current or potential source of drinking water, the screening levels will be updated accordingly.

2 The LOQ exceeds the screening goal. The laboratory detection limit is the lowest possible limit achievable following the EPA analytical method and will be used as the project screening goal. Data will be reported down to the DL; trace values detected between the DL and LOQ will be reported with a "J" qualifier. Any uncertainty associated with the analyte will be discussed in the risk assessment section of the Remedial Investigation report that will be prepared following field activities.

CAS – Chemical Abstracts Service
DL - detection limit
EPA – U.S. Environmental Protection Agency
LOQ – limit of quantitation
NE – not established
pg/L – picograms per liter
QL – quantitation limit
RSL – EPA Regional Screening Level

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil)

Matrix: Soil
Analytical Group: VOCs by EPA 5035/8260B

Analyte	CAS Number	Screening Criteria* (mg/kg)	Screening Criteria Reference	Project QL Goal (mg/kg)	Laboratory-Specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
1,1,1-Trichloroethane	71-55-6	260	ESV[2b]	0.005	0.005	0.0005	0.00023
1,1,2,2-Tetrachloroethane	79-34-5	0.127	ESV[2c]	0.02	0.02	0.0005	0.00035
1,1,2-Trichloroethane	79-00-5	0.4	ESV[2c]	0.005	0.005	0.0005	0.00035
1,1-Dichloroethane	75-34-3	3.6	RSL[1]	0.005	0.005	0.0005	0.00021
1,1-Dichloroethene	75-35-4	11	ESV[2b]	0.005	0.005	0.0005	0.00035
1,2,3-Trichlorobenzene	87-61-6	0.27	ESV[2b]	0.02	0.02	0.002	0.00091
1,2,3-Trichloropropane	96-18-4	0.0051	RSL[1]	0.005	0.005	0.002	0.00083
1,2,4-Trichlorobenzene	120-82-1	0.27	ESV[2b]	0.02	0.02	0.0005	0.00031
1,2,4-Trimethylbenzene	95-63-6	58	RSL[1]	0.01	0.01	0.002	0.00059
1,2-Dibromo-3-chloropropane	96-12-8	0.0053	RSL[1]	0.01	0.01	0.002	0.0017
1,2-Dibromoethane	106-93-4	0.036	RSL[1]	0.01	0.01	0.0005	0.00026
1,2-Dichlorobenzene	95-50-1	0.92	ESV[2b]	0.005	0.005	0.0005	0.00023
1,2-Dichloroethane	107-06-2	0.46	RSL[1]	0.005	0.005	0.0005	0.00031
1,2-Dichloropropane	78-87-5	0.002	ESV[2c]	0.005	0.005	0.0005	0.00044
1,3,5-Trimethylbenzene	108-67-8	780	RSL[1]	0.01	0.01	0.002	0.00055
1,3-Dichloropropane	142-28-9	0.002	ESV[2c]	0.005	0.005	0.0005	0.00025
1,4-Dichlorobenzene	106-46-7	0.88	ESV[2b]	0.005	0.005	0.0005	0.00022
2-Butanone	78-93-3	360	ESV[2b]	0.01	0.01	0.005	0.0038
2-Chlorotoluene	95-49-8	1600	RSL[1]	0.01	0.01	0.0005	0.00023
2-Hexanone	591-78-6	0.36	ESV[2b]	0.01	0.01	0.0020	0.0018

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Analyte	CAS Number	Screening Criteria* (mg/kg)	Screening Criteria Reference	Project QL Goal (mg/kg)	Laboratory-Specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
4-Chlorotoluene	106-43-4	1,600	RSL[1]	0.01	0.01	0.0005	0.00021
4-Methyl-2-pentanone	108-10-1	9.8	ESV[2b]	0.01	0.01	0.005	0.0043
Acetone	67-64-1	1.2	ESV[2b]	0.02	0.02	0.01	0.0062
Benzene	71-43-2	1.2	RSL[1]	0.0005	0.0005	0.0002	0.00013
Bromobenzene	108-86-1	290	RSL[1]	0.02	0.02	0.0005	0.00021
Bromochloromethane	74-97-5	150	RSL[1]	0.005	0.005	0.002	0.00069
Bromodichloromethane	75-27-4	0.29	RSL[1]	0.005	0.005	0.0005	0.00023
Bromoform	75-25-2	15.9	ESV[2c]	0.01	0.01	0.002	0.00079
Bromomethane	74-83-9	0.235	ESV[2c]	0.02	0.02	0.01	0.0094
Carbon Disulfide	75-15-0	0.82	ESV[2b]	0.005	0.005	0.0005	0.00031
Carbon Tetrachloride	56-23-5	0.4	ESV[2c]	0.005	0.005	0.0005	0.00028
Chlorobenzene	108-90-7	2.4	ESV[2b]	0.005	0.005	0.0005	0.00022
Chloroethane	75-00-3	14,000	RSL[1]	0.01	0.01	0.002	0.0015
Chloroform	67-66-3	0.32	RSL[1]	0.005	0.005	0.002	0.00024
Chloromethane	74-87-3	110	RSL[1]	0.01	0.01	0.005	0.0003
cis-1,2-Dichloroethene	156-59-2	23	ESV[2b]	0.005	0.005	0.0005	0.00028
cis-1,3-Dichloropropene	542-75-6	1.8	RSL[1]	0.005	0.005	0.0005	0.00025
Dibromochloromethane	124-48-1	0.73	RSL[1]	0.01	0.01	0.002	0.00057
Dibromomethane	74-95-3	6.5	ESV[2c]	0.005	0.005	0.002	0.00077
Dichlorodifluoromethane	75-71-8	39.5	ESV[2c]	0.01	0.01	0.0005	0.00044
Ethylbenzene	100-41-4	5.8	RSL[1]	0.01	0.01	0.0002	0.00015
Hexachloro-1,3-Butadiene	87-68-3	0.0398	ESV[2c]	0.02	0.02	0.0005	0.00032
Isopropylbenzene	98-82-8	1,900	RSL[1]	0.01	0.01	0.0005	0.00055
m,p-Xylenes	1330-20-7	1.4	ESV[2b]	0.02	0.02	0.0004	0.00027
Methylene Chloride	75-09-2	2.6	ESV[2b]	0.005	0.005	0.002	0.0013

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Analyte	CAS Number	Screening Criteria* (mg/kg)	Screening Criteria Reference	Project QL Goal (mg/kg)	Laboratory-Specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
Methyl-tert-butyl-ether	1634-04-4	47	RSL[1]	0.005	0.005	0.0005	0.0003
Naphthalene	91-20-3	3.8	RSL[1]	0.02	0.02	0.002	0.00081
n-Butylbenzene	104-51-8	3900	RSL[1]	0.02	0.02	0.0002	0.00016
n-Propylbenzene	103-65-1	3,300	RSL[1]	0.01	0.01	0.002	0.0005
o-Xylene	95-47-6	1.4	ESV[2b]	0.01	0.01	0.002	0.00056
Styrene	100-42-5	1.2	ESV[2b]	0.02	0.02	0.002	0.0006
Tetrachloroethene	127-18-4	0.1	ESV[2b]	0.005	0.005	0.0005	0.00021
Toluene	108-88-3	23	ESV[2b]	0.005	0.005	0.002	0.00052
Trans-1,2-Dichloroethene	156-60-5	23	ESV[2b]	0.005	0.005	0.002	0.00051
Trans-1,3-Dichloropropene	542-75-6	1.8	RSL[1]	0.005	0.005	0.002	0.00061
Trichloroethene	79-01-6	0.94	RSL[1]	0.005	0.005	0.0005	0.0003
Trichlorofluoromethane	75-69-4	52	ESV[2b]	0.005	0.005	0.0005	0.00038
Vinyl Chloride	75-01-4	0.059	RSL[1]	0.01	0.01	0.002	0.0005

Notes:

*Value selected based on the most conservative of either human health or ecological risk screening criteria.

1 EPA Residential Regional Screening Levels (RSLs), January 2015. http://www.epa.gov/region9/superfund/prg/index.html.

2 ESV = Ecological screening value taken from one of the following sources:

(a) EPA, 2007, Ecological Soil Screening Level (Eco-SSL) guidance. On-line at: http://www.epa.gov/ecotox/ecossl/index.html, accessed 05/21/16.

(b) Los Alamos National Laboratory (LANL), 2014, ECORISK Database (Release 3.2), Environmental Restoration Project, Los Alamos National Laboratory, Los Alamos, NM, October.

(c) Oak Ridge National Laboratory (ORNL), Risk Assessment Information System (RAIS). On-Line at: http://rais.ornl.gov, accessed 05/26/16

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

CAS – Chemical Abstracts Service
DL – detection limit
EPA – U.S. Environmental Protection Agency
LOD – limit of detection
LOQ – limit of quantitation
mg/kg – milligrams per kilogram
QL – quantitation limit
RSL – EPA Regional Screening Level
VOC – volatile organic compound

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Matrix: Soil
Analytical Group: Semivolatile Organic Compounds by EPA 8270C

Analyte	CAS Number	Screening Criteria* (mg/kg)	Screening Criteria Reference	Project QL (mg/kg)	Laboratory-specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
1,2,4-Trichlorobenzene	120-82-1	0.27[3]	ESV[2b]	5.0	5.0	0.30	0.11
1,2-Dichlorobenzene	95-50-1	0.92[3]	ESV[2b]	2.0	2.0	0.30	0.12
1,4-Dichlorobenzene	106-46-7	0.88	ESV[2b]	0.50	0.50	0.30	0.14
2-Methylnaphthalene	91-57-6	16	ESV[2b]	2.0	2.0	0.30	0.095
2,4,5-Trichlorophenol	95-95-4	0.01[3]	ESV[2c]	0.50	0.50	0.30	0.15
2,4,6-Trichlorophenol	88-06-2	0.01[3]	ESV[2c]	0.50	0.50	0.30	0.16
2,4-Dichlorophenol	120-83-2	0.01[3]	ESV[2c]	0.50	0.50	0.30	0.14
2,4-Dimethylphenol	105-67-9	0.01[3]	ESV[2c]	2.0	2.0	0.30	0.12
2,4-Dinitrophenol	51-28-5	0.0609[3]	ESV[2c]	2.00	2.00	0.80	0.72
2,4-Dinitrotoluene	121-14-2	1.7	RSL[1]	0.50	0.50	0.30	0.15
2,6-Dinitrotoluene	606-20-2	0.36[3]	RSL[1]	2.0	2.0	0.30	0.17
2-Chloronaphthalene	91-58-7	0.0122[3]	ESV[2c]	2.0	2.0	0.30	0.097
2-Chlorophenol	95-57-8	0.39[3]	ESV[2b]	0.50	0.50	0.30	0.14
2-Methyl-4,6-dinitrophenol	534-52-1	4.9[3]	RSL[1]	5.0	5.0	2.0	1.6
2-Methylphenol	95-48-7	0.67	ESV[2b]	0.50	0.50	0.30	0.14
2-Nitroaniline	88-74-4	5.4	ESV[2b]	0.50	0.50	0.30	0.16
3,3'-Dichlorobenzidine	91-94-1	0.646[3]	ESV[2c]	5.0	5.0	2.0	1.1
4-Chloro-3-methylphenol	59-50-7	7.95	ESV[2c]	0.50	0.50	0.30	0.15
4-Chloroaniline	106-47-8	1.0[3]	ESV[2b]	2.0	2.0	0.30	0.12
3/4-Methylphenol	65794-96-9	3,100 / 6,200	RSL[1]	1.0	1.0	0.60	0.24
4-Nitroaniline	100-01-6	5.4	ESV[2b]	0.50	0.50	0.30	0.14
Acenaphthene	83-32-9	29	ESV[2a]	2.0	2.0	0.30	0.099

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Analyte	CAS Number	Screening Criteria* (mg/kg)	Screening Criteria Reference	Project QL (mg/kg)	Laboratory-specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
Anthracene	120-12-7	29	ESV[2a]	2.0	2.0	0.30	0.11
Benzo(a)anthracene	56-55-3	0.15[3]	RSL[1]	0.50	0.50	0.30	0.19
Benzo(a)pyrene	50-32-8	0.40[3]	RSL[1,4]	0.50[2]	0.50[2]	0.30	0.085
Benzo(b)fluoranthene	205-99-2	0.15[3]	RSL[1]	0.50	0.50	0.30	0.084
Benzoic acid	65-85-0	1.0[3]	ESV[2b]	5.0	5.0	0.80	0.78
Benzo(k)fluoranthene	207-08-9	1.1[3]	ESV[2a]	2.0	2.0	0.30	0.11
Benzyl alcohol	100-51-6	120	ESV[2b]	0.50	0.50	0.30	0.15
Bis(2- chloroethoxy)methane	111-91-1	0.302[3]	ESV[2c]	0.50	0.50	0.30	0.12
Bis(2-chloroethyl)ether	111-44-4	0.23[3]	RSL[1]	0.50	0.50	0.30	0.11
Bis(2-chloroisopropyl)ether	39638-32-9 (108-60-1)	4.9	RSL[1]	0.50	0.50	0.30	0.12
Bis(2-ethylhexyl)phthalate	117-81-7	0.02[3]	ESV[2b]	0.50	0.50	0.30	0.096
Butyl Benzyl Phthalate	85-68-7	90	ESV[2b]	0.50	0.50	0.30	0.10
Chrysene	218-01-9	1.1[3]	ESV[2a]	2.0	2.0	0.30	0.094
Dibenz(a,h)anthracene	53-70-3	0.015[3]	RSL[1]	0.50	0.50	0.30	0.090
Diethyl Phthalate	84-66-2	100	ESV[2b]	0.50	0.50	0.30	0.016
Di-n-butyl Phthalate	84-74-2	0.011[3]	ESV[2b]	0.50	0.50	0.30	0.096
Fluoranthene	206-44-0	29	ESV[2a]	2.0	2.0	0.30	0.11
Fluorene	86-73-7	29	ESV[2a]	2.0	2.0	0.30	0.11
Hexachlorobenzene	118-74-1	0.079[3]	ESV[2b]	0.50	0.50	0.30	0.10
Hexachloro-1,3-butadiene	87-68-3	0.0398[3]	ESV[2c]	0.50	0.50	0.30	0.10
Hexachlorocyclopentadiene	77-47-4	0.755[3]	ESV[2c]	5.0	5.0	2.0	0.83
Hexachloroethane	67-72-1	0.596	ESV[2c]	0.50	0.50	0.30	0.11
Indeno(1,2,3-cd)pyrene	193-39-5	0.15[3]	RSL[1]	0.50	0.50	0.30	0.099
Isophorone	78-59-1	139	ESV[2c]	0.50	0.50	0.30	0.12
Naphthalene	91-20-3	3.8[3]	RSL[1]	5.0	5.0	0.30	0.13

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Analyte	CAS Number	Screening Criteria* (mg/kg)	Screening Criteria Reference	Project QL (mg/kg)	Laboratory-specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
Nitrobenzene	98-95-3	2.2	ESV[2b]	2.0	2.0	0.80	0.76
N-Nitroso-di-n-propylamine	621-64-7	0.076[3]	RSL[1]	0.50[2]	0.50	0.30	0.12
N-Nitrosodiphenylamine	86-30-6	0.545	ESV[2c]	0.50	0.50	0.30	0.12
Pentachlorophenol	87-86-5	0.99[3]	RSL[1]	5.0	5.0	2.0	1.3
Phenol	108-95-2	0.79[3]	ESV[2b]	2.0	2.0	0.30	0.14
Pyrene	129-00-0	1.1	ESV[2a]	0.50	0.50	0.30	0.10

Notes:

*Value selected based on the most conservative of either human health or ecological risk screening criteria.

1 EPA Residential Regional Screening Levels (RSLs), January 2015. http://www.epa.gov/region9/superfund/prg/index.html.

2 ESV = Ecological screening value taken from one of the following sources:

(a) EPA, 2007, Ecological Soil Screening Level (Eco-SSL) guidance. On-line at: http://www.epa.gov/ecotox/ecossl/index.html, accessed 05/21/16.

(b) Los Alamos National Laboratory (LANL), 2014, ECORISK Database (Release 3.2), Environmental Restoration Project, Los Alamos National Laboratory, Los Alamos, NM, October.

(c) Oak Ridge National Laboratory (ORNL), Risk Assessment Information System (RAIS). On-Line at: http://rais.ornl.gov, accessed 05/26/16

3 The LOQ exceeds the screening goal. The laboratory detection limit is the lowest possible limit achievable following the EPA analytical method and will be used as the project screening goal. Data will be reported down to the DL; trace values detected between the DL and LOQ will be reported with a "J" qualifier. Any uncertainty associated with the analyte will be discussed in the risk assessment section of the Remedial Investigation report that will be prepared following field activities.

4 Value represents 95% UCL mean background equivalent concentration of benzo(a)pyrene for Northern California soils as taken from Table 2 of the State of California Department of Toxic Substances Control (DTSC) document *Use of the Northern and Southern California Polynuclear Aromatic Hydrocarbon (PAH) Studies in the Manufactured Gas Plant Site Clean Up Process, July 1, 2009* (DTSC, 2009)

CAS – Chemical Abstracts Service
DL – detection limit
DTSC – California Department of Toxic Substances Control
EPA – U.S. Environmental Protection Agency
LOD – limit of detection
LOQ – limit of quantitation
mg/kg – milligrams per kilogram
QL – quantitation limit
RSL – EPA Regional Screening Level

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Matrix: Soil
Analytical Group: Metals by EPA 6020A / (Mercury) 7471A

Analyte	CAS Number	Screening Criteria* (mg/kg)	Screening Criteria Reference	Project QL Goal (mg/kg)	Laboratory-Specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
Aluminum	7429-90-5	35,000	Ambient[1]	25	25	10	3.25
Antimony	7440-36-0	8.5	Ambient[1]	0.5	0.5	0.2	0.13
Arsenic	7440-38-2	36	Ambient[1]	1	1	0.5	0.389
Barium	7440-39-3	330	ESV[2a]	0.5	0.5	0.2	0.112
Beryllium	7440-41-7	0.9[4]	Ambient[1]	1	1	0.5	0.205
Cadmium	7440-43-9	5.2	Ambient[1]	0.5	0.5	0.2	0.12
Chromium	7440-47-3	140	Ambient[1]	0.5	0.5	0.2	0.117
Cobalt	7440-48-4	13	ESV[2a]	0.5	0.5	0.2	0.127
Copper	7440-50-8	120	Ambient[1]	0.5	0.5	0.2	0.116
Lead	7439-92-1	139	Site-Specific Criterion[3]	0.5	0.5	0.2	0.137
Manganese	7439-96-5	1,600	Ambient[1]	0.5	0.5	0.2	0.131
Mercury	7439-97-6	2	Ambient[1]	0.5	0.5	0.2	0.146
Molybdenum	7439-98-7	17	ESV[2b]	0.5	0.5	0.2	0.146
Nickel	7440-02-0	130	Ambient[1]	0.5	0.5	0.2	0.128
Selenium	7782-49-2	0.52	ESV[2a]	0.5	0.5	0.2	0.264
Silver	7440-22-4	4.2	ESV[2a]	0.5	0.5	0.2	0.142
Thallium	7440-28-0	0.05[4]	ESV[2b]	0.5	0.5	0.2	0.105
Vanadium	7440-62-2	190	Ambient[1]	0.5	0.5	0.2	0.142
Zinc	7440-66-6	230	Ambient[1]	5	5	1	0.793

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Notes:

*Value selected based on the most conservative of either human health or ecological risk screening criteria.

[1]Ambient metals concentrations in groundwater at Mare Island as established in *Final Compilation of Technical Memorandum on Ambient Analyses of Metals in Soils and Groundwater, Mare Island, Vallejo, California (Tetra Tech, 2002)*.

2 ESV = Ecological screening value taken from one of the following sources:

(a) EPA, 2007, Ecological Soil Screening Level (Eco-SSL) guidance. On-line at: http://www.epa.gov/ecotox/ecossl/index.html, accessed 05/21/16.

(b) Los Alamos National Laboratory (LANL), 2014, ECORISK Database (Release 3.2), Environmental Restoration Project, Los Alamos National Laboratory, Los Alamos, NM, October.

(c) Oak Ridge National Laboratory (ORNL), Risk Assessment Information System (RAIS). On-Line at: http://rais.ornl.gov, accessed 05/26/16

3 The lead screening value is equal to the sum of DTSC CHHSL + background values. The CHHSL model provides levels (80 mg/kg for residential and 320 mg/kg for industrial) that are based on the amount of lead in the soil that would lead to an incremental increase in blood lead levels of up to 1 µg/dL. The 95th upper confidence limit (UCL) on the mean of the background dataset for lead in Mare Island ambient fill soil is 59 mg/kg (Tetra Tech, 2002) The Navy has agreed not to increase the blood lead levels to more than background + 1 µg/dL. Therefore, the residential screening value for lead at the IA F1 is 59 + 80 mg/kg = 139 mg/kg.

4 The LOQ exceeds the screening goal. The laboratory detection limit is the lowest possible limit achievable following the EPA analytical method and will be used as the project screening goal. Data will be reported down to the DL; trace values detected between the DL and LOQ will be reported with a "J" qualifier. Any uncertainty associated with the analyte will be discussed in the risk assessment section of the Remedial Investigation report that will be prepared following field activities.

CAS – Chemical Abstracts Service
CHHSL – California Human Health Screening Level
dL - deciliter
DL – detection limit
DTSC – California Department of Toxic Substances Control
EPA – U.S. Environmental Protection Agency
LOD – limit of detection
LOQ – limit of quantitation
mg/kg – milligrams per kilogram
QL – quantitation limit
RSL – EPA Regional Screening Level

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Matrix: Soil
Analytical Group: Total Petroleum Hydrocarbons (TPH) by EPA 8015B Modified

Analyte	CAS Number	Screening Criteria (mg/kg)	Screening Criteria Reference[1]	Project QL Goal (mg/kg)	Laboratory-specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
TPH-g	8006-61-9	500	*Site-Specific Tier 2 Environmental Screening Levels*	0.10	0.10	0.050	0.025
TPH-d	68334-30-5	500		5.0	5.0	2.0	1.6
TPH-mo	NE	2,500		25	25	20	5.9

Notes:

[1] Screening levels are site-specific Tier 2 screening levels established at the Investigation Area F1 (IA F1) of former Mare Island Naval Shipyard as described in the *Final Addendum to Technical Memorandum: Evaluation of Extent of Contamination Where Total Petroleum Hydrocarbon Sample Results Exceed Tier 2 Screening Levels at Investigation Area F1, Former Mare Island Naval Shipyard* (Tetra Tech, 2012).

CAS – Chemical Abstracts Service
DL – detection limit
EPA – U.S. Environmental Protection Agency
LOD – limit of detection
LOQ – limit of quantitation
mg/kg – milligrams per liter
NE – not established
QL – quantitation limit
TPH-d – total petroleum hydrocarbons as diesel
TPH-g – total petroleum hydrocarbons as gasoline
TPH-mo – total petroleum hydrocarbons as motor oil

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Matrix: Soil
Analytical Group: Polychlorinated biphenyls by EPA 8082

Analyte	CAS Number	Screening Criteria* (mg/kg)	Screening Criteria Reference	Project QL Goal (mg/kg)	Laboratory-Specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
Aroclor-1016	12674-11-2	1.0	ESV[2b]	0.05	0.05	0.025	0.014
Aroclor-1221	11104-28-2	0.15	RSL[1]	0.05	0.05	0.025	0.013
Aroclor-1232	11141-16-5	0.15	RSL[1]	0.05	0.05	0.025	0.011
Aroclor-1242	53469-21-9	0.041	ESV[2b]	0.05	0.05	0.025	0.012
Aroclor-1248	12672-29-6	0.0072[3]	ESV[2b]	0.05	0.05	0.025	0.014
Aroclor-1254	11097-69-1	0.041[3]	ESV[2b]	0.05	0.05	0.025	0.012
Aroclor-1260	11096-82-5	0.24	RSL[1]	0.05	0.05	0.025	0.011

Notes:

*Value selected based on the most conservative of either human health or ecological risk screening criteria.

1 EPA Residential Regional Screening Levels (RSLs), January 2015, available at http://www.epa.gov/region9/superfund/prg/rsl-table.html.

2 ESV = Ecological screening value taken from one of the following sources:

(a) EPA, 2007, Ecological Soil Screening Level (Eco-SSL) guidance. On-line at: http://www.epa.gov/ecotox/ecossl/index.html, accessed 05/21/16.

(b) Los Alamos National Laboratory (LANL), 2014, ECORISK Database (Release 3.2), Environmental Restoration Project, Los Alamos National Laboratory, Los Alamos, NM, October.

(c) Oak Ridge National Laboratory (ORNL), Risk Assessment Information System (RAIS). On-Line at: http://rais.ornl.gov, accessed 05/26/16

3 The LOQ exceeds the screening goal. The laboratory detection limit is the lowest possible limit achievable following the EPA analytical method and will be used as the project screening goal. Data will be reported down to the DL; trace values detected between the DL and LOQ will be reported with a “J” qualifier. Any uncertainty associated with the analyte will be discussed in the risk assessment section of the Remedial Investigation report that will be prepared following field activities.

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

mg/kg – milligrams per kilogram
CAS – Chemical Abstracts Service
DL – detection limit
EPA – U.S. Environmental Protection Agency
LOD – limit of detection
LOQ – limit of quantitation
QL – quantitation limit

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Matrix: Soil
Analytical Group: Dioxins/Furans by EPA 8290A, Low Concentration

Analyte	CAS Number	Screening Criteria* (pg/g)	Screening Criteria Reference	Project QL Goal (pg/g)	Laboratory-Specific Limits		
					LOQ (pg/g)	LOD (pg/g)	DL (pg/g)
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6	0.29[3]	ESV[2b]	2.0	2.0	0.2	0.074
Total Hexachlorodibenzo-p-dioxin	N/A	100	RSL[1]	5.0	5.0	0.2	0.131

Notes:

*Value selected based on the most conservative of either human health or ecological risk screening criteria.

[1] EPA Residential Regional Screening Levels (RSLs), January 2015, available at http://www.epa.gov/region9/superfund/prg/rsl-table.html.

2 ESV = Ecological screening value taken from one of the following sources:

(a) EPA, 2007, Ecological Soil Screening Level (Eco-SSL) guidance. On-line at: http://www.epa.gov/ecotox/ecossl/index.html, accessed 05/21/16.

(b) Los Alamos National Laboratory (LANL), 2014, ECORISK Database (Release 3.2), Environmental Restoration Project, Los Alamos National Laboratory, Los Alamos, NM, October.

(c) Oak Ridge National Laboratory (ORNL), Risk Assessment Information System (RAIS). On-Line at: http://rais.ornl.gov, accessed 05/26/16

3 The LOQ exceeds the screening goal. The laboratory detection limit is the lowest possible limit achievable following the EPA analytical method and will be used as the project screening goal. Data will be reported down to the DL; trace values detected between the DL and LOQ will be reported with a "J" qualifier. Any uncertainty associated with the analyte will be discussed in the risk assessment section of the Remedial Investigation report that will be prepared following field activities.

CAS – Chemical Abstracts Service
DL – detection limit
EPA – U.S. Environmental Protection Agency
LOD – limit of detection
LOQ – limit of quantitation
N/A – not applicable
pg/g – picograms per gram
QL – quantitation limit

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Matrix: Soil
Analytical Group: Organochlorine Pesticides by EPA 8081A

Analyte	CAS Number	Screening Criteria* (mg/kg)	Screening Criteria Reference	Project QL Goal (mg/kg)	Laboratory-Specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
4,4'-DDD	72-54-8	0.21	ESV[2a]	0.005	0.005	0.002	0.0016
4,4'-DDE	72-55-9	0.21	ESV[2a]	0.005	0.005	0.002	0.0015
4,4'-DDT	50-29-3	0.21	ESV[2a]	0.005	0.005	0.002	0.0017
Aldrin	309-00-2	0.031	RSL[1]	0.005	0.005	0.002	0.0016
Alpha Chlordane	5103-71-9	0.085	RSL[1]	0.005	0.005	0.002	0.0016
Alpha-BHC	319-84-6	0.085	RSL[1]	0.005	0.005	0.002	0.0016
Beta-BHC	319-85-7	0.27	ESV[2b]	0.005	0.005	0.002	0.0013
Chlordane	57-74-9	0.27	ESV[2b]	0.050	0.050	0.025	0.016
Delta-BHC	319-86-8	0.0094	ESV[2b]	0.005	0.005	0.002	0.0013
Dieldrin	60-57-1	0.0049[3]	ESV[2a]	0.005	0.005	0.002	0.0016
Endosulfan I	959-98-8	0.64	ESV[2b]	0.005	0.005	0.002	0.0013
Endosulfan II	33213-65-9	0.64	ESV[2b]	0.005	0.005	0.002	0.0014
Endosulfan Sulfate	1031-07-8	0.64	ESV[2b]	0.005	0.005	0.002	0.0017
Endrin	72-20-8	0.0014[3]	ESV[2b]	0.005	0.005	0.002	0.0018
Endrin Aldehyde	7421-93-4	0.0014[3]	ESV[2b]	0.005	0.005	0.002	0.0012
Endrin Ketone	53494-70-5	0.0014[3]	ESV[2b]	0.005	0.005	0.002	0.0017
Gamma Chlordane	5103-74-2	0.56	RSL[1]	0.005	0.005	0.002	0.0016

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Analyte	CAS Number	Screening Criteria* (mg/kg)	Screening Criteria Reference	Project QL Goal (mg/kg)	Laboratory-Specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
Gamma-BHC	58-89-9	0.0094	ESV[2b]	0.005	0.005	0.002	0.0017
Heptachlor	76-44-8	0.059	ESV[2b]	0.005	0.005	0.002	0.0016
Heptachlor Epoxide	1024-57-3	0.059	RSL[1]	0.005	0.005	0.002	0.0018
Hexachlorobenzene	118-74-1	0.079	ESV[2b]	0.005	0.005	0.002	0.0016
Methoxychlor	72-43-5	5	ESV[2b]	0.005	0.005	0.002	0.0016
Toxaphene	8001-35-2	0.48	RSL[1]	0.100	0.100	0.050	0.032

Notes:

*Value selected based on the most conservative of either human health or ecological risk screening criteria.

[1] EPA Residential Regional Screening Levels (RSLs),January 2015, available at http://www.epa.gov/region9/superfund/prg/rsl-table.html.

2 ESV = Ecological screening value taken from one of the following sources:

(a) EPA, 2007, Ecological Soil Screening Level (Eco-SSL) guidance. On-line at: http://www.epa.gov/ecotox/ecossl/index.html, accessed 05/21/16.

(b) Los Alamos National Laboratory (LANL), 2014, ECORISK Database (Release 3.2), Environmental Restoration Project, Los Alamos National Laboratory, Los Alamos, NM, October.

(c) Oak Ridge National Laboratory (ORNL), Risk Assessment Information System (RAIS). On-Line at: http://rais.ornl.gov, accessed 05/26/16

3 The LOQ exceeds the screening goal. The laboratory detection limit is the lowest possible limit achievable following the EPA analytical method and will be used as the project screening goal. Data will be reported down to the DL; trace values detected between the DL and LOQ will be reported with a "J" qualifier. Any uncertainty associated with the analyte will be discussed in the risk assessment section of the Remedial Investigation report that will be prepared following field activities.

CAS – Chemical Abstracts Service
DL – detection limit
LOD – limit of detection
LOQ – limit of quantitation
mg/kg – milligrams per kilogram
NE – not established
QL – quantitation limit
RSL – EPA Regional Screening Level

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Matrix: Soil
Analytical Group: Chlorinated Herbicides by EPA 8151A

Analyte	CAS Number	Screening Criteria* (mg/kg)	Screening Criteria Reference	Project QL Goal (mg/kg)	Laboratory-Specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
2,4,5-T	93-76-5	0.596	ESV[2c]	0.010	0.010	0.0025	0.0011
2,4,5-TP (Silvex)	93-72-1	0.109	ESV[2c]	0.010	0.010	0.0025	0.0023
2,4-D	94-75-7	0.0272[3]	ESV[2c]	0.100	0.100	0.025	0.014
2,4-DB	94-82-6	490	RSL[1]	0.100	0.100	0.025	0.016
Dalapon	75-99-0	1,800	RSL[1]	0.250	0.250	0.120	0.073
Dicamba	1918-00-9	1,800	RSL[1]	0.010	0.010	0.0025	0.0012
Dichlorprop	120-36-5	NE	NE	0.100	0.100	0.025	0.017
Dinoseb	88-85-7	0.0218[3]	ESV[2c]	0.050	0.050	0.012	0.0051
MCPA	94-74-6	0.00005[3]	ESV[2c]	10.0	10.0	2.5	2.1
MCPP	93-65-2	62.0	RSL[1]	10.0	10.0	5.0	3.2

Notes:

*Value selected based on the most conservative of either human health or ecological risk screening criteria.

[1] EPA Residential Regional Screening Levels (RSLs), January 2015, available at http://www.epa.gov/region9/superfund/prg/rsl-table.html.

2 ESV = Ecological screening value taken from one of the following sources:

(a) EPA, 2007, Ecological Soil Screening Level (Eco-SSL) guidance. On-line at: http://www.epa.gov/ecotox/ecossl/index.html, accessed 05/21/16.

(b) Los Alamos National Laboratory (LANL), 2014, ECORISK Database (Release 3.2), Environmental Restoration Project, Los Alamos National Laboratory, Los Alamos, NM, October.

(c) Oak Ridge National Laboratory (ORNL), Risk Assessment Information System (RAIS). On-Line at: http://rais.ornl.gov, accessed 05/26/16

3 The LOQ exceeds the screening goal. The laboratory detection limit is the lowest possible limit achievable following the EPA analytical method and will be used as the project screening goal. Data will be reported down to the DL; trace values detected between the DL and LOQ will be reported with a "J" qualifier. Any uncertainty associated with the analyte will be discussed in the risk assessment section of the Remedial Investigation report that will be prepared following field activities.

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

CAS – Chemical Abstracts Service
DL – detection limit
LOD – limit of detection
LOQ – limit of quantitation
mg/kg – milligrams per kilogram
NE – not established
QL – quantitation limit
RSL – EPA Regional Screening Level

SAP Worksheet #15.2 – Reference Limits and Evaluation Table (Soil) (Continued)

Matrix: Soil
Analytical Group: Organotins by GC/MS Select Ion Monitoring (Krone et al, 1989)

Analyte	CAS Number	Screening Criteria* (mg/kg)	Screening Criteria Reference	Project QL Goal (mg/kg)	Laboratory-Specific Limits		
					LOQ (mg/kg)	LOD (mg/kg)	DL (mg/kg)
Dibutyltin	1191-48-6	18.0	RSL[1]	0.003	0.003	0.00073	N/A
Monobutyltin	1118-46-3	NE	NE	0.003	0.003	0.0014	N/A
Tributyltin	1461-22-9	18.0	RSL[1]	0.003	0.003	0.0015	N/A

Notes:

*Value selected based on the most conservative of either human health or ecological risk screening criteria.

[1] EPA Residential Regional Screening Levels (RSLs), January 2015, available at http://www.epa.gov/region9/superfund/prg/rsl-table.html.

CAS – Chemical Abstracts Service
DL – detection limit
EPA – U.S. Environmental Protection Agency
GC/MS – gas chromatogram/mass spectrometer
LOD – limit of detection
LOQ – limit of quantitation
mg/kg – milligrams per kilogram
N/A – not applicable
NE – not established
QL – quantitation limit
RSL – EPA Regional Screening Level

SAP Worksheet #16 – Project Schedule / Timeline Table

Activities	Organization	Dates		Deliverable
		Anticipated Date(s) of Initiation	Anticipated Date of Completion	
Preparation of Internal Draft SAP	NOREAS	9/25/2012	11/16/2012	Internal Draft SAP
DON Review	NAVFAC SW	11/19/2012	12/31/2012	NAVFAC Comments
Preparation of Draft SAP	NOREAS	1/1/2014	3/27/2014	Draft SAP
Agency Review	EPA, DTSC, Water Board	3/28/2014	5/30/2014	Agency Comments
Draft SAP RTCs	NOREAS	6/2/2014	6/16/2014	NOREAS RTCs
Agency Approval of RTCs	EPA, DTSC, Water Board	6/17/2014	7/16/2014	Agency Comments
Internal Draft Final SAP Revisions	NOREAS	7/17/2014	8/4/2014	Internal Draft Final SAP
DON Review	NAVFACSW	8/4/2014	9/5/2014	NAVFAC SW Comments
Agency Review	EPA, DTSC, Water Board	3/15/2015	05/08/2015	Agency Comments
Draft Final SAP RTCs	NOREAS	05/09/2014	06/26/2015	NOREAS RTCs
Final SAP	NOREAS	06/26/2015	07/08/2015	Final SAP

Notes:

DON – U.S. Department of the Navy
DTSC – Department of Toxic Substances Control
EPA – U.S. Environmental Protection Agency
NAVFAC SW – Naval Facilities Command, Southwest
NOREAS – NOREAS, Inc.
RTC – response to comment
SAP – Sampling and Analysis Plan
Water Board – Regional Water Quality Control Board

SAP Worksheet #17 – Sampling Design and Rationale

NOREAS will conduct an RI to assess the nature and horizontal and vertical extent of potential contaminants at the SSA. Results of the previous site assessments, investigations, and removal actions (see Work Plan Section 2.0) were reviewed and evaluated to determine the overall approach for this RI. In addition to the evaluation of previous investigation results, the Installation Restoration Program (CERCLA), Munitions Response Program, UST, and Toxic Substances Control Act environmental programs were considered during the development of the investigative approach.

As a result, a total of 52 soil borings and nine groundwater monitoring wells are proposed for this RI. The locations of the proposed soil borings and groundwater wells are illustrated on Figures 3 through 9. Detailed descriptions of the soil and groundwater investigation approaches, including the proposed sample types, locations (depth), and analytical parameters are provided in the Work Plan Section 4.0 and in WS #18 and are briefly summarized below. In addition, detailed procedures for soil and groundwater sampling are provided in WS #14.

In the event that additional samples or sampling locations are required to evaluate the extent of a particular impact, based on field observations at the time of the investigation, additional soil borings and/or groundwater monitoring wells may be completed under this RI Work Plan/SAP at the discretion of the NOREAS field geologist and upon approval of the BRAC RPM.

Soil Sampling

The soil sampling elements of the RI will focus on assessing the potential presence of chemical and/or MC contaminants in vadose zone soils based on information regarding past uses/activities at a given location and/or the results of previous investigations. In general, historical use information and/or historical sample data were evaluated from the following types of site features:

- Building Areas
- SWMUs
- Historic MEC Sites
- Oven/Primer Pit Areas
- Other areas of interest (drums and tanks uncovered during MEC NTCRA)

Based on the information reviewed, a number of site features at the SSA were selected for soil sampling as part of this RI. A list of the specific sites that were evaluated for investigation, including a summary of the historical use and sampling data, is provided in Table 4-1 of the Work Plan. The locations of the proposed RI soil boring and sampling locations for the buildings are illustrated on Figures 3 through 9.

SAP Worksheet #17 – Sampling Design and Rationale (Continued)

Groundwater Sampling

The main objectives of the groundwater investigation will be to (1) investigate hydrogeologic conditions, (2) determine the nature and extent of potential chemical and explosives contaminants in groundwater, and (3) to evaluate the general quality of the groundwater at the SSA with respect potential beneficial use. To achieve these objectives, a total of nine 2-inch diameter groundwater monitoring wells is proposed for this RI. The proposed locations of groundwater monitoring wells are depicted on Figure 3 and Figure 9. Upon completion, the newly installed groundwater monitoring wells will be developed using standard well development procedures.

Currently, no groundwater monitoring wells are located in the SSA. As part of the evaluation of contaminant impacts to groundwater and their potential risks to human health and the environment, general hydrogeologic conditions such as hydraulic gradient and flow patterns beneath the site will be evaluated. The locations of the proposed groundwater monitoring wells were selected primarily to provide information with respect to the hydrogeologic conditions at the SSA.

Following their installation and development, groundwater elevation data collected will be collected from the proposed wells to determine the water table elevations, hydraulic gradient, and predominant flow directions. Given the proximity to Carquinez Strait and San Pablo Bay, groundwater elevations at the SSA are expected to fluctuate in response to tidal influences. Care will be taken to collect water levels in all nine wells within the shortest amount of time as possible. However, a formal tidal study is not planned at this time.

SAP Worksheet #18 – Sampling Locations and Methods/SOP Requirements Table

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]	Number of Samples	Sampling SOP Reference
BUILDINGS							
Former Bldg. A193 (Former Mine Anchor Facility Annex)	None	SSARI-B193B01-0.5	0.5[c]	Soil	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals	1	WS #14
		SSARI-B193B01-5	5.0			1	WS #14
		SSARI-B193B01-10	10.0			1	WS #14
	SWMU 93 + SWMU 106	SSARI-B193B02-0.5	0.5[c]			1	WS #14
		SSARI-B193B02-5	5.0			1	WS #14
		SSARI-B193B02-10	10.0			1	WS #14
Bldg. A195 (Ordnance Segregation/Hazardous Waste Storage)	SWMU 93 + SWMU 106	SSARI-B195B01-0.5	0.5[c,d]			1	WS #14
		SSARI-B195B01-5	5.0			1	WS #14
		SSARI-B195B01-10	10.0			1	WS #14
	None	SSARI-B195B02-0.5	0.5[c,d]			1	WS #14
		SSARI-B195B02-5	5.0			1	WS #14
		SSARI-B195B02-10	10.0			1	WS #14
Bldg. A259 (Mine Anchor Assembly and Advanced Weapons Container Maintenance)	None	SSARI-B259B01-0.5	0.5[c,d]			1	WS #14
		SSARI-B259B01-5	5.0			1	WS #14
		SSARI-B259B01-10	10.0			1	WS #14
		SSARI-B259B02-0.5	0.5[c,d]			1	WS #14
		SSARI-B259B02-5	5.0			1	WS #14
		SSARI-B259B02-10	10.0			1	WS #14
Structure A296 Explosives Safe Haven	None	SSARI-B296B01-0.5	0.5[c,d]		TPH-g, TPH-d, TPH-mo, and metals	1	WS #14
		SSARI-B296B01-5	5.0			1	WS #14
		SSARI-B296B01-10	10.0			1	WS #14
	SWMU 93 + SWMU 106	SSARI-B296B02-0.5	0.5[c]		VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals	1	WS #14
		SSARI-B296B02-5	5.0			1	WS #14
		SSARI-B296B02-10	10.0			1	WS #14

SAP Worksheet #18 – Sampling Locations and Methods/SOP Requirements Table (Continued)

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]	Number of Samples	Sampling SOP Reference
SWMUs							
SWMU 93	None	SSARI-S93B01-0.5	0.5[c]	Soil	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs,	1	WS #14
		SSARI-S93B01-5	5.0			1	WS #14
		SSARI-S93B01-10	10.0			1	WS #14
	Building A259 + Former MEC Site in Grid AF011	SSARI-S93B02-0.5	0.5[c]		VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals	1	WS #14
		SSARI-S93B02-5	5.0			1	WS #14
		SSARI-S93B02-10	10.0			1	WS #14
	None	SSARI-S93B03-0.5	0.5[c]		VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals	1	WS #14
		SSARI-S93B03-5	5.0			1	WS #14
		SSARI-S93B03-10	10.0			1	WS #14
		SSARI-S93B04-0.5	0.5[c]			1	WS #14
		SSARI-S93B04-5	5.0			1	WS #14
		SSARI-S93B04-10	10.0			1	WS #14
SWMU 106	SWMU 93	SSARI-S106B01-0.5	0.5[c]			1	WS #14
		SSARI-S106B01-5	5.0			1	WS #14
		SSARI-S106B01-10	10.0			1	WS #14
		SSARI-S106B02-0.5	0.5[c]			1	WS #14
		SSARI-S106B02-5	5.0			1	WS #14
		SSARI-S106B02-10	10.0			1	WS #14
	None	SSARI-S106B03-0.5	0.5[c]			1	WS #14
		SSARI-S106B03-5	5.0[b]			1	WS #14
		SSARI-S106B03-10	10.0[b]			1	WS #14
	Former MEC Site in Grid AI011	SSARI-S106B04-0.5	0.5[c]		VOCs, SVOCs, TPH-g, TPH-d, TPH-mo, PCBs, and metals	1	WS #14
		SSARI-S106B04-5	5.0			1	WS #14
		SSARI-S106B04-10	10.0			1	WS #14
	Former MEC Site in Grids AH011	SSARI-S106B05-0.5	0.5[c]			1	WS #14
		SSARI-S106B05-5	5.0			1	WS #14
		SSARI-S106B05-10	10.0			1	WS #14

SAP Worksheet #18 – Sampling Locations and Methods/SOP Requirements Table (Continued)

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]	Number of Samples	Sampling SOP Reference
SWMU 106	SWMU 93 + Former MEC Site AG009	SSARI-S106B06-0.5	0.5[c]	Soil	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals	1	WS #14
		SSARI-S106B06-5	5.0			1	WS #14
		SSARI-S106B06-10	10.0			1	WS #14
	Former MEC Site in Grids AF010/AG010	SSARI-S106B07-0.5	0.5[c]			1	WS #14
		SSARI-S106B07-5	5.0			1	WS #14
		SSARI-S106B07-10	10.0			1	WS #14
	Building A259 + Former MEC Site – disposal pits in Grid AF011	SSARI-S106B08-0.5	0.5[c]			1	WS #14
		SSARI-S106B08-5	5.0			1	WS #14
		SSARI-S106B08-10	10.0			1	WS #14
	None	SSARI-S106B09-0.5	0.5[c]		VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals	1	WS #14
		SSARI-S106B09-5	5.0			1	WS #14
		SSARI-S106B09-10	10.0			1	WS #14
	Former MEC Site – disposal pits in Grid AE010	SSARI-S106B10-0.5	0.5[c]		VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals	1	WS #14
		SSARI-S106B10-5	5.0			1	WS #14
		SSARI-S106B10-10	10.0			1	WS #14
	Former MEC Site in Grid AE009	SSARI-S106B11-0.5	0.5[c]			1	WS #14
		SSARI-S106B11-5	5.0[b]			1	WS #14
		SSARI-S106B11-10	10.0[b]			1	WS #14
	Oven/Primer Pits	SSARI-S106B12-0.5	0.5[c]			1	WS #14
		SSARI-S106B12-5	5.0			1	WS #14
		SSARI-S106B12-10	10.0			1	WS #14
	None	SSARI-S106B13-0.5	0.5[c]		VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals	1	WS #14
		SSARI-S106B13-5	5.0			1	WS #14
		SSARI-S106B13-10	10.0			1	WS #14
		SSARI-S106B14-0.5	0.5[c]			1	WS #14
		SSARI-S106B14-5	5.0			1	WS #14
		SSARIS106B14-10	10.0			1	WS #14

SAP Worksheet #18 – Sampling Locations and Methods/SOP Requirements Table (Continued)

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]	Number of Samples	Sampling SOP Reference
FORMER MEC SITES							
Former MEC Site (disposal pit AH010/011 + former deck marker location)	None	SSARI-MECB01-0.5	0.5[c]	Soil	Metals	1	WS #14
		SSARI-MECB01-5	5.0			1	WS #14
		SSARI-MECB01-10	10.0			1	WS #14
		SSARI-MECB02-0.5	0.5[c]			1	WS #14
		SSARI-MECB02-5	5.0			1	WS #14
		SSARI-MECB02-10	10.0			1	WS #14
		SSARI-MECB03-0.5	0.5[c]			1	WS #14
		SSARI-MECB03-5	5.0			1	WS #14
		SSARI-MECB03-10	10.0			1	WS #14
		SSARI-MECB04-0.5	0.5[c]			1	WS #14
		SSARI-MECB04-5	5.0			1	WS #14
		SSARI-MECB04-10	10.0			1	WS #14
Former MEC Site (disposal pit AE011)		SSARI-MECB05-0.5	0.5[c]			1	WS #14
		SSARI-MECB05-5	5.0[b]			1	WS #14
		SSARI-MECB05-10	10.0[b]			1	WS #14
Former MEC Site (disposal pit AE010)		SSARI-MECB06-0.5	0.5[c]			1	WS #14
		SSARI-MECB06-5	5.0			1	WS #14
		SSARI-MECB06-10	10.0			1	WS #14
OVEN/PRIMER PITS							
Oven/Primer Pit Area (wetlands)	None	SSARI-PPB01-0.5	0.5[c]	Soil	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, metals, and dioxins/furans	1	WS #14
		SSARI-PPB01-5	5.0			1	WS #14
		SSARI-PPB01-10	10.0			1	WS #14
		SSARI-PPB02-0.5	0.5[c]			1	WS #14
		SSARI-PPB02-5	5.0			1	WS #14
		SSARI-PPB02-10	10.0			1	WS #14
		SSARI-PPB03-0.5	0.5[c]			1	WS #14
		SSARI-PPB03-5	5.0			1	WS #14
		SSARI-PPB03-10	10.0			1	WS #14
		SSARI-PPB04-10	10.0			1	WS #14
		SSARI-PPB05-10	10.0			1	WS #14
		SSARI-PPB06-10	10.0			1	WS #14

SAP Worksheet #18 – Sampling Locations and Methods/SOP Requirements Table (Continued)

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]	Number of Samples	Sampling SOP Reference
OTHER AREAS – TANKS (AJ015) AND DRUMS (AA009)							
Tanks/Dry Wells (DGM Grid AJ015)	None	SSARI-STB01-2	2.0	Soil	VOCs and PCBs	1	WS #14
		SSARI-STB01-5	5.0			1	WS #14
		SSARI-STB02-2	2.0			1	WS #14
		SSARI-STB02-5	5.0			1	WS #14
		SSARI-STB03-2	2.0			1	WS #14
		SSARI-STB03-5	5.0			1	WS #14
Tank Conveyance Pipeline (DGM Grid AJ015)		SSARI-STB04-2	2.0		VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, PCBs, and metals	1	WS #14
		SSARI-STB04-5	5.0			1	WS #14
		SSARI-STB05-2	2.0			1	WS #14
		SSARI-STB05-5	5.0			1	WS #14
		SSARI-STB06-2	2.0			1	WS #14
		SSARI-STB06-5	5.0			1	WS #14
		SSARI-STB07-2	2.0			1	WS #14
		SSARI-STB07-5	5.0			1	WS #14
		SSARI-STB08-2	2.0			1	WS #14
		SSARI-STB08-5	5.0			1	WS #14
		SSARI-STB09-2	2.0			1	WS #14
		SSARI-STB09-5	5.0			1	WS #14
Buried Drums (DGM Grid AA009)		SSARI-BDB01-0.5	0.5		SVOCs (including PAHs), TPH-d, and TPH-mo	1	WS #14
		SSARI-BDB01-5	5.0[b]			1	WS #14
		SSARI-BDB01-10	10.0[b]			1	WS #14

SAP Worksheet #18 – Sampling Locations and Methods/SOP Requirements Table (Continued)

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]	Number of Samples	Sampling SOP Reference
SOIL SAMPLES FROM MONITORING WELL BORINGS							
SSA-MW01	Former drums and tanks in Grids AI015 and AJ015	SSARI-MW1SB-0.5	0.5[c]	Soil	VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals	1	WS #14
		SSARI-MW1SB-5	5.0			1	WS #14
		SSARI-MW1SB-10	10.0			1	WS #14
SSA-MW02	Former MEC Site AH011	SSARI-MW2SB-0.5	0.5			1	WS #14
		SSARI-MW2SB-5	5.0			1	WS #14
		SSARI-MW2SB-10	10.0			1	WS #14
SSA-MW03	SWMU 106 + Former MEC Site AF011	SSARI-MW3SB-0.5	0.5			1	WS #14
		SSARI-MW3SB-5	5.0			1	WS #14
		SSARI-MW3SB-10	10.0			1	WS #14
SSA-MW04	SWMU 106 + Former MEC Site AE010	SSARI-MW4SB-0.5	0.5			1	WS #14
		SSARI-MW4SB-5	5.0			1	WS #14
		SSARI-MW4SB-10	10.0			1	WS #14
SSA-MW05	SWMU 106 + Oven/Primer Pits	SSARI-MW5SB-0.5	0.5			1	WS #14
		SSARI-MW5SB-5	5.0			1	WS #14
		SSARI-MW5SB-10	10.0			1	WS #14
SSA-MW06	Former drums in AA009	SSARI-MW6SB-0.5	0.5			1	WS #14
		SSARI-MW6SB-5	5.0			1	WS #14
		SSARI-MW6SB-10	10.0			1	WS #14
SSA-MW07	Building A195	SSARI-MW7SB-0.5	0.5			1	WS #14
		SSARI-MW7SB-5	5.0			1	WS #14
		SSARI-MW7SB-10	10.0			1	WS #14
SSA-MW08	South of Oven/Primer Pit Area	SSARI-MW8SB-0.5	0.5[c]			1	WS #14
		SSARI-MW8SB-5	5.0			1	WS #14
		SSARI-MW8SB-10	10.0			1	WS #14
SSA-MW09	Southwest portion of SSA	SSARI-MW9SB-0.5	0.5[c]			1	WS #14
		SSARI-MW9SB-5	5.0			1	WS #14
		SSARI-MW9SB-10	10.0			1	WS #14

SAP Worksheet #18 – Sampling Locations and Methods/SOP Requirements Table (Continued)

Target Sampling Location	Secondary Target(s)	Sample Identification Number	Planned Depth[a] (feet bgs)	Matrix	Analytical Group[b]	Number of Samples	Sampling SOP Reference
GROUNDWATER SAMPLE LOCATIONS							
SSA-MW01	Groundwater	SSA-MW01-001	TBD[4]	Water	VOCs, SVOCs (including PAHs), TPH-g, PCBs, TPH-d, TPH-mo, metals, and TDS	1	WS #14
SSA-MW02		SSA-MW02-001	TBD[4]			1	WS #14
SSA-MW03		SSA-MW03-001	TBD[4]			1	WS #14
SSA-MW04		SSA-MW04-001	TBD[4]			1	WS #14
SSA-MW05		SSA-MW05-001	TBD[4]		VOCs, SVOCs (including PAHs), TPH-g, PCBs, dioxins/furans[5], TPH-d, TPH-mo, metals, and TDS	1	WS #14
SSA-MW06		SSA-MW06-001	TBD[4]		VOCs, SVOCs (including PAHs), TPH-g, PCBs, PH-d, TPH-mo, metals, and TDS	1	WS #14
SSA-MW07		SSA-MW07-001	TBD[4]			1	WS #14
SSA-MW08		SSA-MW08-001	TBD[4]			1	WS #14
SSA-MW09		SSA-MW09-001	TBD[4]			1	WS #14

Notes:

a. Planned depth only, actual depth may be adjusted in the field based on observations of potential evidence for contaminant impact (staining, elevated head space measurements. etc.).
b. Organotins will be analyzed only in the event that ABM is encountered or identified.
c. No analysis for VOCs for the 0.5 feet bgs sample at this location.
d. Include analyses for organochlorine pesticides for the 0.5 feet bgs sample collected from this location.
e. Groundwater samples will be collected from the depth corresponding with the middle of the screened interval for each well, as determined from the total depth as installed.
f. Groundwater samples from well SSA-MW05 may be analyzed for dioxins/furans in the event that they are detected in the soil samples from the Oven/Primer Pit area.

Well/boring identification by location is shown on Figures 4 through 9.

bgs – below ground surface
Bldg. – building
DGM – digital geophysical mapping
MEC – munitions and explosives of concern
PAH – polycyclic aromatic hydrocarbon
PCB – polychlorinated biphenyl
SOP – standard operating procedure
SVOC – semi-volatile organic compound
SWMU – solid waste management unit
TBD – to be determined
TDS – total dissolved solid
TPH-d – total petroleum hydrocarbons as diesel
TPH-g – total petroleum hydrocarbons as gasoline
TPH-mo – total petroleum hydrocarbons as motor oil
VOC – volatile organic compound

SAP Worksheet #19 – Analytical Methods/SOPs/Preservation/Holding Time Requirements Table

Matrix	Analytical Group	Analytical and Preparation Method (SOP Reference)	Containers	Sample Volume	Preservation Requirements	Maximum Holding Time (preparation/ analysis)
Water	VOCs	EPA 5030B/8260B (M212 & M311)	40-mL VOA vial	3 x 40-mL vials	pH<2, HCl, 4 + 2 °C	14 days
Water	SVOCs	EPA 3510C/8270C (M200 & M404)	1-L Amber Glass	1 x 1 L	4°C ± 2	7 days to extraction/ 40 days for analysis
Water	TPH-g	EPA 5030B/8015B Mod. (M505)	40-mL VOA vial	2 x 40-mL vials	pH<2, HCl, 4 + 2 °C	14 days
Water	TPH-d, TPH-mo	EPA 3510C/8015B Mod. (M507)	1-L Amber Glass	1 x 1-L	4 °C ± 2 °C	7 days to extraction/ 40 days for analysis
Water	PCBs	EPA 3510C/8082 (M407)	1-L Amber Glass	1 x 1-L	4 °C ± 2 °C	7 days to extraction/ 40 days for analysis
Water	Dioxins/Furans	EPA Method 8290A (BRL-SOP-00405& 00406)	1-L Amber Glass	4 x 1-L	4 °C ± 2 °C	30 days to extraction/ 45 days for analysis
Water	Metals (total)	EPA 3010A/6020A (M610)	250-mL HDPE	250-mL HDPE	pH<2, nitric acid	180 days
Water	TDS	EPA 160.1 (M713)	1-L HDPE	1 x 1-L	Cool to 4 °C ± 2 °C	7 days
Soil	VOCs	EPA 5035/8260B (M213 & M311)	One TerraCore® Sample Kit	30 g	Cool to 4 °C ± 2 °C	14 days
Soil	SVOCs	EPA 3545/8270C (M200 & M404)	4-oz glass jar	20 g	Cool to 4 °C ± 2 °C	14 days to extraction/ 40 days for analysis
Soil	TPH-g	EPA 5035B/8015B Mod. (M213 & M505)	One TerraCore® Sample Kit	30 g	Cool to 4 °C ± 2 °C	14 days
Soil	TPH-d & TPH-mo	EPA 3520C/8015B Mod. (M507)	4-oz glass jar	10 g	Cool to 4 °C ± 2 °C	14 days
Soil	Metals (total)	EPA 3050B/6020A (M610)	4-oz glass jar	2 g	Cool to 4 °C ± 2 °C	180 days

SAP Worksheet #19 – Analytical Methods/SOP/Preservation/Holding Time Requirements Table (Continued)

Matrix	Analytical Group	Analytical and Preparation Method (SOP Reference)	Containers	Sample Volume	Preservation Requirements	Maximum Holding Time (preparation/ analysis)
Soil	PCBs	EPA 3545/8082 (M407)	4-oz glass jar	20 g	Cool to 4 °C ± 2 °C	14 days to extraction/ 40 days for analysis
Soil	Pesticides	EPA 3545/8081A (M400)	4-oz glass jar	20 g	Cool to 4 °C ± 2 °C	14 days to extraction/ 40 days for analysis
Soil	Dioxins/Furans	EPA Method 8290A (BRL-SOP-00405& 00406)	100-mL amber glass	2 x 5 g	Cool to 4 °C ± 2 °C	30 days to extraction/ 45 days for analysis
Soil	Organotins	Krone et al (M442)	4-oz glass jar	20 g	Cool to 4 °C ± 2 °C	14 days

Notes:

°C – degrees Celsius
EPA – U.S. Environmental Protection Agency
g – grams
HCl – hydrochloric acid
HDPE – high-density polyethylene
L – liter
mL – milliliters
Mod. - modified
PCBs – polychlorinated biphenyls
SOP – standard operating procedure
SVOC – semivolatile organic compound
TDS – total dissolved solids
TPH-d – total petroleum hydrocarbons as diesel
TPH-g – total petroleum hydrocarbons as gasoline
TPH-mo – total petroleum hydrocarbons as motor oil
VOA – volatile organic analysis
VOC – volatile organic compound

SAP Worksheet #20.1 – Field Quality Control Sample Summary Table (Soil Matrix Samples)[a]

Matrix	Analytical Group	No. of Sampling Locations	No. of Field Duplicates	No. of MS/MSDs	No. of Equip. Blanks[b]	No. of Source Blanks[c]	No. of VOA Trip Blanks[d]	Estimated Quantities of Samples to Laboratories
Soil	VOCs	92	0	5	17	1	0	115
Soil	SVOCs	140	0	7	17	1	0	165
Soil	TPH-g and TPH-d/mo	140	0	7	17	1	0	165
Soil	PCBs	92	0	5	0	0	0	97
Soil	Pesticides	6	0	1	0	0	0	7
Soil	Organotins	6	0	1	0	0	0	7
Soil	Metals	155	0	8	17	1	0	181
Soil	Dioxins/Furans	12	0	0	0	0	0	12

Notes:

a. Field duplicates will not be collected for soil samples during this investigation due to anticipated heterogeneous nature of soil matrix.
b. Equipment blank samples will be collected at a rate of one sample per piece of equipment, per day of sampling.
c. One source blank sample will be collected per source. It is anticipated that only one source will be used during this investigation.
d. Trip blanks are not required for soil samples.

MS/MSDs – matrix spike/matrix spike duplicate
PCBs – polychlorinated hydrocarbons
SVOCs – semivolatile organic compounds
TPH- g – total petroleum hydrocarbon as gasoline
TPH- d/mo – total petroleum hydrocarbon as diesel and motor oil
VOA – volatile organic analysis
VOCs – volatile organic compounds

SAP Worksheet #20.2 – Field Quality Control Sample Summary Table (Groundwater Matrix Samples)[a]

Matrix	Analytical Group	No. of Sampling Locations	No. of Field Duplicates	No. of MS/MSDs	No. of Equip. Blanks[b]	No. of Source Blanks[c]	No. of VOA Trip Blanks[d]	Estimated total No. of Samples to Laboratory
Water	VOCs	9	1	1	1	1	1	14
Water	SVOCs	9	1	1	1	1	0	13
Water	TPH-g & TPH-d/mo	9	1	1	1	1	0	13
Water	PCBs	9	1	1	0	0	0	11
Water	Metals	9	1	1	1	1	0	13
Water	TDS	9	0	0	0	0	0	9
Water	Dioxins/Furans	2	1	0	0	0	0	3

Notes:

a. Field blanks will not be collected for PCBs, and dioxins/furans during this RI as these analytes are not affected by potential background and carry over contamination.
b. Estimated. Equipment blank samples will be collected at a rate of one sample per piece of equipment, per day of sampling.
c. Estimated. One source blank sample will be collected per source. It is anticipated that only one source will be used.
d. Estimated. One per cooler per sampling day.

MS/MSDs – matrix spike/matrix spike duplicate
PCBs – polychlorinated biphenyls
SVOCs – semi-volatile organic compounds
TDS – total dissolved solids
TPH-g – total petroleum hydrocarbons as gasoline
TPH-d/mo – total petroleum hydrocarbons as diesel and motor oil
VOA – volatile organic analysis
VOCs – volatile organic compounds

SAP Worksheet #21 – Project Sampling SOP References Table

Sampling SOPs will not be utilized in this project. Sampling and sample handling procedures are detailed within WS #14.

SAP Worksheet #22 – Field Equipment Calibration, Maintenance, Testing, and Inspection Table

Field Equipment	Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference	Comments
Water Quality Meter	Perform calibration checks[1]	Daily	Automatic calibration with standards passes	If standards do not pass, contact technical support. If problem cannot be corrected, a new meter will be obtained.	Sampling personnel	User manual provided by manufacturer	No additional comments.
Photoionization Detector	Perform calibration checks[1]	Daily	Automatic calibration with standards passes	If standards do not pass, contact technical support. If problem cannot be corrected, a new meter will be obtained.	Sampling personnel	User manual provided by manufacturer	No additional comments.
Bladder Pump	Perform calibration checks[1]	Daily	Follow manufacturer instruction	Recalibrate	Sampling personnel	User manual provided by manufacturer	No additional comments.
Turbidimeter	Perform calibration checks[1]	Daily	Follow manufacturer instruction	Recalibrate	Sampling personnel	User manual provided by manufacturer	No additional comments.
Magnetometer	Perform function checks	Each borehole	Positive response to ferrous metal	Replace non-functioning equipment	UXO personnel	User manual provided by manufacturer	No additional comments.

Notes:

[1] A function check is first performed on the equipment. The calibration gas or liquids are tested to ensure that it falls within manufacturer's criteria. If the function check is acceptable, then the instrument is ready for use. Otherwise, the instrument will be calibrated according to manufacturer's instructions.

SOP – Standard Operating Procedure
UXO – unexploded ordnance

SAP Worksheet #23 – Analytical SOP References Table

Lab SOP Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Matrix and Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)	Variances from DoD QSM 4.2 (Y/N)
M212 & M311	Purge & Trap/VOCs by GC/MS, Rev3.1/Rev 0.0	Definitive	Groundwater/VOCs by EPA 8260B	GC/MS	Calscience	N	N
M213 & M311	Closed-System Purge and Trap/VOCs by GCMS – Rev1.0/0.0	Definitive	Soil/VOCs by EPA 5035/8260B	GC/MS	Calscience	N	N
M200 & M404	SVOCs by GC/MS Rev4.7	Definitive	Groundwater/Soil/ SVOCs by EPA 8270C	GC/MS	Calscience	N	N
M610	EPA Method 6020, ICP-MS, Rev5.2	Definitive	Groundwater/Soil/ Trace Metals by EPA 6020A	ICP-MS	Calscience	N	N
M619	EPA Method 7470A, Mercury in Liquid Waste, Rev3.0	Definitive	Groundwater/ Mercury by EPA 7470A	CVAA	Calscience	N	N
M713	TDS (Filterable Residue), Gravimetric, Rev2.6	Definitive	Groundwater/TDS by Standard Method 2540 C or EPA 160.1	Gravimetric	Calscience	N	N
M407	EPA Method 8082, Polychlorinated Biphenyls As Aroclors by Gas Chromatography, Rev3.5	Definitive	Groundwater/Soil/PCBs by EPA 8082	GC	Calscience	N	N
M400	Organochlorine Pesticides by GC, Rev 5.0	Definitive	Soil/Pesticides by EPA 8081A	GC	Calscience	N	N
M620	EPA Method 7471A, Mercury in Solid or Semisolid Waste, Rev3.3	Definitive	Soil/Mercury by EPA 7471A	CVAA	Calscience	N	N
M442	Organotins via Krone et al., (1989) by GC/MS and SIM	Definitive	Soil/Organotins by Krone et al	GC/MS SIM	Calscience	N	N

SAP Worksheet #23 – Analytical SOP References Table (Continued)

Lab SOP Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Matrix and Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)	Variances from DoD QSM 4.2 (Y/N)
M505/M507	EPA 8015B: Total Petroleum Hydrocarbons by GC/FID – Rev1.1/0.0	Definitive	Groundwater/Soil/TPH by EPA 8015B (Modified)	GC/FID	Calscience	N	N
M414	Nitroaromatics and Nitroamines By HPLC, Rev2.4	Definitive	Groundwater/Soil/ Explosives by EPA 8330	HPLC	Calscience	N	N
BRL SOP-00406	Dioxins and Furans by HRGC HRMS in Water & Soil (EPA 8290A), Rev10	Definitive	Groundwater/Soil/Dioxins/ Furans – HRMS by EPA8290A	HRMS (Micromass Autospec Ultima)	Maxxam	N	N
BRL SOP-00405	Dioxin and Furan Extracts Cleanup, Rev2	Definitive	Groundwater/Soil/Dioxins/ Furans – HRMS by EPA8290A	HRMS	Maxxam	N	N
BRL SOP-00407	Dioxin and Furan Extraction in Water and Soil Samples, Rev3	Definitive	Groundwater/Soil/Dioxins/ Furans – HRMS by EPA8290A	HRMS	Maxxam	N	N

Notes:
Calscience – Eurofins Calscience Inc.
CVAA – cold-vapor atomic emission spectroscopy
EPA – U.S. Environmental Protection Agency
GC/FID – gas chromatograph/flame ionization detector
GC/MS – gas chromatograph/mass spectrometer
HPLC – High-Performance Liquid Chromatography
HRMS – high-resolution mass spectrometry
ICP-MS – inductively coupled plasma-mass spectrometry
Maxxam – Maxxam Analytics Laboratories
SIM – selected ion monitoring
SOP – standard operating procedure
SVOC – semivolatile organic compound
TDS – total dissolved solids
VOC – volatile organic compound

SAP Worksheet #24 – Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Person Responsible for CA
GC/MS – VOCs	BFB Tuning	Prior to calibration and every 12 hours during sample analysis	m/z — Relative Abundance Criteria 50 — 15 − 40% of m/z 95 75 — 30 − 60% of m/z 95 95 — Base peak 100% rel. abun. 9 — 5 − 9% of m/z□95 173 — < 2% □f m/z 174 174 — > 50% of m/z 95 175 — 5 − 9% of m/z 174 176 — > 95% but < 101% of m/z 174 177 — 5 − 9% of m/z 176	Retune instrument and verify.	Analyst
GC/MS	Minimum 5-point ICAL for all analytes	Initially, after the BFB Tune Check, after major maintenance and as needed thereafter	Average retention factor - VOC's VOC- SPCCs: ≥ 0.30 for chlorobenzene and 1,1,2,2-tetrachloroethane, ≥0.1 for chloromethane, bromoform, and 1,1-dichloroethane RSD for RFs for CCCs: VOCs - ≤30% and one option below if required by project: 1): RSD for each analyte ≤ 15% 2): linear least squares regression r ≥ 0.995 when RSD >15% 3): non-linear – COD r2 ≥ 0.99 (minimum of 6 points)	Locate the source of the problem. If expected RFs are not met, check for standard degradation or perform instrument maintenance to correct the problem then repeat ICAL.	Analyst
GC/MS	ICV Second Source Standard	Immediately after ICAL	VOCs: %D for each CCC is ≤ 20%, and the daily RRF for each SPCC is ≥ 0.30 for chlorobenzene and 1,1,2,2-tetrachloroethane, and >0.1 for chloromethane, bromoform, and 1,1-dichloroethane	Prepare fresh standard and reanalyze ICV to rule out standard degradation or inaccurate injection. If problem persists, perform instrument maintenance to correct the problem and repeat ICAL.	Analyst

SAP Worksheet #24 – Analytical Instrument Calibration Table (Continued)

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Person Responsible for CA
GC/MS	CCV	Daily, following the BFB tune check, before sample analysis, and every 12 hours of analysis time	VOCs: %D for each CCC is ≤ 20%, and the daily RRF for each SPCC is ≥ 0.30 for chlorobenzene and 1,1,2,2-tetrachloroethane, ≥0.1 for chloromethane, bromoform, and 1,1-dichloroethane	Prepare fresh standard and reanalyze CCV to rule out standard degradation or inaccurate injection. If problem persists, perform instrument maintenance to correct the problem and repeat ICAL.	Analyst
GC/MS	Retention time Window position Establishment for each analyte and surrogate	Once per ICAL	Position shall be set using the midpoint standard of the ICAL curve. Updated with CCV as needed.	N/A	Analyst
GC/MS	Evaluation of RRT	With each standard and sample	RRT of ea. target analyte in each calibration standard within ± 0.06 RRT units.	Identify possible cause for the nonconformance, then rerun ICAL.	Analyst
HRMS – Dioxins/Furans	MS Tuning	Prior to calibration and every 12 hours during sample analysis	Refer to method for specific ion criteria.	Retune instrument and verify. Rerun affected samples. Flagging criteria are not appropriate and problem must be corrected. No samples may be accepted without a valid tune.	Analyst
HRMS – Dioxins/Furans	ICAL	As needed	%RSD <20%, Unlabeled analytes %RSD <20%, Labeled analytes	If the acceptance criteria were not met, re-calibration is performed before any samples may be analyzed.	Analyst
HRMS – Dioxins/Furans	ICV	1 per ICAL, analyzed after ICAL, before field samples	%RSD <50 % for Native and Labeled analytes	If the acceptance criteria were not met, re-calibration is performed before any samples may be analyzed.	Analyst

SAP Worksheet #24 – Analytical Instrument Calibration Table (Continued)

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Person Responsible for CA
HRMS – Dioxins/Furans	CCV	1 per analytical run. Analytical run not to exceed 12 hours.	%RSD 20% Unlabeled Analytes %RSD 20% Labeled Analytes	If the criterion has not achieved corrective action, re-calibration is performed before any samples may be analyzed. Corrective action may include re-analysis of the samples.	Analyst
GC	Minimum 5-point ICAL for all analytes	Initially, as needed thereafter	RSD ≤ 20% for all analytes, or linear least squares regression r > 0.995	Locate the source of the problem. If expected RSD is not met, check for standard degradation or perform instrument maintenance to correct the problem then repeat ICAL.	Analyst
GC	ICV/ Second Source Standard	Immediately after ICAL	All analytes within ±20% D	Prepare fresh standard and reanalyze ICV to rule out standard degradation or inaccurate injection. If problem persists perform instrument maintenance to correct the problem and repeat ICAL.	Analyst
GC	CCV	Every 12 hours	All analytes within ±15% D	Prepare fresh standard and reanalyze CCV to rule out standard degradation or inaccurate injection. If problem persists perform instrument maintenance to correct the problem and repeat ICAL.	Analyst
ICP-MS	Hardware Tuning	Minimum every 24 hours	- Mass Calibration: within ±0.1 amu of the true value - Resolution Check: <0.9 amu full width at 10% peak height - % RSD: 5% for replicates	Maintenance, re-tune and verify.	Analyst

SAP Worksheet #24 – Analytical Instrument Calibration Table (Continued)

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Person Responsible for CA
ICP-MS	ICAL for all analytes. Minimum one high standard and a calibration blank	Daily ICAL prior to sample analysis	No acceptance criteria unless more than one standard is used, in which case r ≥ 0.995	Prepare fresh standard and reanalyze ICV to rule out standard degradation or inaccurate injection. If problem persists perform instrument maintenance and repeat ICAL.	Analyst
ICP-MS	ICV Second source Standard	Once after each ICAL, prior to sample analysis	± 10% of true value	Prepare fresh standard and reanalyze ICV to rule out standard degradation or inaccurate injection. If still out, perform instrument maintenance and repeat ICAL and ICV.	Analyst
ICP-MS	LLICV Standard	Following the ICV, prior to sample analysis	%RSD = 5% %D ± 20% of true value	Prepare fresh standard and reanalyze LLICV to rule out standard degradation or inaccurate injection. If problem persists perform instrument maintenance and repeat ICAL.	Analyst
ICP-MS	CCV	Prior to sample analysis, after every 10 field samples and at the end of the analysis sequence.	± 10% of true value	Correct problem, re-run calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since the last successful calibration verification.	Analyst
ICP-MS	ICSA/AB	Following the ICB, prior to sample analysis	80%-120% recovery; evaluate non-interferent ICSA results with absolute values ≥2x DL	Terminate analysis, correct problem, recalibrate instrument, check calibration, and re-run all samples analyzed since last compliant ICS.	Analyst
ICP-MS	ICB	Following ICV, prior to sample analysis	No detects ≥ ½ LOQ	Determine source of blank contamination and correct problem. Reanalyze with all associated samples	Analyst

SAP Worksheet #24 – Analytical Instrument Calibration Table (Continued)

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Person Responsible for CA
ICP-MS	Continuing Calibration Blank	Following CCV, prior to sample analysis, after every 10 samples, and at end of analysis sequence	No detects ≥ ½ LOQ	Determine source of blank contamination and correct problem. Reanalyze with all associated samples	Analyst
CVAA	ICAL – miniumum calibration blank + 5 points	Daily ICAL prior to sample analysis	r ≥ 0.995	Locate the source of the problem. If expected RSD is not met, check the standard degradation or perform instrument maintenance to correct the problem then repeat ICAL.	Analyst
CVAA	ICV Second source Standard	Immediately after ICAL	± 10% of true value	Prepare fresh standard and reanalyze ICV to rule out standard degradation or inaccurate injection. If still out, perform instrument maintenance and repeat ICAL and ICV.	Analyst
CVAA	CCV	Prior to sample analysis, after every 10 field samples and at the end of the analysis sequence.	± 10% of true value	Correct problem, re-run calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since the last successful calibration verification.	Analyst
CVAA	ICB	Following ICV, prior to sample analysis	No detects ≥ ½ LOQ	Determine source of blank contamination and correct problem. Reanalyze with all associated samples	Analyst

SAP Worksheet #24 – Analytical Instrument Calibration Table (Continued)

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Person Responsible for CA
CVAA	Continuing Calibration Blank	Following CCV, prior to sample analysis, after every 10 samples, and at end of analysis sequence	No detects ≥ ½ LOQ	Determine source of blank contamination and correct problem. Reanalyze with all associated samples	Analyst
Micromass Autospec Ultima HRMS	5-point. ICAL	EPA 8290A Midpoint CS3 every 12hrs 5 pt. as necessary	EPA 8290A Unlabeled analytes < 20% RSD Labeled analytes < 30% Analyte retention time is within +3sec from internal Signal to noise > 10 standards > 2.5 samples Ion Abundance Ratio +15%	Instrument Maintenance Instrument parameters adjusted (retuned) Standards reanalyzed	Analyst

Notes:

%RSD – percent relative standard deviation
%D – percent difference
amu – atomic mass unit
BFB – bromfluorobenzene
CA – corrective action
CCC – calibration check compound
CCV – continuing calibration verification
COD – coefficient of determination
GC/MS – gas chromatograph/mass spectrometer
HRMS – high-resolution mass spectrometer
ICAL – initial calibration
ICB – initial calibration blank
ICP-MS – inductively coupled plasma-mass spectrometry
ICS – interference check solution
ICSA – interference check solution - A (high concentration)
ICV – Initial Calibration Verification
LLICV – Low-Level Initial Calibration Verification
N/A – not applicable
QL – quantitation limit
RF – response factor
RRF – relative response factor
RRT – relative retention time
RSD – relative standard deviation
SPCC – system performance check compound
VOC – volatile organic compound

SAP Worksheet #25 – Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person
All Instrumentation/ Equipment	Parameter Setup	Physical check	Physical check	Initially; prior to ICAL, CCV or verification as required by SOP or Method	Predetermined optimum parameter settings	Reset if incorrect	Analyst
GC/MS	Tune MS	Analyze tune Standard	Tune standard passes criteria	Initially and every 12 hours following	Refer to methods for Tune criteria	Retune MS	Analyst
GC	Change septum, clean injection port, change or clip column, install new liner, change trap	Response factors and chromatogram review	Instrument performance and sensitivity	As needed	CCV pass criteria	Clean/replace injector port, cut additional column, replace column, reanalyze CCV, recalibrate instrument	Analyst
ICP/ICP-MS	ICSA/ICSAB	Instrument Performance	Conformance to interference check	Prior to sample analysis	Within + 20% of expected value	Reanalyze ICS. If problem persists, perform maintenance, repeat calibrations and reanalyze all associated samples.	Analyst
ICP/ICP-MS	ICB/CCB	Instrument Performance	Instrument contamination check	After every ICV/CCV	No analytes detected > 1/2 RL or above LOD as applicable to project	Determine possible source of contamination, correct the problem, reanalyze calibration blank and all associated samples.	Analyst

SAP Worksheet #25 – Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table (Continued)

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person
HRMS - Micromass Autospec Ultima	• Inner /Outer ion source • Autosampler • GC column • Septa • Injection port liner	EPA 8290A	• Helium flow • Vacuum • GC column performance	Frequency determined by instrument remaining in calibration and free of interference	Passing calibration	Retune, recalibrate, reinject affected samples, reanalyze affected samples	Analyst

Notes:

CCV – continuing calibration verification
EPA – U.S. Environmental Protection Agency
GC – gas chromatograph
GC/MS – gas chromatograph/mass spectrometer
HRMS – high-resolution mass spectrometer
ICAL – initial calibration
ICP-MS – inductively coupled plasma-mass spectrometry
MS – mass spectrometer

SAP Worksheet #26 – Sample Handling System

Sample Handling System

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization): NOREAS Sampling Personnel
Sample Packaging (Personnel/Organization): NOREAS Sampling Personnel
Coordination of Shipment (Personnel/Organization): NOREAS Project Chemist
Type of Shipment/Carrier: Laboratory Courier or Commercial Courier
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Laboratory Sample Custodian
Sample Custody and Storage (Personnel/Organization): Laboratory Sample Custodian
Sample Preparation (Personnel/Organization): Laboratory Sample Preparation Group
Sample Determinative Analysis (Personnel/Organization): Laboratory Bench Chemist
SAMPLE ARCHIVING
Field Sample Storage (No. of days from sample collection): 60 days
Sample Extract/Digestate Storage (No. of days from extraction/digestion): 120 days
Biological Sample Storage (No. of days from sample collection): N/A
SAMPLE DISPOSAL
Personnel/Organization: Laboratory Sample Custodian
Number of Days from Analysis: 3 months

SAP Worksheet #27 – Sample Custody Requirements Table

Field Documentation

All information pertinent to field sampling will be recorded in a field logbook to maintain the integrity and traceability of samples. All samples will be properly labeled and coolers custody sealed before they are transported to the laboratory, and will be accompanied by completed COC documentation. All documentation will be recorded in a field logbook in indelible ink.

Sample Number

All samples submitted to the analytical laboratories will be uniquely numbered, as listed in WS #18. The sample number will be recorded in the field logbook and on the labels and COC form when the sample is collected. A complete description of the sample and sampling conditions will be recorded in the field logbook and referenced using the unique sample identification number.

Sample Labeling

Sample labels are necessary to prevent misidentification of samples. Sample labels will be filled out in indelible ink and affixed to sample containers when the sample is collected. Each sample label will be covered with clear tape. Each sample container will be labeled with the following, at a minimum:

- Company name
- Sample identification number
- Sample collection date (month/day/year)
- Time of collection (24-hour clock)
- Sampler's initials
- Analyses required
- Preservative (if any)

Chain-of-Custody Procedures

To establish the documentation necessary to trace sample possession from the time of collection through analysis and disposal, a COC record will be completely filled out and will accompany every sample. Samples will be delivered to the laboratory for analysis as soon as practicable. A COC record will accompany all samples. A copy of the COC form is provided in Attachment 1.

The following will be recorded on the COC record:

- Project name
- Project location
- Project number

SAP Worksheet #27 – Sample Custody Requirements Table (Continued)

- Sample ID
- Sampler name
- Sampler signature
- Project contact
- Air bill number (if applicable)
- Date of sample collection
- Time of sample collection to the nearest minute, 24-hour clock
- Sample type (matrix)
- Turnaround time
- Laboratory name
- Number of sample containers
- Analysis required
- Comments
  - MS/MSD samples
  - Observations specific to sample
  - Field filtered
- Transfer signature to relinquish samples
  - The sampler will be the first person to relinquish sample possession
- Courier/laboratory representative signature (for commercial carrier, record air bill number here [if applicable])
- Date/time (of custody transfer)
- Laboratory instruction
- Data package requirement (Level III or IV)

Field Logbooks

A permanently bound field logbook with consecutively numbered pages, used for sampling activities only, will be assigned to this project. All entries will be recorded in indelible ink. The logbook pages will be signed by the responsible sampler at the end of each workday, and any unused portions of the logbook pages will be crossed out, signed, and dated.

If it is necessary to transfer the logbook to another person, the person relinquishing the logbook will sign and date the last page used, and the person receiving the logbook will sign and date the next page to be used.

SAP Worksheet #27 – Sample Custody Requirements Table (Continued)

At a minimum, the logbook will contain the following information:

- Project name and location
- Date and time
- Personnel in attendance
- General weather information
- Work performed
- Field observations
- Sampling performed, including specifics such as location, type of sample, type of analyses, and sample identification
- Descriptions of deviations from this SAP
- Problems encountered and corrective action taken
- Identification of field QC samples
- QC activities
- Verbal or written instructions

Sample Handling and Shipping

This procedure will be followed for water samples:

Immediately after sample labeling, custody seals will be affixed to each sample container. For vials or other small containers, the custody seal will be placed on the outside of the first resealable bag; then the container will be placed in a second resealable bag. This will prevent any contact with the adhesive from the custody seal and the sample. Other sample containers will be placed in double-resealable plastic bags to protect the sample from moisture, and to prevent breakage and potential cross-contamination during transportation to the laboratory. All glass sample containers will be protected with bubble wrap first, if transported by a commercial carrier. Vials should be wrapped with bubble wrap, then placed in a resealable bag, a custody seal placed over the bag, and then placed in another resealable bag.

Each cooler will be shipped with a temperature blank. A temperature blank is a vial filled with tap water and stored in the cooler during sample collection and transportation. The temperature of the cooler will be recorded by the laboratory on the COC record immediately upon receipt of the samples.

Samples transported by a laboratory-assigned courier will be packed in a sample cooler with sufficient ice (cooler will be approximately half full of wet ice that is below and above sample containers). Two custody seals will be taped across the cooler lid: one seal in the front and one seal in the back. The COC record will be completed and signed by the courier. The cooler and

SAP Worksheet #27 – Sample Custody Requirements Table (Continued)

the top two copies (white and pink) of the COC record will then be released to the courier for transportation to the laboratory.

Samples to be shipped by commercial carrier will be packed in a sample cooler lined with a plastic bag. Ice will be double-bagged and placed at the bottom of the cooler; one layer of sample containers will be placed on the ice, and more double-bagged ice will be placed on top of the containers. This will be repeated until the cooler is filled with ice as the top layer in the cooler. The COC record will include the air bill number, and the Received By box will be labeled with the commercial courier's name. The top two copies of the COC record will be sealed in a double-resealable bag and then taped to the inside of the sample cooler lid. The cooler will be taped shut with strapping tape. Two custody seals will be taped across the cooler lid: one seal in the front and one seal in the back. Clear tape will be applied to the custody seals to prevent accidental breakage during shipment. The pouch for the air bill will be placed on the cooler and secured with clear tape. The air bill will be completed for priority overnight delivery and placed in the pouch. If multiple coolers are being shipped, the original air bill will be placed on the cooler with the COC record, and copies of the air bill will be placed on the other coolers. The number of packages should be included on each air bill (1 of 2, 2 of 2). Saturday deliveries should be coordinated with the laboratory in advance, and field sampling personnel, or their designee, must ensure that Saturday delivery stickers are placed on each cooler by the commercial courier.

Document Corrections

Changes or corrections on any project documentation will be made by crossing out the erroneous item with a single line and initialing (by the person performing the correction) and dating the correction. The original item, although erroneous, must remain legible beneath the crossed-out line. The new information should be written clearly above the crossed-out item.

Laboratory Sample Custody and Documentation

The integrity and traceability of samples from the time they are collected, through the time data are reported, are essential in any sampling and analysis program. The handling of the samples and transferring of custody must be well documented, given the evidentiary nature of the analytical data.

The sample custodian will sign the COC from the courier or FedEx®, inventory each shipment, and note on the original COC record any discrepancy in the sample custody, temperature of the cooler, or broken samples. The laboratory will note any discrepancies on the sample receipt form. The laboratory project manager will immediately notify the Project Chemist, who, in consultation with the project team, will provide instructions in writing to the laboratory.

SAP Worksheet #28.1 – Laboratory QC Samples Table (VOCs)

Matrix	Water/Soil
Analytical Group	VOCs
Analytical Method / SOP Reference	EPA 5030/5035/8260B M212/M311

QC Sample	Frequency/ Number	Method/SOP QC Acceptance Limit	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blank	1/batch of 20 field samples	No detects ≥ ½ LOQ	If sufficient sample volume is available, reanalyze blank, QC and affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy	No detects ≥ ½ LOQ
LCS/LCSD	1/batch of 20 field samples	See Attachment A-3	If sufficient sample volume is available, reanalyze QC and affected samples. If volume is not sufficient, qualify data as needed. Discuss in narrative.	Analyst	Accuracy, Precision	See Attachment A-3
MS/MSD	1/batch of 20 field samples	See Attachment A-3	None if LCS/LCSD passes – Flag data.	Analyst	Accuracy, Precision	See Attachment A-3
Surrogate Spikes	All environmental and laboratory QC samples	See Attachment A-3	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy/Bias	See Attachment A-3
Internal Standards	All environmental and laboratory QC samples	-50% to +100%	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy	-50% to +100%

Notes:

EPA – U.S. Environmental Protection Agency
LCS – laboratory control sample
LCSD – laboratory control sample duplicate
MS/MSD – matrix spike/ matrix spike duplicate
QC – quality control
LOQ – limit of quantitation
SOP – standard operating procedure
VOC – volatile organic compound

SAP Worksheet #28.2 – Laboratory QC Samples Table (SVOCs)

Matrix	Water/Soil
Analytical Group	SVOCs
Analytical Method / SOP Reference	EPA 8270C M404

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blank	1/batch of 20 field samples	No detects ≥ ½ LOQ	If sufficient sample volume is available, reanalyze blank, QC and affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy/Bias - Contamination	No detects ≥ ½ LOQ
LCS/LCSD	1/batch of 20 field samples	See Attachment A-3	If sufficient sample volume is available, reanalyze QC and affected samples. If volume is not sufficient, qualify data as needed. Discuss in narrative.	Analyst	Accuracy, Precision	See Attachment A-3
MS/MSD	1/batch of 20 field samples	See Attachment A-3	None if LCS/LCSD passes – Flag data.	Analyst	Accuracy, Precision	See Attachment A-3
Surrogate Spikes	All environmental and laboratory QC samples	See Attachment A-3	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy/Bias	See Attachment A-3
Internal Standards	All environmental and laboratory QC samples	-50% to +100%	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy	-50% to +100%

Notes:

EPA – U.S. Environmental Protection Agency
LCS – laboratory control sample
LCSD – laboratory control sample duplicate
LOQ – limit of quantitation
MS/MSD – matrix spike/matrix spike duplicate
QC – quality control
SOP – standard operating procedure
SVOC – semivolatile organic compound

SAP Worksheet #28.3 – Laboratory QC Samples Table (Metals)

Matrix	Water/Soil
Analytical Group	Metals
Analytical Method / SOP Reference	EPA 6020A/M610

QC Sample	Frequency/ Number	Method/SOP QC Acceptance Limit	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blank	1/batch	No detects ≥ ½ LOQ	If sufficient sample volume is available, reanalyze blank, QC and affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy, Bias, Contamination	No detects ≥ ½ LOQ
LCS/LCSD	1/batch	80%-120% 0 - 20%	If sufficient sample volume is available, reanalyze QC and affected samples. If volume is not sufficient, qualify data as needed. Discuss in narrative.	Analyst	Accuracy, Precision	80%-120% 0 - 20%
MS/MSD	1/batch	75-125% 0 - 20%	None if LCS/LCSD passes – Qualify data as matrix effect.	Analyst	Accuracy, Precision	75-125% 0 - 20%
Internal Standards	Every QC and environmental sample	Intensity within 30% - 120% if the ICAL	Reanalyze new sample aliquot	Analyst	Accuracy	Intensity within 30% - 120% if the ICAL
Post-digestion Spike	1/batch	75%-125%	None – or perform MSA if required by project.	Analyst	Accuracy, Precision	75%-125%
Serial Dilution	1/batch	≤10%	None – or perform PDS/PDSD if required by project.	Analyst	Accuracy	10%

Notes:

EPA – U.S. Environmental Protection Agency
ICAL – initial calibration
LCS – laboratory control sample
LCSD – laboratory control sample duplicate
LOQ – limit of quantitation
MS – matrix spike
MSA – method of standard addition
MSD – matrix spike duplicate
PDSD – post-digest spike duplicate
QC – quality control
PDS – post-digest spike
SOP – standard operating procedure

SAP Worksheet #28.4 – Laboratory QC Samples Table (Pesticides / PCBs)

Matrix	Soil
Analytical Group	Pesticides/PCBs
Analytical Method / SOP Reference	8081A/8082/ M400/M407

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blank	1/batch	No detects ≥ ½ LOQ	If sufficient sample volume is available, reanalyze blank, QC and affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy/Bias - Contamination	No detects ≥ ½ LOQ
LCS/LCSD	1/batch	See Attachment A-3	If sufficient sample volume is available, reanalyze QC and affected samples. If volume is not sufficient, qualify data as needed. Discuss in narrative.	Analyst	Accuracy, Precision	See Attachment A-3
MS/MSD	Project designated sample matrix QC	See Attachment A-3	None – refer to LCS/LCSD-Flag/discuss in narrative.	Analyst	Matrix interference/Accuracy/ Bias/Precision	See Attachment A-3
Surrogate Spikes	Every analytical sample	See Attachment A-3	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy/Bias	See Attachment A-3

Notes:

LCS – laboratory control sample
LOQ limit of quantitation
MS – matrix spike
PCBs – polychlorinated biphenyls
SOP – standard operating procedure
LCSD – laboratory control sample duplicate
MB – method blank
MSD – matrix spike duplicate
QC – quality control

SAP Worksheet #28.5 – Laboratory QC Samples Table (TPH as Gasoline, Diesel, and Motor Oil)

Matrix	Water/Soil
Analytical Group	TPH (as Gasoline, Diesel, and Motor Oil)
Analytical Method / SOP Reference	8015B/M505/ M507

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blank	1/batch	No detects ≥ ½ LOQ	If sufficient sample volume is available, reanalyze blank, QC and affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy/Bias – Contamination	No detects ≥ ½ LOQ
LCS/LCSD	One per sample preparation batch	See Attachment A-3	If sufficient sample volume is available, reanalyze QC and affected samples. If volume is not sufficient, qualify data as needed. Discuss in narrative.	Analyst	Accuracy, Precision	See Attachment A-3
MS/MSD	Project designated sample matrix QC	See Attachment A-3	None – refer to LCS/LCSD-Flag/discuss in narrative.	Analyst	Matrix interference/Accuracy/ Bias/Precision	See Attachment A-3
Surrogate Spikes	Every analytical sample	See Attachment A-3	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy/Bias	See Attachment A-3

Notes:

LCS – laboratory control sample
LCSD – laboratory control sample duplicate
LOQ limit of quantitation
MS – matrix spike
MSD – matrix spike duplicate
QC – quality control
SOP – standard operating procedure
TPH – total petroleum hydrocarbons

SAP Worksheet #28.6 – Laboratory QC Samples Table (Dioxins/Furans)

Matrix	Water/Soil
Analytical Group	Dioxins/Furans (Low Level)
Analytical Method / SOP Reference	EPA 8290A/ BRL SOP-00406

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blank	1 per extraction batch	No detects ≥ ½ LOQ	The source of the contamination is investigated and eliminated before proceeding with further analysis. Corrective actions are: 1. Samples ND – report without qualification 2. Samples >10X contamination level – report with qualification 3. Samples <10x contamination – re-extract and reanalyze. Insufficient sample - qualify and footnote	Analyst/Prep Analyst	Acceptable Level or Absence of interference/ contamination	No detects ≥ ½ LOQ
LCS/LCSD	1 per extraction batch	%Recovery = (Calculated Value/True Value) *100%	Source of poor recovery is investigated and eliminated before proceeding with further analysis, corrective actions are: 1. Biased high, samples ND – report without qualifications. 2. Biased low – re-extract and reanalyze. Insufficient volume – qualify and footnote	Analyst/Prep Analyst	Laboratory Accuracy/Method bias in ideal matrix	%Recovery = (Calculated Value/True Value) *100%

SAP Worksheet #28.6 – Laboratory QC Samples Table (Dioxins/Furans) (Continued)

Matrix	Water/Soil
Analytical Group	Dioxins/Furans (Low Level)
Analytical Method / SOP Reference	EPA 8290A/ BRL SOP-00406

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator	Measurement Performance Criteria
MS/MSD	1 per 20 samples or one for each extraction batch	%Recovery = (Calculated Value - Sample Value/True Value) *100% Recovery if matrix spiked internal standards 40-135% Native analyte recoveries 80-140%	If the recoveries indicate that the problem is procedure related, re-extraction and re-analysis is required. If the recoveries indicate that the failures are matrix-related, refer to Blank Spike as measure of method performance in clean matrix. The project Chemist will be contacted and a decision will be made to either report the data as is with a notation in the analytical narrative or if the samples should be re-extract and re-analyzed.	Analyst/Prep Analyst	Matrix interference/ Accuracy/ Bias/Precision	%Recovery = (Calculated Value - Sample Value/True Value) *100%
Surrogate Spikes	Every sample	%Recovery = (Calculated Value/True Value) *100%	Reason for poor recoveries is investigated and eliminated before further analytical activities. Corrective actions are: 1. High bias, samples ND – report without qualification. 2. Low bias – reextract and reanalyze. Insufficient volume – qualify and footnote	Analyst/Prep Analyst	Individual sample preparation efficiency control	%Recovery = (Calculated Value/True Value) *100%

SAP Worksheet #28.6 – Laboratory QC Samples Table (Dioxins/Furans) (Continued)

Matrix	Water/Soil
Analytical Group	Dioxins/Furans (Low Level)
Analytical Method / SOP Reference	EPA 8290A/ BRL SOP-00406

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Internal standards	Every sample	40 – 135% as per method EPA 8290A	If failure is due to instrument performance issues, the problem must be identified, corrected, and the sample must be re-analyzed. If no instrument problem is found the sample must be re-extracted. If upon re-analysis the responses are still not within limits, the problem may be considered sample matrix interference and results flagged.	Analyst	Extraction efficiency control	Meets method acceptance criteria 40-135%

Notes:

LCS – laboratory control sample
LCSD – laboratory control sample duplicate
LOQ limit of quantitation
MB – method blank
MS – matrix spike
MSD – matrix spike duplicate
QC – quality control
SOP – standard operating procedure

SAP Worksheet #28.7 – Laboratory QC Samples Table (Organotins)

Matrix	Soil
Analytical Group	Organotins
Analytical Method / SOP Reference	Krone et al Method/M442

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blank	1/batch	No detects ≥ ½ LOQ	If sufficient sample volume is available, reanalyze blank, QC and affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy/Bias – Contamination	No detects ≥ ½ LOQ
LCS/LCSD	One per sample preparation batch	% Recovery: 50 - 120% RPD: 0 – 20%	If sufficient sample volume is available, reanalyze QC and affected samples. If volume is not sufficient, qualify data as needed. Discuss in narrative.	Analyst	Accuracy, Precision	% Recovery: 50 - 120% RPD: 0 – 20%
MS/MSD	Project designated sample matrix QC	% Recovery: 37 - 127% RPD: 0 – 26%	None – refer to LCS/LCSD-Flag/discuss in narrative.	Analyst	Matrix interference/ Accuracy/ Bias/Precision	% Recovery: 37 - 127% RPD: 0 – 26%
Surrogate Spikes	Every analytical sample	19 – 121%	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy/Bias	19 – 121%

Notes:

LCS – laboratory control sample
LOQ limit of quantitation
MS – matrix spike
QC – quality control
WS – Worksheet
LCSD – laboratory control sample duplicate
MB – method blank
MSD – matrix spike duplicate
SOP – standard operating procedure
RPD - relative percent difference

SAP Worksheet #29 – Project Documents and Records Table

Document	Where Maintained
Field notes/logbook	Project file at NOREAS
Daily contractor quality control report	Project file at NOREAS
Daily progress report	Project file at NOREAS
Chain-of-custody forms	Project file at NOREAS; NAVFAC SW
Laboratory raw data package	Project file at NOREAS; NAVFAC SW
Audit/assessment checklists/reports	Project file at NOREAS; Eurofins Calscience Inc.,
Corrective action forms/reports	Project file at NOREAS; Calscience
Laboratory equipment calibration logs	Calscience; Maxxam Analytics
Sample preparation logs	Calscience; Maxxam Analytics
Run logs	Calscience ; Maxxam Analytics
Sample disposal records	Calscience ; Maxxam Analytics
Validated data	Project file at NOREAS; NAVFAC SW
Data Package	Project file at NOREAS; NAVFAC SW

Notes:

NAVFAC SW – Naval Facilities Engineering Command Southwest
The project file will be maintained by the Project Manager and the Project Chemist.

SAP Worksheet #30 – Analytical Services Table

Matrix	Analytical Group	Sample Locations/ID Number	Analytical Methods	Data Package Turnaround Time[1]	Laboratory / Organization[2,3] (name and address, contact person and telephone number)	Backup Laboratory / Organization (name and address, contact person and telephone number)
Water	VOCs SVOCs TPH-g TPH-d/mo Metals TDS PCBs	SSA-MW01 – SSA-MW09 (See WS #18)	8260B 8270C 8015B Mod. 8015B Mod. 6020A/7470A 160.1 8082 8330	5 business days	Eurofins Calscience Inc. 7440 Lincoln Way Garden Grove, CA Richard Villafania 714-895-5494	EMAX Laboratories, Inc. 1835 W. 205th Street Torrance, CA 90501 Richard Beauvil 310-618-8889
Water	Dioxins/ Furans	SSA-MW01 – SSA-MW09 (See WS #18)	8290A	21 days	Maxxam Analytics 6740 Campobello Rd., Mississauga, ON Canada L5N 2L8 Ivana Vukovic 905-817-5784 or 800-668-0639	ALS Environmental (formerly Columbia Analytical Services) 19408 Park Row, Suite 320 Houston, Texas 77084 Michael Cosson 713-266-1599
Soil	VOCs SVOCs TPH-g TPH-d/mo Metals PCBs	Oven/Primer Pit Area; SWMU 93 Outfall; MEC; Former Radium Button Location; Former Bldgs.; Drum Area (See WS #18)	8260B 8270C 8015B Mod. 8015B Mod. 6020A/7471A 8082 8330	5 business days	Eurofins Calscience Inc. 7440 Lincoln Way Garden Grove, CA Richard Villafania 714-895-5494	EMAX Laboratories, Inc. 1835 W. 205th Street Torrance, CA 90501 Richard Beauvil 310-618-8889
Soil	Dioxins/ Furans	Oven/Primer Pit Area (See WS #18)	8290A	21 days	Maxxam Analytics 6740 Campobello Rd., Mississauga, ON Canada L5N 2L8 Ivana Vukovic 905-817-5784 or 800-668-0639	ALS Environmental (formerly Columbia Analytical Services) 19408 Park Row, Suite 320 Houston, Texas 77084 Michael Cosson 713-266-1599

SAP Worksheet #30 – Analytical Services Table (Continued)

Matrix	Analytical Group	Sample Locations/ID Number	Analytical Methods	Data Package Turnaround Time[1]	Laboratory / Organization[2,3] (name and address, contact person and telephone number)	Backup Laboratory / Organization (name and address, contact person and telephone number)
Soil + ABM (where present)	Organotins[4]	Drum area; Former Bldg. A195 MEC Sites Grids AE009, AE011, and AJ013 (only if ABM found)	Krone et al. (GC/MS SIM)	10 business days	Eurofins Calscience Inc. 7440 Lincoln Way Garden Grove, CA Richard Villafania 714-895-5494	EMAX Laboratories, Inc. 1835 W. 205th Street Torrance, CA 90501 Richard Beauvil 310-618-8889
Soil	Pesticides	Former Bldg. A195, Bldg A259, Bldg A296	8081A	10 business days	Eurofins Calscience Inc. 7440 Lincoln Way Garden Grove, CA Richard Villafania 714-895-5494	EMAX Laboratories, Inc. 1835 W. 205th Street Torrance, CA 90501 Richard Beauvil 310-618-8889

Notes:

[1] Preliminary data are due in 5 business days for most methods, unless otherwise directed on the COC form by NOREAS. For specialty tests, preliminary data are due within 15 business days. Final data packages are due in 10 business days.
[2] Identified analytical laboratories are certified by State of California ELAP and accredited by the DoD ELAP (See Attachment A-2).
[3] Primary laboratory will be Eurofins Calscience, Inc. Specialty tests will be subcontracted to Maxxam Analytics directly through the primary laboratory.
[4] Organotins will be analyzed only in the event that ABM is encountered or identified.

ABM – abrasive blast material
COC – chain-of-custody form
DoD – Department of Defense
ELAP – Environmental Laboratory Accreditation Program
EPA – U.S. Environmental Protection Agency
GC/MS – gas chromatography/mass spectrometry
PCB – polychlorinated biphenyls
SIM – select ion monitoring
SVOC – semivolatile organic compounds
TPH – total petroleum hydrocarbons
TPH-d – total petroleum hydrocarbons as diesel
TPH-g – total petroleum hydrocarbons as gasoline
TPH-mo – total petroleum hydrocarbons as motor oil
VOC – volatile organic compound
WS – Worksheet

SAP Worksheet #31 – Planned Project Assessments Table

Assessment Type	**Frequency**	**Internal or External**	**Organization Performing Assessment**	**Person(s) Responsible for Performing Assessment** (title and organizational affiliation)	**Person(s) Responsible for Responding to Assessment Findings** (title and organizational affiliation)	**Person(s) Responsible for Identifying and Implementing Corrective Actions** (title and organizational affiliation)	**Person(s) Responsible for Monitoring Effectiveness of CA** (title and organizational affiliation)
Readiness review	Once	Internal	NOREAS	QCM, NOREAS	Project Manager, NOREAS	Project Manager, NOREAS	Project Manager and QCM, NOREAS
Field sampling surveillance	Once at the beginning, once during, and once toward the end of field sampling activities	Internal	NOREAS	QCM, NOREAS	Project Manager, NOREAS	Project Manager, NOREAS	Project Manager and QCM, NOREAS
Management review	Once	Internal	NOREAS	QCM, NOREAS	Project Manager, NOREAS	Project Manager, NOREAS	QCM, NOREAS
Laboratory verification	Prior to identifying a laboratory for the project	Internal	NOREAS	Project Chemist, NOREAS	Project Manager, Calscience	Quality Assurance Manager, Calscience	QCM, NOREAS
Facility notification	48 hours prior to start of fieldwork	Internal	NOREAS	Project Manager, NOREAS	Project QAO, NOREAS	Project Manager, NOREAS	Project Manager, NOREAS
Vendors notifications	48 hours prior to start of sampling	Internal	NOREAS	Project Manager, NOREAS	Project QAO, NOREAS	Project Manager, NOREAS	Project Manager, NOREAS
Field audit	1 per startup of the sampling	Internal	NOREAS	Project Chemist, NOREAS	Project QAO, NOREAS	Project Chemist and Project QAO, NOREAS	Project Manager, NOREAS

Notes:

CA – corrective action
Calscience - Eurofins Calscience Inc.
NOREAS – NOREAS, Inc.
QAO – Quality Assurance Officer
QC – Quality Control
QCM – Quality Control Manager

SAP Worksheet #31 – Planned Project Assessments Table (Continued)

Laboratory Verification

Contracted laboratories must be certified by the state of California through the Department of Public Health ELAP for analysis of constituents of concern for each method specified. In addition, the laboratories must successfully complete the DoD ELAP laboratory evaluation process prior to receiving any project samples for analysis. Laboratory verification consists of ensuring that ELAP certifications of primary and secondary laboratories have not expired and that both laboratories have been evaluated by the DoD ELAP. Laboratory certificates are provided in Attachment A-2. In addition, prior to start of sampling, variances reported by the laboratories are acceptable and meet the project quality objectives listed in this SAP.

Facility Notification

At least 48 hours prior to start of sampling, NOREAS will notify the DON Points of Contact including the Resident Officer in Charge of Construction, BRAC Facilities Coordinator and the BRAC PMO CSA listed in WS #3 regarding the commencement of the field activities, and coordinate.

Vendors Notifications

Sampling containers shall be ordered with the off-site laboratory at least 7 days prior to start of sampling event, and the supplies shall be checked to meet the SOP requirements listed in WS #19.

Field Audits

Prior to start of the project, a visit to the project site will be performed to verify site conditions. Throughout the duration of the project, field documentation and sample receipt forms will be reviewed as needed.

The Project Manager and senior technical staff may schedule and/or perform field audits. All nonconformances must be corrected and objective evidence of the correction, either through additional on-site reviews or documentation provided to the QCM and the project manager. The audit team may issue a corrective-action request form to identify and schedule specific corrective actions to be undertaken and completed by the project team. The QCM is responsible to verify that any required corrective actions are completed. The QCM has the authority to stop work if a non-conformance critical to data usability is identified.

Project QA will be a function of the Program QCM, who is assigned the authority to inspect all activities and may stop work if activities detrimental to the quality of the work product are detected. Project personnel will evaluate compliance of the laboratory QA program and procedures with *Installation Restoration Chemical Data Quality Manual* requirements (NFESC 1999). Oversight may include internal and external audits, documentation of findings, and reports of corrective action. The Program QCM will coordinate a management review of any deficiencies that are noted.

SAP Worksheet #32 – The Assessment Findings and Corrective Action Responses

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (name, title, organization)	Timeframe of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response (name, title, organization)	Timeframe for Response
Readiness Review	List of items to be completed	Project Manager, NOREAS	48 hours after the meeting	A list of completed items	QCM, NOREAS	5 days
Field Sampling Surveillance	Surveillance Report	Project Manager, NOREAS	7 days after completion of the inspection	Corrective Action Report	QCM, NOREAS	5 days after notification
Data Review Surveillance	Surveillance Report	Project Manager, NOREAS	7 days after completion of the inspection	Corrective Action Report	Project Manager, QCM, NOREAS	14 days after notification
Management Review	Surveillance Report	Project Manager, NOREAS	7 days after completion of the inspection	Corrective Action Report	QCM, NOREAS	14 days after notification

Notes:

NOREAS, NOREAS, Inc.
QAO – Quality Assurance Officer
QCM – Quality Control Manager

SAP Worksheet #33 – QA Management Reports Table

Type of Report	**Frequency** (daily, weekly monthly, quarterly, annually, etc.)	**Projected Delivery Date(s)**	**Person(s) Responsible for Report Preparation** (title and organizational affiliation)	**Report Recipient(s)** (title and organizational affiliation)
Field Sampling Surveillance Report	Once at startup of sampling	Deficiencies will be discussed with the project team on the day surveillance is conducted. Report will be issued 10 days after surveillance date.	Project Chemist, NOREAS	Project Manager, QCM, NOREAS
Management Review Report	Once during field activities	Report will be issued 10 days after management review is completed.	QCM, NOREAS	Project Manager, Program Manager, NOREAS
Remedial Investigation and Feasibility Study Report	Once after field activities have been completed	Approximately 180 days after final laboratory data has been validated (dependent on agency review time).	QCM, Project Manager NOREAS	Project Manager, Program Manager, NOREAS, RPM, NAVFAC SW

Notes:

QA quality assurance
NAVFAC SW – Naval Facilities Engineering Command Southwest
NOREAS, NOREAS, Inc.
QCM – Quality Control Manager
RPM – Remedial Project Manager

SAP Worksheet #34 – Verification (Step I) Process Table

Verification Input	Description	Internal / External	Responsible for Verification (name, organization)
Field logbook	Field logbooks will be reviewed and placed in the project file upon project completion.	Internal	Field Sampling Personnel, QCM, NOREAS
Chain-of-custody forms	Chain-of-custody forms will be reviewed upon their completion and verified for completeness. A copy of the chain-of-custody will be retained in the project file, and the original and remaining copies taped inside the container for shipment.	Internal	Field Sampling Personnel, NOREAS
Sample login sheets	Sample login information will be reviewed and verified for completeness in accordance with the chain-of-custody forms.	Internal External	Project Chemist, NOREAS Laboratory Project Manager, Calscience/Maxxam Analytics
Laboratory data prior to release	Laboratory data will be reviewed and verified for completeness against analyses requested on the chain-of-custody forms.	External	Laboratory Project Manager, Calscience/Maxxam Analytics
Laboratory final data packages	All laboratory data packages will be verified by the laboratory performing the work for completeness and technical accuracy prior to submittal. Data packages will then be reviewed by the Project Chemist for completeness. Subsequently, data packages will be evaluated externally according to the data validation procedures specified in WS #36 of this SAP.	Internal External External	Project Chemist, NOREAS Laboratory Project Manager, Calscience/Maxxam Analytics Laboratory Data Consultants, Inc.
Electronic data deliverables	All EDDs will be verified by the laboratory performing the work for completeness and technical accuracy prior to submittal. All received EDDs will be verified against the hard-copy laboratory data packages.	External Internal	Laboratory Project Manager, Calscience/Maxxam Analytics Project Chemist, NOREAS

Notes:

EDD – electronic data deliverable
NOREAS, NOREAS, Inc.
QCM – Quality Control Manager
SAP – Sampling and Analysis Plan
WS – Worksheet

SAP Worksheet #35 – Validation (Step IIa and IIb) Process Table

Step IIa/IIb	Validation Input	Description	Responsible for Validation (Name, Organization)
IIa	Communication	Establish that required communication procedures were followed by field or laboratory personnel.	Project Manager, NOREAS QCM, NOREAS
IIa	Sampling Methods and Procedures	Establish that the required sampling methods were used and that any deviations were noted. Verify that the sampling procedures and field measurements met performance criteria and that any deviations were documented.	QC Manager, NOREAS
IIa	Holding Times	Verify that samples were analyzed within holding times specified in method, procedure, or contract requirements. If holding times were not met, confirm that deviations were documented, that appropriate notifications were made to the laboratory.	Analyst–primary; supervisor or peer–secondary, Calscience/Maxxam Analytics
IIa	Analytes	Verify that required lists of analytes were reported as specified in the SAP.	Analyst–primary; supervisor or peer–secondary Calscience/Maxxam Analytics
IIa	Analytical Methods and Procedures	Verify that the required analytical methods were used and that any deviations were noted. Verify that the QC samples met performance criteria and that any deviations were documented.	Analyst–primary; supervisor or peer–secondary, Calscience/Maxxam Analytics
IIa	Data Qualifiers	Verify that the laboratory data qualifiers were defined in the laboratory data package and applied as specified.	Analyst–primary; supervisor or peer–secondary, Calscience/Maxxam Analytics Project Chemist, NOREAS
IIb	Sampling Plan	Determine whether the sampling plan was executed as specified (i.e., the number, location, and type of field samples were collected and analyzed as specified in the SAP).	Project Chemist, NOREAS
IIb	Sampling Procedures	Evaluate whether sampling procedures were followed with respect to equipment and proper sampling support (e.g., techniques, equipment, decontamination, volume, temperature, preservative).	Project Chemist, NOREAS
IIa/IIb	Field Duplicates	Compare results of field duplicates with criteria established in the SAP.	Project Chemist, NOREAS LDC,
IIa/IIb	Project Quantitation Limits	Determine that LOQs were achieved, as outlined in the SAP.	Project Chemist, NOREAS LDC,

SAP Worksheet #35 – Validation (Step IIa and IIb) Process Table (Continued)

Step IIa/IIb	Validation Input	Description	Responsible for Validation (Name, Organization)
IIa/IIb	Performance Criteria	Evaluate QC data against performance criteria in the SAP.	LDC

Notes:

IIa – Compliance with methods, procedures, and contracts
IIb – Comparison with measurement performance criteria in the SAP
LDC – Laboratory Data Consultants, Incorporated
Calscience – Eurofins Calscience Inc.
QC – Quality Control
QCM – Quality Control Manager
SAP – Sampling and Analysis Plan

SAP Worksheet #36 – Analytical Data Validation (Steps IIa and IIb) Summary Table

Step IIa / IIb	Matrix	Analytical Group	Validation Criteria1	Data Validator (title and organizational affiliation)
IIa	Water	VOCs	In accordance with Calscience SOPs M212/M311, DoD QSM, NAVFAC SW EWI#1, and EPA Level III and IV guidelines.	Linda Rauto Project Manager, LDC, Inc.
IIa	Soil	VOCs	In accordance with Calscience SOPs M213/M311, DoD QSM, NAVFAC SW EWI#1, and EPA Level III and IV guidelines.	Linda Rauto Project Manager, LDC, Inc.
IIa	Water/Soil	SVOCs	In accordance with Calscience SOP M404, DoD QSM, NAVFACSW EWI#1, and EPA Level III and IV guidelines.	Linda Rauto Project Manager, LDC, Inc.
IIa	Water/Soil	Metals & Mercury	In accordance with Calscience SOPs M601 & M619/M620, DoD QSM, NAVFAC SW EWI#1, and EPA Level III and IV guidelines.	Linda Rauto Project Manager, LDC, Inc.
IIa	Water/Soil	TPH-gasoline, -diesel, and –motor oil	In accordance with Calscience SOPs M505 & M507, DoD QSM, NAVFAC SW EWI#1, and EPA Level III and IV guidelines.	Linda Rauto Project Manager, LDC, Inc.
IIa	Water	Total Dissolved Solids	In accordance with Calscience SOP M713, DoD QSM, NAVFACSW EWI#1, and EPA Level III and IV guidelines.	Linda Rauto Project Manager, LDC, Inc.
IIa	Water/Soil	PCBs	In accordance with Calscience SOP M407, DoD QSM, NAVFACSW EWI#1, and EPA Level III and IV guidelines.	Linda Rauto Project Manager, LDC, Inc.
IIa	Water/Soil	Explosives	In accordance with Calscience SOP M414, DoD QSM, NAVFACSW EWI#1, and EPA Level III and IV guidelines.	Linda Rauto Project Manager, LDC, Inc.
IIa	Soil	Organochlorine Pesticides	In accordance with Calscience SOP M400, DoD QSM, NAVFACSW EWI#1, and EPA Level III and IV guidelines.	Linda Rauto Project Manager, LDC, Inc.

SAP Worksheet #36 – Analytical Data Validation (Steps IIa and IIb) Summary Table (Continued)

Step IIa / IIb	Matrix	Analytical Group	Validation Criteria1	Data Validator (title and organizational affiliation)
IIa	Soil	Organotins	In accordance with Calscience SOP M442, DoD QSM, NAVFACSW EWI#1, and EPA Level III and IV guidelines.	Linda Rauto Project Manager, LDC
IIa	Water/Soil	Dioxins/Furans	In accordance with Maxxam Analytics BRL SOP-00405/00406/00407, DoD QSM, NAVFACSW EWI#1, and EPA Level III and IV guidelines.	Linda Rauto Project Manager, LDC

Notes:

1 Level III validation involves review of final laboratory data and QC samples provided by the laboratory. Level IV validation involves the same review as level III and also includes recalculation of results using raw laboratory data.

IIa – Compliance with methods, procedures, and contracts
IIb – Comparison with measurement performance criteria in the SAP
DoD – Department of Defense
EPA – U.S. Environmental Protection Agency
EWI – Environmental Work Instruction
Laboratory Data Consultants, Inc.
NAVFAC SW – Naval Facilities Engineering Command Southwest
PCBs – polychlorinated biphenyls
QSM – Quality Systems Manual Version 4.2
SOP – standard operating procedure
SVOC – semivolatile organic compound
VOC – volatile organic compound

SAP Worksheet #37 – Usability Assessment

NOREAS Project Chemist will perform the data usability assessment for this project in accordance with the *EPA National Functional Guidelines for Organic Methods Data Review* (EPA 2008), *EPA National Functional Guidelines for Inorganic Methods Data Review* (EPA 2004), SWDIV EW#1 (3EN2.1) (NFESC 2001), EPA methods, and the specifications of the SAP. Analytical DQOs will be assessed through application of precision, accuracy, representativeness, completeness, and comparability (PARCC) parameters to ensure that the data are of sufficient quality to meet the project objectives.

Analytical data will be obtained using published, standard methods in a State of California Department of Health Services and DoD ELAP-certified analytical laboratories. The analytical methods, project-specific reporting limits (LOQs), and QC acceptance limits to be followed for this project are those specified in Tables in WS #15 and WS #28 of this SAP and the *DoD Quality Systems Manual (QSM) for Environmental Laboratories* (Version 4.2) (DoD 2010). The following subsections describe each of the PARCC parameters and how they will be assessed during this project.

Precision

Precision is the degree of mutual agreement between individual measurements of the same property under similar conditions. Usually, combined field and laboratory precision is evaluated by collecting and analyzing field duplicates and then calculating the variance between the samples, typically as a relative percent difference.

$$RPD = \frac{|A - B|}{\frac{(A + B)}{2}} \text{ X } 100\%$$

Where:

A = First duplicate concentration
B = Second duplicate concentration

Field sampling precision is evaluated by analyzing field duplicate samples. Field duplicates will be collected and analyzed at a frequency of 10 percent for groundwater samples. Field duplicates will not be collected for soil matrix samples due to anticipated heterogeneity of this matrix.

Laboratory analytical precision is evaluated by analyzing laboratory duplicates and/or MS and MSD. MS/MSD samples will be prepared for all constituents for this project with the exception of waste profile samples. The results of the analysis of each MS/MSD pair will be used to calculate relative percent difference for evaluating analytical precision. The field precision acceptability guidance limit for this project will be 30 percent for groundwater samples when both sample and its duplicate concentrations are greater than 10 times the reporting limit.

SAP Worksheet #37 – Usability Assessment (Continued)

Accuracy

Accuracy is the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations. Analytical accuracy is determined by comparing the percent recovery of analytes spiked into a LCS against an established control limit. The following formula is used for calculating accuracy based on percent recovery of a specific analyte:

$$\text{Percent Recovery} = \frac{S - C}{T} \text{ x } 100$$

Where:

S = Measured spike sample concentration
C = Sample concentration
T = True or expected concentration of the spike

Analytical accuracy will be evaluated using the MS and MSD samples, LCSs, surrogate standards (organic methods only), and method blanks. MS and MSD samples will be prepared and analyzed at a frequency of 5 percent (one in 20 field samples) for groundwater and soil samples. LCSs are also analyzed at a rate of 5 percent. Surrogate standards, where applicable, are added to each field and laboratory QC sample analyzed for organic constituents.

Field accuracy will be assessed by collecting and analyzing field QC samples: equipment rinsate, trip blank, and source water, as appropriate. These field QC samples will be used to evaluate the potential for target analytes to enter samples as a result of sampling and handling processes.

Laboratories may use the advisory limits until the in-house statistically-based control limits are developed for each analytical method and sample matrix; however, these limits may not exceed the acceptance criteria provided in the DoD QSM (Version 4.2) (DoD 2010). Results that fall outside the accuracy goals will be further evaluated based on the results of other laboratory or field QC samples.

Representativeness

Representativeness, a qualitative parameter, expresses the degree to which sample data accurately and precisely represent the characteristics of a population, variations in a parameter at a sampling point, or an environmental condition that they are intended to represent. Representative data will be obtained for this project through careful selection of sampling locations and analytical parameters. Representative data will also be obtained through proper collection and handling of samples to avoid interference and minimize contamination.

SAP Worksheet #37 – Usability Assessment (Continued)

Representativeness of data will also be ensured through the consistent application of standardized field and laboratory procedures. Field blanks (if appropriate) and laboratory blank samples will be evaluated for the presence of potential contaminants to aid in evaluating the representativeness of sample results. Data determined to be non-representative, by comparison with existing data, will be used only if accompanied by appropriate qualifiers and limits of uncertainty.

Completeness

Completeness is a measure of the percentage of project-specific data that are determined to be valid. Valid data are obtained when samples are collected and analyzed in accordance with standardized QC procedures outlined in this SAP and when none of the QC criteria that affect data usability are exceeded. Completeness will be evaluated and determined as part of the data quality assessment process when all data validation is completed. For completeness evaluation, valid results are all results not qualified as rejected ("R"). The goal for completeness is 95 percent for aqueous samples and 90 percent for soil samples and is determined by dividing the number of usable sample results by the total number of sample results planned for this investigation.

In addition, the completeness goal for meeting method holding times will be 100 percent for this investigation. If these goals are not achieved, the source of nonconformity will be evaluated to determine whether resampling or reanalysis is necessary.

Comparability

Comparability expresses the confidence with which one data set can be compared with another. Comparability of data will be achieved by consistently following standard field and laboratory procedures, published analytical methods, reporting formats, and by using standard measurement units in reporting analytical data.

Method Sensitivity (Detection Limit, Limit of Detection, and Limit of Quantitation)

Detection limit is the smallest analyte concentration that can be demonstrated to be different from zero or a blank concentration at the 99 percent level of confidence. The limit of detection is defined as the smallest concentration of an analyte that must be present in a sample matrix in order to be detected at a high level of confidence (99 percent). The LOQ (a.k.a. reporting limit) represents the lowest concentration of an analyte that produces a quantitative result within specified limits of precision and accuracy. For DoD projects, the LOQs are typically set at or above the concentration of the lowest initial calibration standard (DoD 2010). Analytical methods for this project have been selected so that the LOQs for each target analyte are below the project action/screening limits listed in WS #15, as allowed by the analytical method.

SAP Worksheet #37 – Usability Assessment (Continued)

Data Quality Assessment

After data are validated by a third-party data validation company, the NOREAS Project Chemist will assess field and laboratory QC. The PARCC parameters will be determined and evaluated as described above. The Project Chemist will review the data validation reports for any deviations, and application of the data qualifiers to data, and for meeting project DQOs. The following data usability qualifiers will be used:

J	–	Indicates an estimated value
U	–	Indicates the analyte was analyzed for but not detected
R	–	Quality control indicates the data is not usable
UJ	–	Indicates the analyte was analyzed for but not detected. The sample detection limit is an estimated value

Data qualifiers will be used to indicate uncertainties associated with the data. The assigned qualifiers will be entered into the validation code field in the database. The Project Chemist will prepare a data quality assessment report that will summarize the findings of the data assessment and discuss the usability of the data to be included in the final report.

Analytical data will be reported in tabular format to be included in the report. The electronic data in NEDD format will be submitted to the NIRIS database within 30 days of completion of validation, as described in *EWI EVR.6, Environmental Data Management and Required Electronic Delivery Standards* (SWDIV 2005). An e-mail confirmation received by NOREAS will be forwarded to the project file.

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FIGURES

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Y:\Shared\GIS_CAD_GIN\Figures\Mare Island\SSA\00 Mare Island Vicinity Map.mxd

LEGEND

Mare Island Base Boundary

N

0 2.5 5 10 Miles

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VALLEJO, CALIFORNIA
SAMPLING AND ANALYSIS PLAN

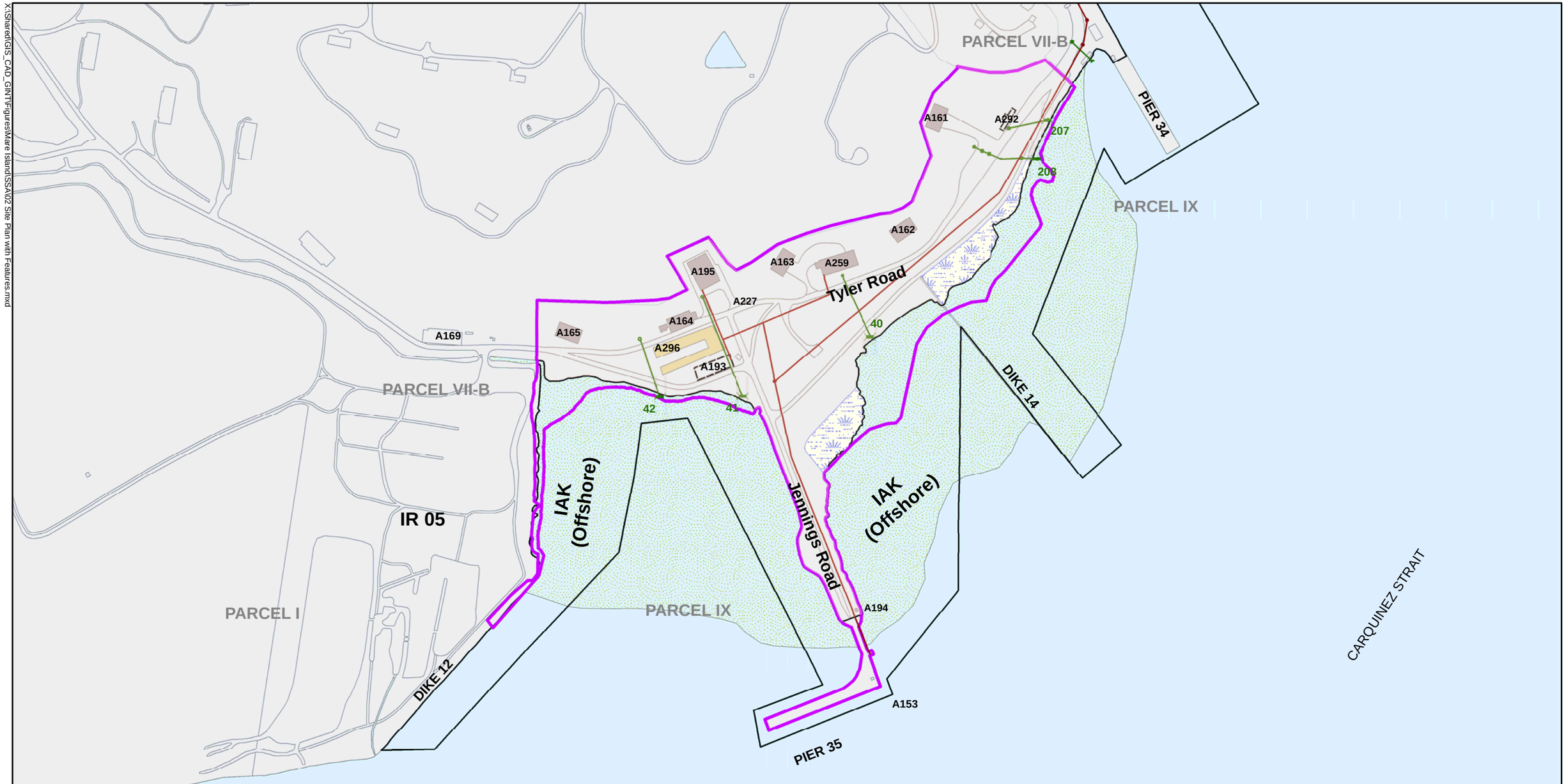
FIGURE 1

MARE ISLAND VICINITY MAP

NOREAS

DATE: APRIL 2014
CONTRACT NO.: N62473-12-C-4812
DCN: NRS-4812-0000-0002

X:\Shared\GIS_CAD_GINT\Figures\Mare Island\SSA\02 Site Plan with Features.mxd



LEGEND

- INVESTIGATION AREA (IA)
- TRANSFER PARCEL BOUNDARY
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM SEWER DRAIN LINE (SWMU 93)
- INVESTIGATION AREA K (IAK)
- STORM SEWER OUTFALLS (SWMU 93)
- BUILDINGS
- REMOVED BUILDING
- SOUTH SHORE AREA BOUNDARY FOR RI
- WETLANDS
- TIDAL MUDFLATS
- EXPLOSIVES SAFE HAVEN

N

0 200 400 800 Feet

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FIGURE 2

SITE PLAN WITH FEATURES

NOREAS

DATE: JULY 2015
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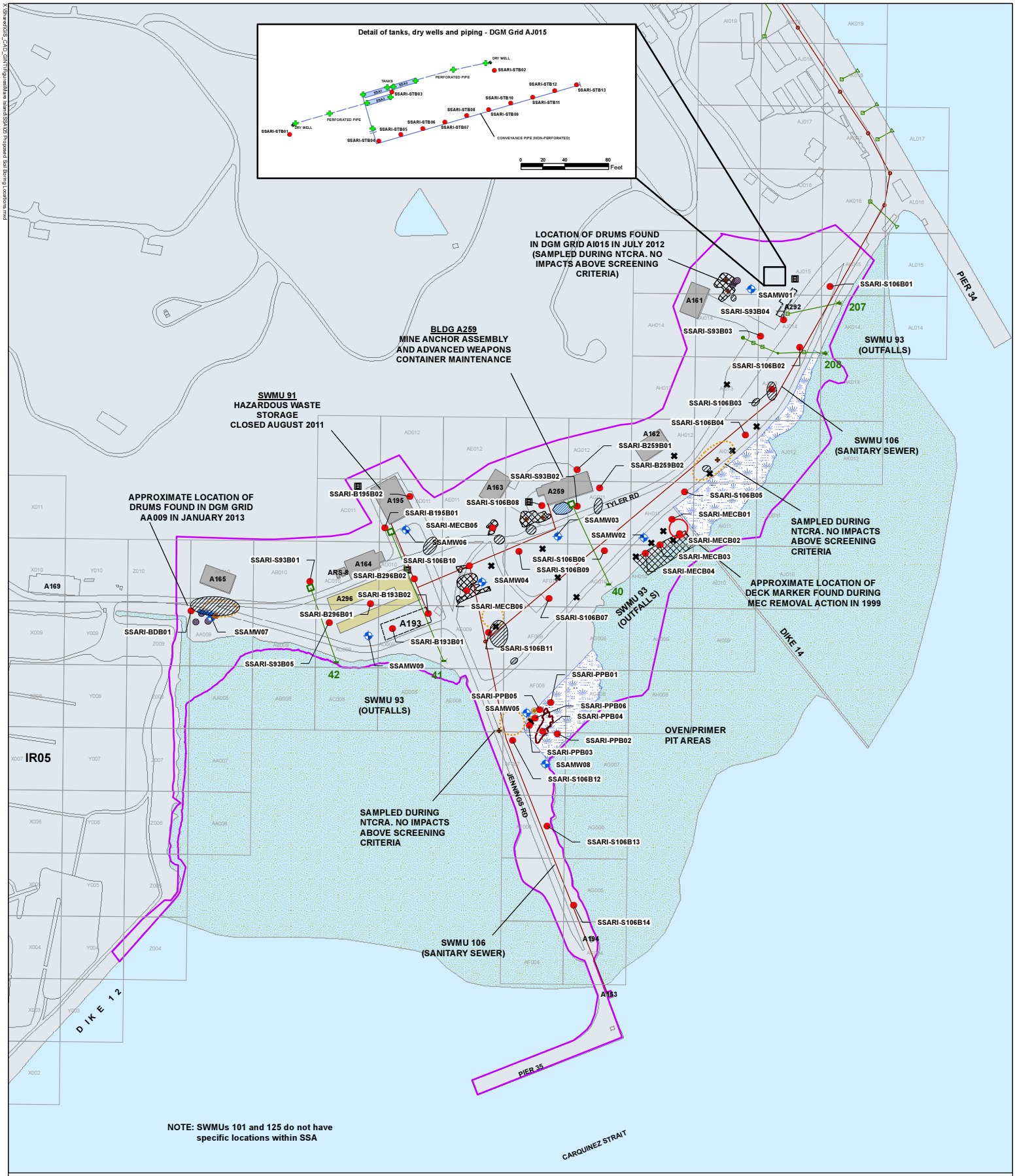
DCN: NRS-4812-0000-0010



NOTE: SWMUs 101 and 125 do not have specific locations within SSA

LEGEND

- PROPOSED BORING LOCATIONS
- REMOVED MUNITIONS AND EXPLOSIVES OF CONCERN (MEC) LOCATION
- PROPOSED GROUNDWATER MONITORING WELL
- BURIED DRUMS (REMOVED)
- OVEN PIT
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM DRAIN LINE
- FORMER UNDERGROUND STORAGE TANK LOCATION
- SWMU — SOLID WASTE MANAGEMENT UNIT
- ABRASIVE BLAST MATERIAL
- STORM SEWER OUTFALLS (SWMU 93)
- DISPOSAL PIT AREA
- UNRESOLVED PIT AREA
- SOUTH SHORE AREA BOUNDARY FOR
- REMOVED BUILDING
- EXPLOSIVES SAFE HAVEN
- NON-PIT AREAS WHERE HIGH DENSITY OF MEC ITEMS REMOVED
- PRIMER PIT (REMOVED)
- BUILDINGS
- WETLANDS
- TIDAL MUDFLATS
- NTCRA Sample Location (Metals, SVOCs, TPH)
- NTCRA Sample Location (Metals, Explosives)
- NTCRA Sample Location (Metals, VOCs, SVOCs, PCBs, TPH)
- NTCRA Sample Location (Metals, VOCs, SVOCs, PCBs, Pesticides, Dioxins/Furans, Explosives, Herbicides, TPH)
- STORM DRAIN (SWMU 93)

N

0 150 300 600 Feet

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FIGURE 3

SUMMARY OF PROPOSED SOIL AND GROUNDWATER SAMPLING LOCATIONS

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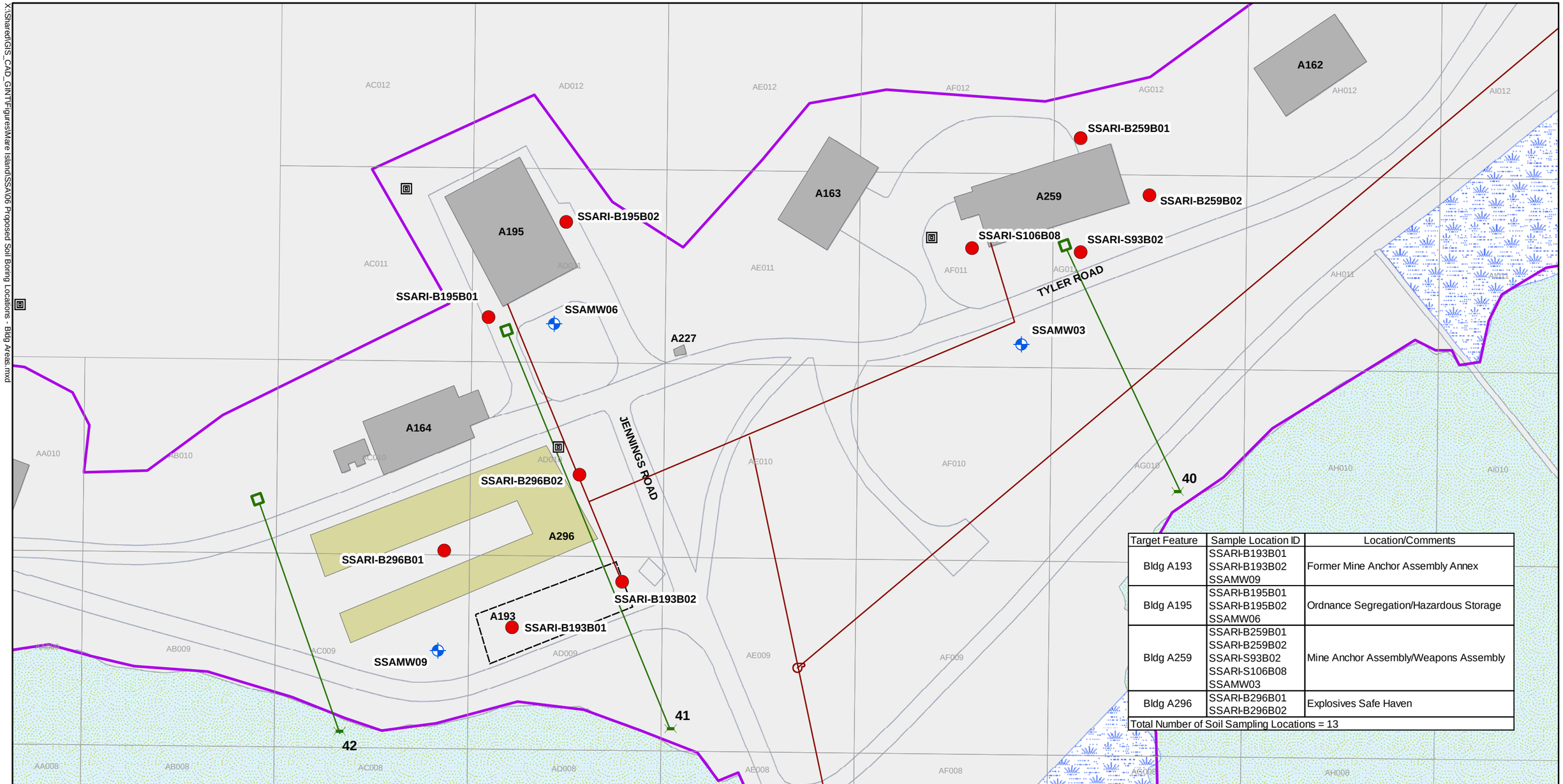
DATE: JUNE 2015
CONTRACT NO.: N62473-12-C-4812
DCN: NRS-4812-0000-0010

X:\Shared\GIS_CAD_GIN\Figures\Mare Island\SSA\06 Proposed Soil Boring Locations - Bldg Areas.mxd



Target Feature	Sample Location ID	Location/Comments
Bldg A193	SSARI-B193B01 SSARI-B193B02 SSAMW09	Former Mine Anchor Assembly Annex
Bldg A195	SSARI-B195B01 SSARI-B195B02 SSAMW06	Ordnance Segregation/Hazardous Storage
Bldg A259	SSARI-B259B01 SSARI-B259B02 SSARI-S93B02 SSARI-S106B08 SSAMW03	Mine Anchor Assembly/Weapons Assembly
Bldg A296	SSARI-B296B01 SSARI-B296B02	Explosives Safe Haven
Total Number of Soil Sampling Locations = 13		

LEGEND

- PROPOSED BORING LOCATION
- PROPOSED GROUNDWATER MONITORING WELL
- STORM SEWER OUTFALLS (SWMU 93)
- FORMER UNDERGROUND STORAGE TANK LOCATION
- BUILDINGS
- SOUTH SHORE AREA BOUNDARY
- REMOVED BUILDING
- EXPLOSIVES SAFE HAVEN
- WETLANDS
- TIDAL MUDFLATS
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM SEWER DRAIN LINE (SWMU 93)
- STORM DRAIN (SWMU 93)

N

0 50 100 200 Feet

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SAMPLING AND ANALYSIS PLAN

FIGURE 4

PROPOSED SOIL SAMPLING LOCATIONS - BUILDING AREAS

NORESAS

DATE: JUNE 2015
CONTRACT NO.: N62473-12-C-4812
DCN: NRS-4812-0000-0010

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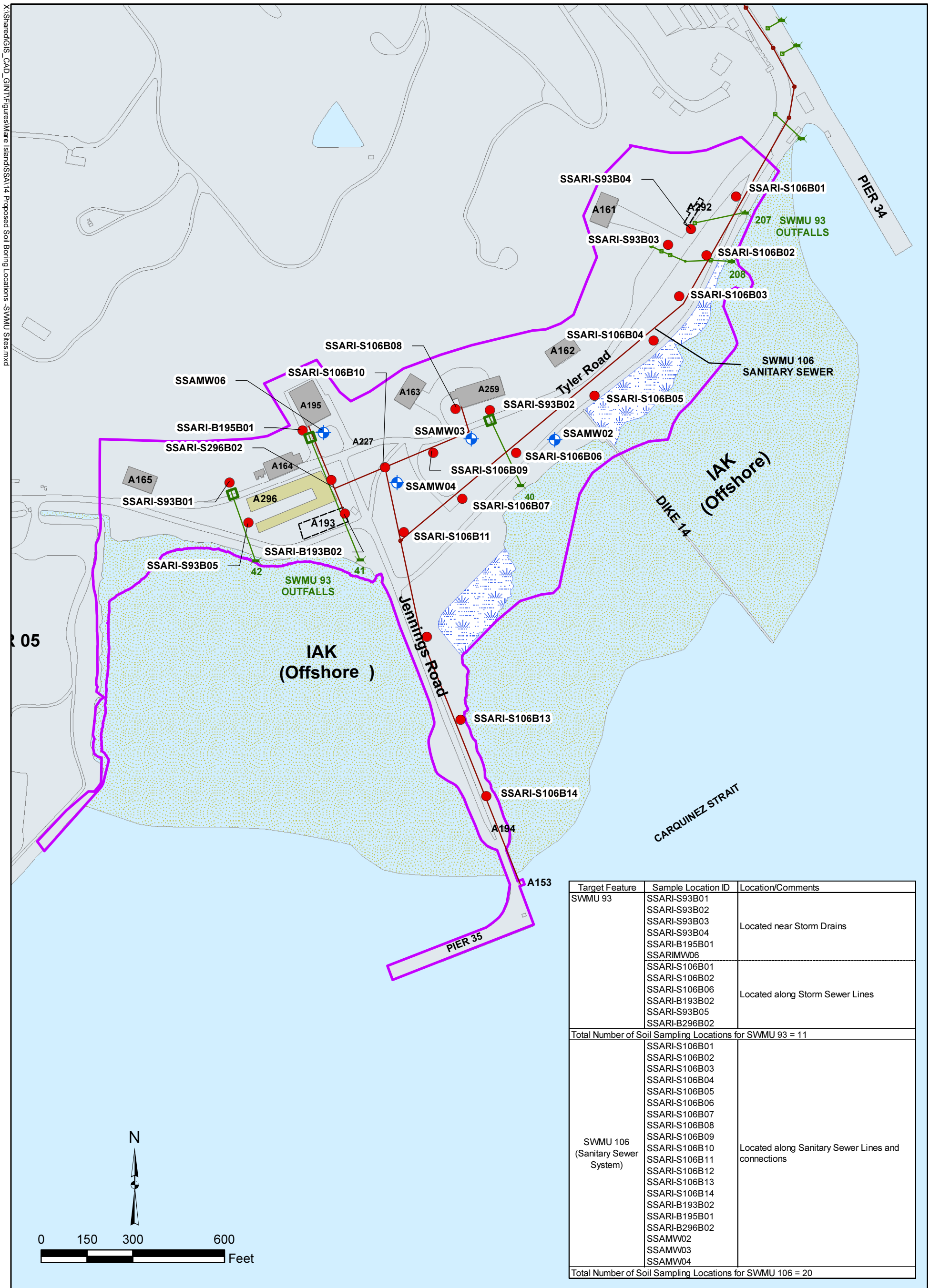

Target Feature	Sample Location ID	Location/Comments
SWMU 93	SSARI-S93B01 SSARI-S93B02 SSARI-S93B03 SSARI-S93B04 SSARI-B195B01 SSARIMW06	Located near Storm Drains
	SSARI-S106B01 SSARI-S106B02 SSARI-S106B06 SSARI-B193B02 SSARI-S93B05 SSARI-B296B02	Located along Storm Sewer Lines
Total Number of Soil Sampling Locations for SWMU 93 = 11		
SWMU 106 (Sanitary Sewer System)	SSARI-S106B01 SSARI-S106B02 SSARI-S106B03 SSARI-S106B04 SSARI-S106B05 SSARI-S106B06 SSARI-S106B07 SSARI-S106B08 SSARI-S106B09 SSARI-S106B10 SSARI-S106B11 SSARI-S106B12 SSARI-S106B13 SSARI-S106B14 SSARI-B193B02 SSARI-B195B01 SSARI-B296B02 SSAMW02 SSAMW03 SSAMW04	Located along Sanitary Sewer Lines and connections
Total Number of Soil Sampling Locations for SWMU 106 = 20		

LEGEND

- PROPOSED BORING LOCATION
- PROPOSED GROUNDWATER MONITORING WELL
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM SEWER DRAIN LINE (SWMU 93)
- IAK INVESTIGATION AREA K
- SWMU SOLID WASTE MANAGEMENT UNIT
- STORM DRAIN (SWMU 93)
- STORM SEWER OUTFALLS (SWMU 93)
- SOUTH SHORE AREA BOUNDARY
- REMOVED BUILDING
- BUILDINGS
- WETLANDS
- TIDAL MUDFLATS
- EXPLOSIVES SAFE HAVEN

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FIGURE 5

PROPOSED SOIL SAMPLING LOCATIONS
SWMU SITES

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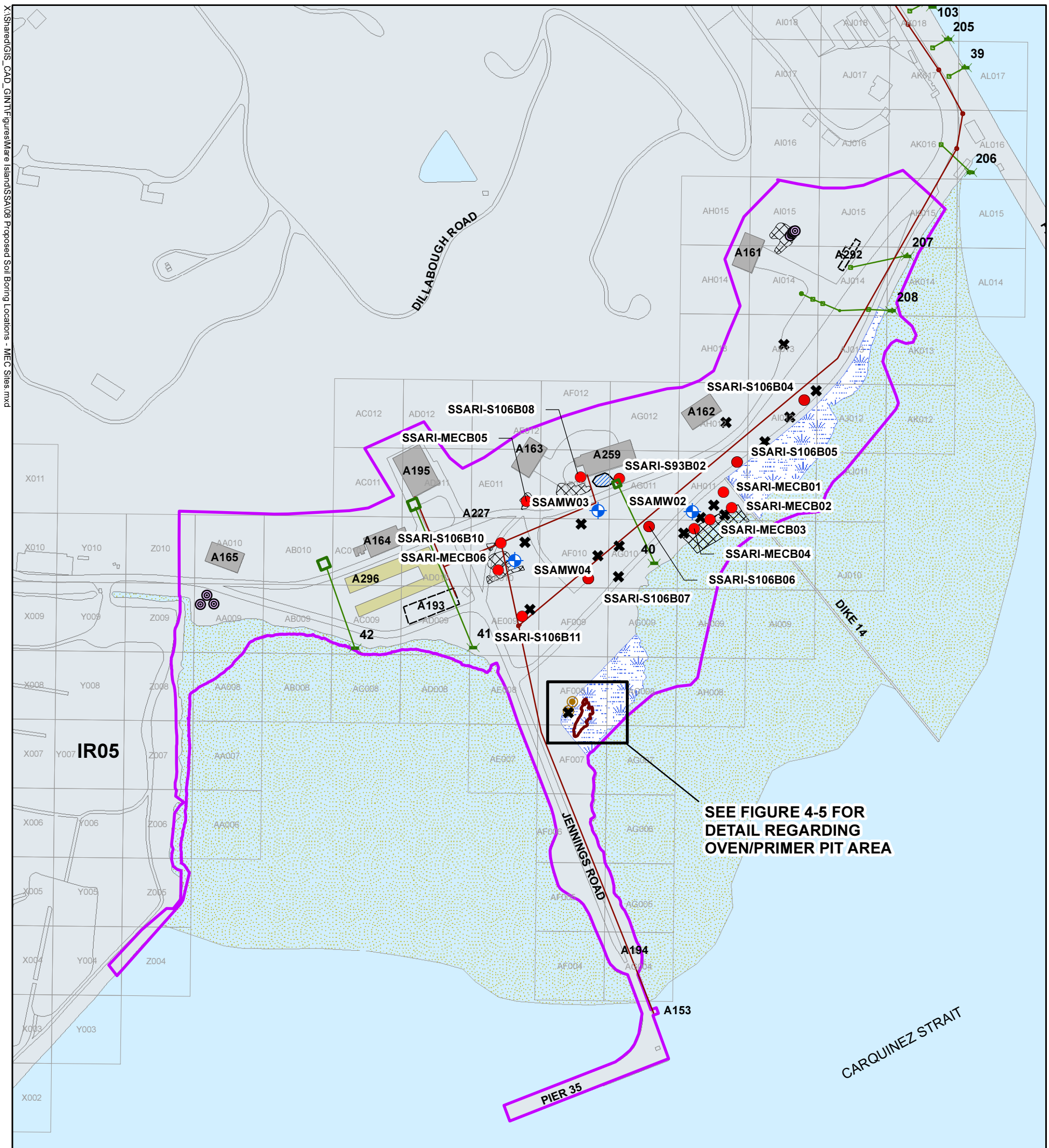
CONTRACT NO.: N62473-12-C-4812
DCN: NRS-4812-0000-0010



Target Feature	Sample Location ID	Location/Comments
Former MEC Sites	SSARI-MECB01	Disposal Pit in DGM Grids AH010/AH011 + deck marker recovered near Dike 14
	SSARI-MECB02	
	SSARI-MECB03	
	SSARI-MECB04	
	SSARI-MECB05	Disposal pit in DGM Grid AE011
	SSARI-MECB06	Disposal pit in DGM Grid AE010
	SSARI-S93B02	Disposal pit in DGM Grid AF011/AG011
	SSARI-S106B04	Disposal pit in DGM Grid AF011
	SSARI-S106B05	
	SSARI-S106B06	
	SSARI-S106B07	
	SSARI-S106B08	
	SSARI-S106B10	
	SSARI-S106B11	
	SSAMW02	
	SSAMW03	
	SSAMW04	
Total Number of Soil Sampling Locations = 17		
*See Figure 4-5 for soil sampling locations in the Oven/Primer Pit area		

LEGEND

- PROPOSED BORING LOCATION
- PROPOSED GROUNDWATER MONITORING WELL
- RECOVERED MUNITIONS AND EXPLOSIVE OF CONCERN (MEC)
- FORMER BURIED DRUM LOCATION
- OVEN PIT
- PRIMER PIT (REMOVED)
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM SEWER DRAIN LINE (SWMU 93)
- STORM DRAIN (SWMU 93)
- STORM SEWER OUTFALLS (SWMU 93)
- SOUTH SHORE AREA BOUNDARY
- BUILDINGS
- REMOVED BUILDING
- DISPOSAL PIT AREA
- UNRESOLVED PIT AREA (AF011)
- WETLANDS
- TIDAL MUDFLATS
- EXPLOSIVES SAFE HAVEN

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FIGURE 6

PROPOSED SOIL SAMPLING LOCATIONS - MEC SITES

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DATE: FEBRUARY 2015
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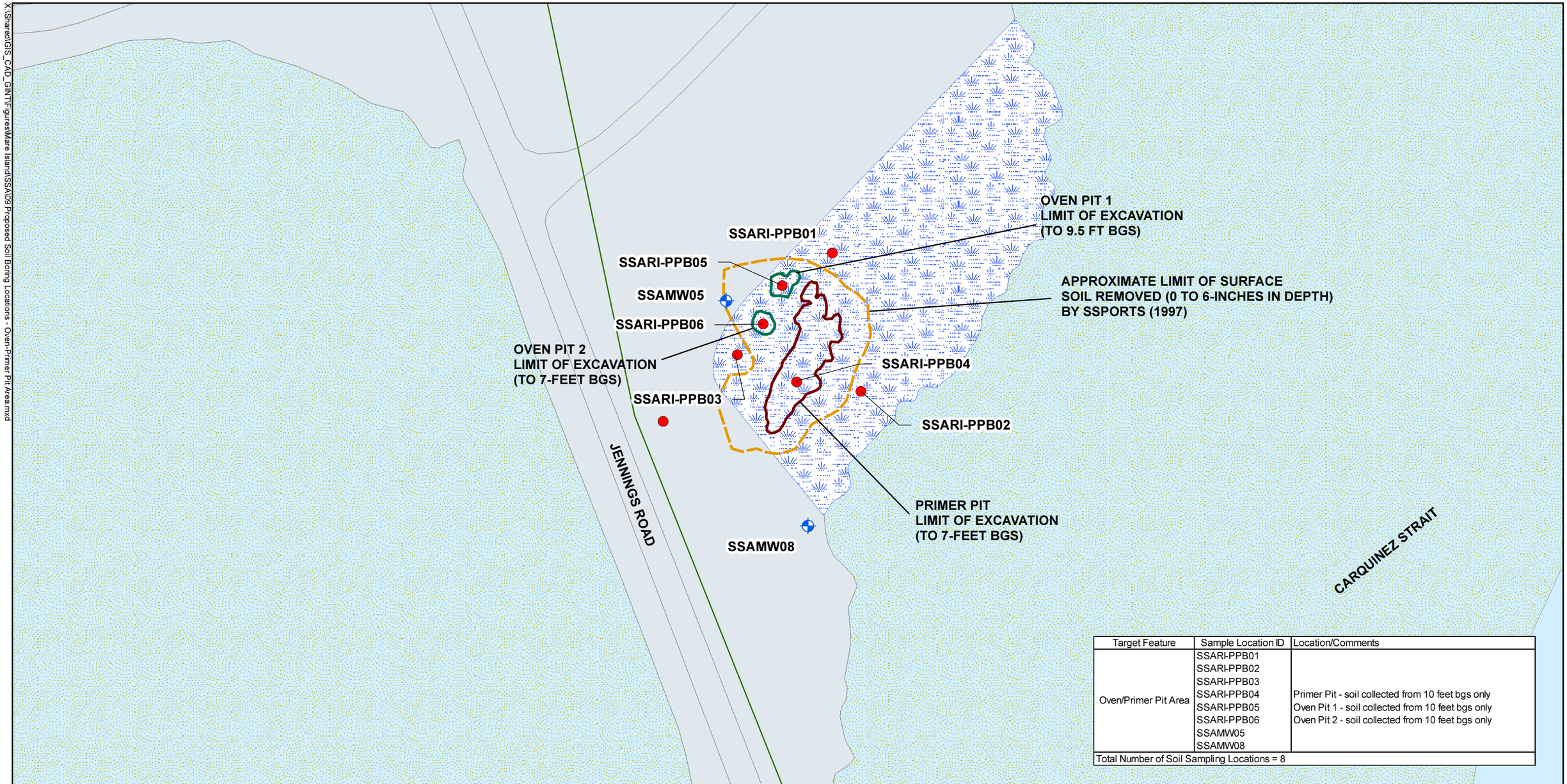
X:\Shared\GIS_CAD_GINT\Figures\Mare Island\SSA\09 Proposed Soil Boring Locations - Oven-Primer Pit Area.mxd



Target Feature	Sample Location ID	Location/Comments
Oven/Primer Pit Area	SSARI-PPB01	
	SSARI-PPB02	
	SSARI-PPB03	
	SSARI-PPB04	Primer Pit - soil collected from 10 feet bgs only
	SSARI-PPB05	Oven Pit 1 - soil collected from 10 feet bgs only
	SSARI-PPB06	Oven Pit 2 - soil collected from 10 feet bgs only
	SSAMW05	
	SSAMW08	
Total Number of Soil Sampling Locations = 8		

LEGEND

- PROPOSED BORING LOCATION
- PROPOSED GROUNDWATER MONITORING WELL
- SANITARY SEWER PIPELINE (SWMU 106)
- WETLANDS
- PRIMER PIT
- OVEN PITS
- BGS BELOW GROUND SURFACE
- LIMIT OF SURFACE SOIL EXCAVATION
- TIDAL MUDFLATS

N

0 35 70 140 Feet

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FIGURE 7

PROPOSED SOIL SAMPLING LOCATIONS - OVEN/PRIMER PIT AREAS

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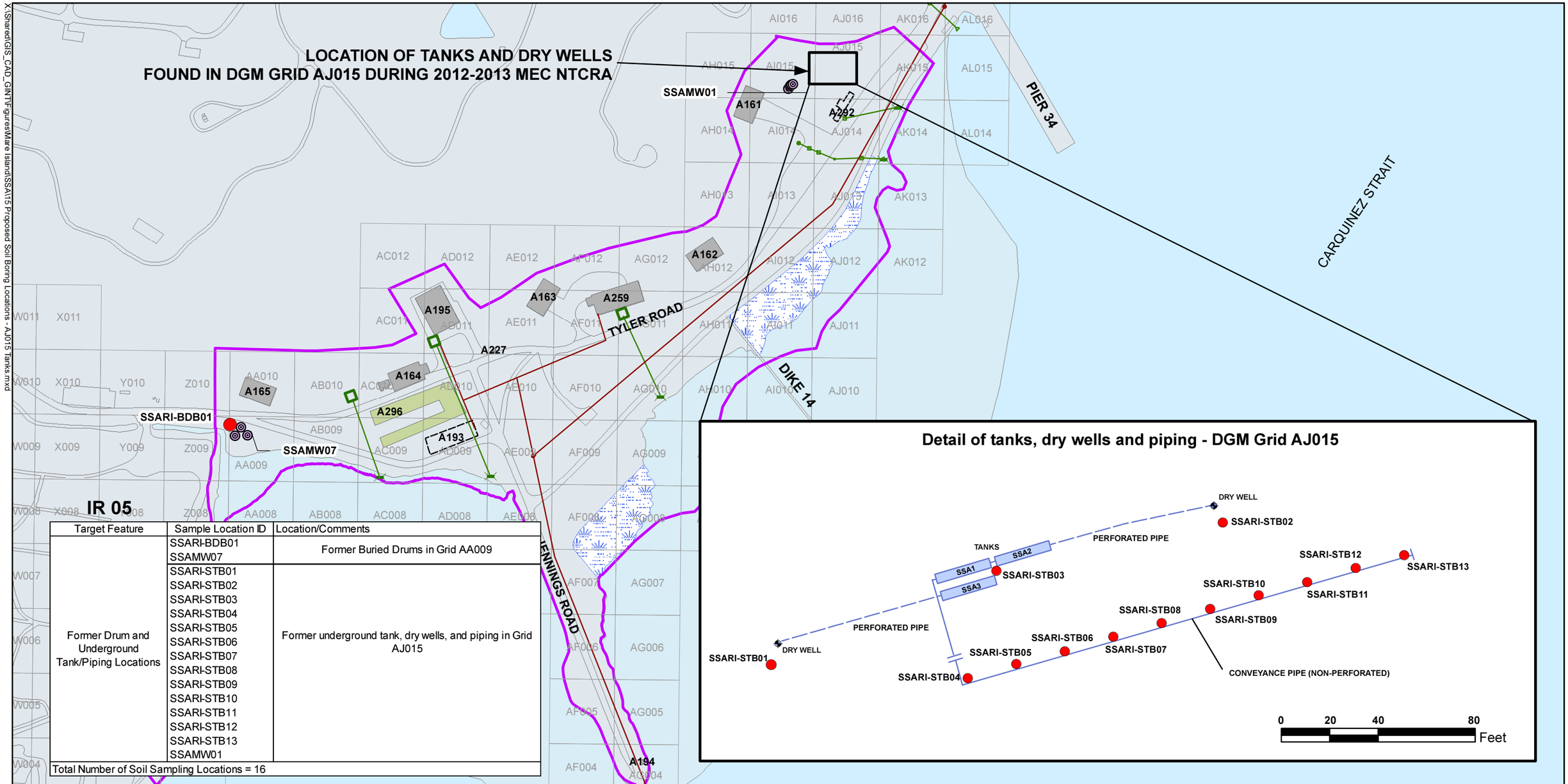
CONTRACT NO.: N62473-12-C-4812
DCN: NRS-4812-0000-0010

X:\Shared\GIS_CAD_GIN\Figures\Mare Island\SSA\15 Proposed Soil Boring Locations - AJ015 Tanks.mxd



Target Feature	Sample Location ID	Location/Comments
Former Drum and Underground Tank/Piping Locations	SSARI-BDB01 SSAMW07	Former Buried Drums in Grid AA009
	SSARI-STB01 SSARI-STB02 SSARI-STB03 SSARI-STB04 SSARI-STB05 SSARI-STB06 SSARI-STB07 SSARI-STB08 SSARI-STB09 SSARI-STB10 SSARI-STB11 SSARI-STB12 SSARI-STB13 SSAMW01	Former underground tank, dry wells, and piping in Grid AJ015
Total Number of Soil Sampling Locations = 16		

LEGEND

- PROPOSED BORING LOCATION
- PROPOSED GROUNDWATER MONITORING WELL
- FORMER BURIED DRUM LOCATION (REMOVED)
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM SEWER DRAIN LINE
- STORM SEWER OUTFALLS (SWMU 93)
- SOUTH SHORE AREA BOUNDARY
- REMOVED BUILDING
- BUILDINGS
- WETLANDS
- EXPLOSIVES SAFE HAVEN
- FORMER DRY WELL
- STORM DRAIN (SWMU 93)

N

0 150 300 600 Feet

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FIGURE 8

PROPOSED SOIL SAMPLING LOCATIONS
TANKS (GRID AJ015) AND DRUMS (GRID AA009)

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DATE: JUNE 2015
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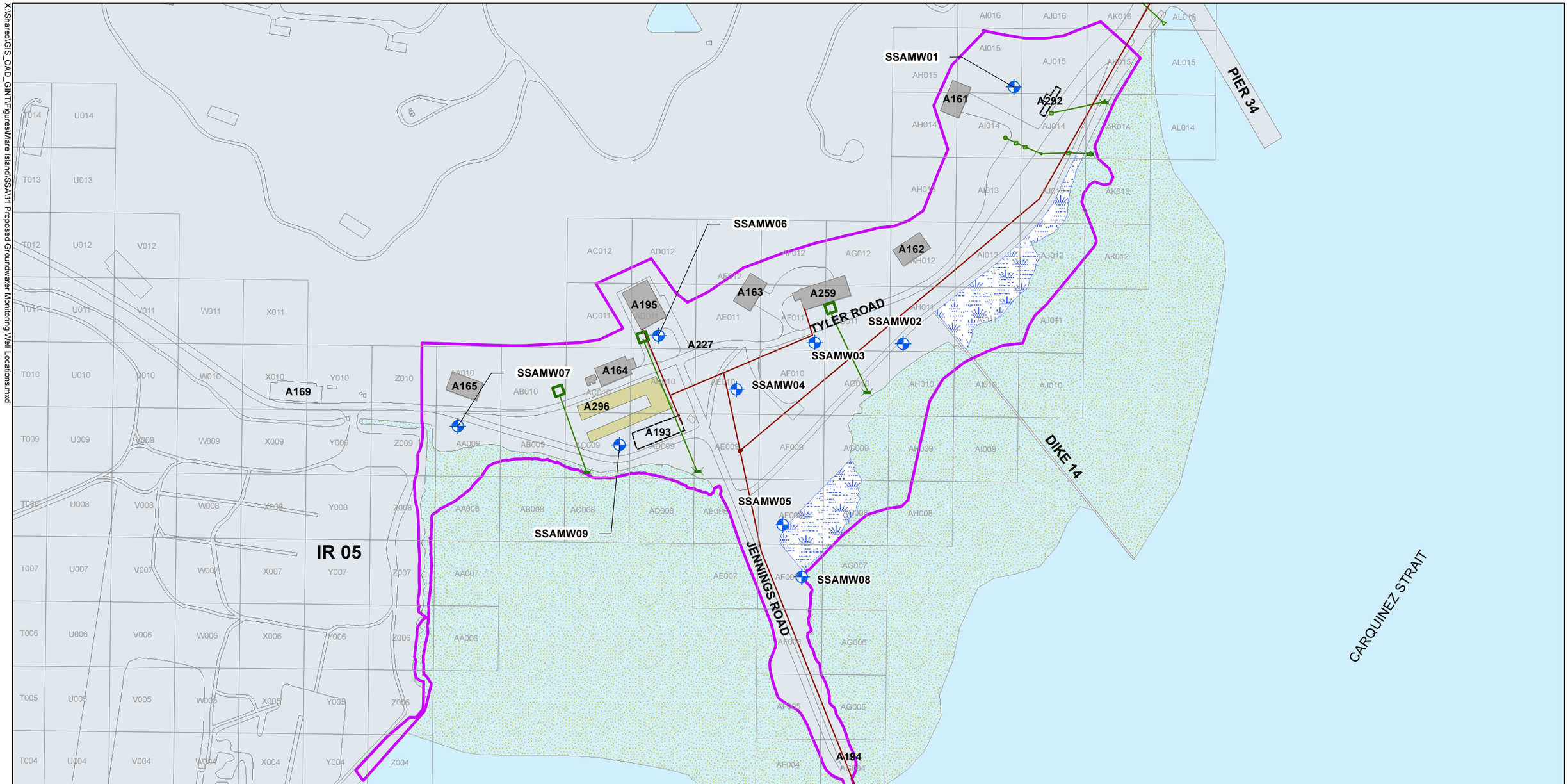
DCN: NRS-4812-0000-0010

X:\Shared\GIS_CAD_GINT\Figures\Mare Island\SSA\11 Proposed Groundwater Monitoring Well Locations.mxd



LEGEND

- PROPOSED GROUNDWATER MONITORING WELL
- SANITARY SEWER PIPELINE (SWMU 106)
- STORM SEWER DRAIN LINE
- STORM SEWER OUTFALLS (SWMU 93)
- SOUTH SHORE AREA BOUNDARY
- REMOVED BUILDING
- BUILDINGS
- WETLANDS
- TIDAL MUDFLATS
- EXPLOSIVES SAFE HAVEN
- STORM DRAIN (SWMU 93)

N

0 150 300 600 Feet

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SAMPLING AND ANALYSIS PLAN

FIGURE 9

PROPOSED GROUNDWATER MONITORING WELL LOCATIONS

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DCN: NRS-4812-0000-0010

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ATTACHMENT A-1

CHAIN-OF-CUSTODY FORM, LOW-FLOW PURGING & SAMPLING SHEET, BORING LOG AND FIELD CALIBRATION FORM

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NOREAS
Environmental Engineering and Science

CHAIN-OF-CUSTODY RECORD

COC No. MINS-0001
PAGE 1 of 1

Project Name/No:	Mare Island Naval Shipyard Remedial Investigation	Purchase Order No.	
Project Location:	South Shore Area Parcels VI & VIIB	Laboratory Name:	Calscience Environmental Lab
Company Name:	NOREAS, Inc.	Laboratory Contact:	Richard Villafania
Address:	16501 Scientific Way Irvine, CA 92618	Laboratory Address:	7440 Lincoln Way, Garden Grove, CA 92841-1427
Project Manager:	Jeff Brenner	Laboratory Phone:	(714) 895-5494
Phone/Fax No.	(949) 467-9106 or (949) 439-5402		
Project Contact:	Sevda K. Aleckson	Airbill No.	
Contact Phone:	(949) 467-9117 or (949) 510-8610		

Laboratory SDG No:

ANALYSES REQUIRED

Sample ID	Sampling Location	Date	Time	Matrix	QC Level (3/4)	Unpreserved	Preserved	# of Containers	VOCs (EPA 8260B)	TPH-G (EPA 8015B Mod.)	TPH-D/MO (EPA 8015B Mod.)	SVOCs (EPA 8270C)	PCBs (EPA 8082)	Metals (EPA 6010B/7470/7471)	Explosives (EPA 8330)	Dioxins/Furans (EPA 8290A)*	Radium-226 (EPA 905 Mod.)*	TDS (EPA 160.1)	EnCore/TerraCore Prep (EPA 5035	MS/MSD

Special Instructions: *Dioxin samples to be subcontracted to Maxxam Analytics and Radiological test to be subcontracted to GEL Environmental.

Turnaround Time: ☐ *24 HR* ☐ *48 HR* ☐ *72 HR*
☐ *STANDARD* *OR* ☐ _____

Matrix: W: Groundwater or Drinking water; S: Soil; W: Waste

Sampler(s) Name(s):

Relinquished By (signature):	Date	Received By (signature)	Date
Company	Time	Company	Time
Relinquished By (signature):	Date	Received By (signature)	Date
Company	Time	Company	Time

Sample Condition Upon Receipt (For Laboratory Use)

Cooler Temp (°C):

Sample Condition: ☐ **Intact** ☐ **Broken**

Cooler Seal: ☐ **Intact** ☐ **Broken**

DISTRIBUTION: White - Laboratory; Blue - Project File

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FIELD CALIBRATION FORM

Project Name: _____

Calibration by: _____ Date: _____

	Pre-Sampling	Post-Sampling
Time:		

pH/TEMPERATURE/CONDUCTIVITY/DISSOLVED OXYGEN METER

Instrument Manufacturer: _____ Model: _____

Instrument Serial Number: _____

CALIBRATION SOLUTIONS / STANDARDS

Solution Manufacturer	Solution	Lot Number	Expiration Date
Pine Env.	Auto Cal (pH 4, Conductivity, & Turbidity)		
Pine Env.	pH 10		
Pine Env.	pH 7		
Pine Env.	ORP		
Pine Env.	Sodium Sulfide		

INSTRUMENT CHECK-OUT

Solution Parameters	Standard Solution	Instrument Response	
		Pre-Sampling	Post-Sampling
pH Buffer	4.00		
	7.00		
	10.00		
Dissolved Oxygen[1]	0% Saturation		
	100% Saturation		
Conductivity	4.49 mS/cm		
Turbidity (NTUs)	0		
ORP	240 mV		
Temperature	NA		

[1] Instrument response was calibrated to the air (i.e. 100% saturation) and to a concentrated sodium sulfite solution (i.e. zero oxygen/ 0% saturation) per manufactures instructions.

Comments: _____

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NOREAS
Environmental Engineering and Science

LOW-FLOW PURGING AND SAMPLING DATA SHEET

Project Name: _____ Well Number: _____
Project Number: _____ Equipment: _____
Date: _____ Sample ID: _____ Time: _____
Site Personnel: _____ Duplicate ID: _____ Time: _____

Reference: Top of Casing	Before	After
Depth to Water (ft)		
Depth of Well (ft)		
Depth to Top of Screen (ft)		
Screen Length (ft)		
Pump Depth (ft)		
Pump Rate (mL/min)		
Sample Pump Rate (mL/min)		
System Volume (mL)		

Total Volume Purged (mL): _____

System Volume (mL) = (2.4*H)+470
where
2.4mL/ft = tubing volume per foot (1/8" I.D.)
H = length of tubing in feet
470 mL = Bladder volume + Flowthru cell volume

Time	pH	Specific Conductivity (µS/cm)	Dissolved Oxygen (mg/L)	Temp. (^oC)	ORP (mV)	Turbidity (NTU)	Depth to Water (ft)	Cum. Volume (mL)	Comments
Stability:	± 0.1 units	± 3 %	± 0.3 mg/L	± 1^oC	± 20 mV	± 10 %			

Field Tests:

Note 1: Stabilization criteria may change based on project-specific requirements.

Note 2: Samples were collected directly from pump unless otherwise noted.

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NOREAS
Environmental Engineering and Science

SUBSURFACE EXPLORATION LOG

BORING/WELL ID NUMBER:

Page __ of __

CLIENT:
PROJECT NUMBER:
LOCATION:

GEOLOGIST:
DATE DRILLED:
DRILLING COMPANY:

TOTAL DEPTH:
DRILLING METHOD:
SAMPLE METHOD:

Depth (ft bgs)		Time (24 hr)	FID/PID (ppm)		GEOLOGIC DESCRIPTION														USCS Soil Class. Symbol	Lithologic Contact (ft bgs)
			Soil Sample / Soil Cuttings	Breathing Zone	% gravel	% sand	% non-plastic fines	% plastic fines	Grading	Lithologic Name/Soil Type	Color	Moisture	Density	Consistency	Plasticity	Angularity	Max. grain size	Additonal Observations		
Notes:					> 1/4 inch	visible -1/4 in.	visible with hand lens	not visible	poorly vs. well	See USCS flow Charts. Describe sand and gravel grading, ie, fine to coarse grained	Use Munsell color chart if available	Dry Moist Wet	Course: v. loose loose md. dense dense v. dense	Fines: v. soft soft md. Stiff v.stiff hard	high med low non	A Sa Sr R	in inches	odor, staining, minerology, stucture, cementation, other distinctive charateristics		

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ATTACHMENT A-2

LABORATORY ACCREDITATION LETTERS

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CERTIFICATE OF ACCREDITATION

ANSI-ASQ National Accreditation Board/ACLASS
500 Montgomery Street, Suite 625, Alexandria, VA 22314, 877-344-3044

This is to certify that

Calscience Environmental Laboratories, Inc.
17440 Lincoln Way
Garden Grove, CA 92841

has been assessed by ACLASS
and meets the requirements of

ISO/IEC 17025:2005 and DoD-ELAP

while demonstrating technical competence in the field(s) of

TESTING

Refer to the accompanying Scope(s) of Accreditation for information regarding the types of tests to which this accreditation applies.

ADE-1864

Certificate Number

ACLASS Approval

Certificate Valid: 04/25/2014-04/25/2016
Version No. 001 Issued: 04/28/2014

This laboratory is accredited in accordance with the recognized International Standard ISO/IEC 17025:2005. This accreditation demonstrates technical competence for a defined scope and the operation of a laboratory quality management system (*refer to joint ISO-ILAC-IAF Communiqué dated January 2009*).

SCOPE OF ACCREDITATION TO ISO/IEC 17025:2005 & DoD-ELAP

Calscience Environmental Laboratories, Inc.

17440 Lincoln Way, Garden Grove, CA 92841
Larry Lem Phone: 714-895-5494
LLem@calscience.com www.calscience.com

TESTING

Valid to: April 25, 2016 Certificate Number: ADE- 1864

I. Environmental

MATRIX	SPECIFIC TEST or GROUP of ANALYTES**	SPECIFICATION OR STANDARD METHOD (all SW846 unless specified)	* KEY EQUIPMENT OR TECHNOLOGY USED
Air	Fixed Gases	ASTM D-1946	GC-TCD
Air	Air Hydrocarbons	Calscience SOP M374/ BTXE APH	GC-MS
Air	Air VOCs	EPA TO-15	GC-MS
Air	Sorbent Tube VOCs	EPA TO-17 (M)	GC-MS
Air	Air Hydrocarbons	EPA TO-3 (M)	GC-FID
Aqueous	Dissolved Gases	RSK-175 (M)	GC-FID
Aqueous	Hexavalent Chromium (Cr VI)	EPA 218.6	IC
Aqueous	Anions	EPA 300.0	IC
Aqueous	Ammonia	EPA 350.1	Segmented Flow Analyzer (SFA)
Aqueous	Metals	EPA 7470A	CVAA

MATRIX	SPECIFIC TEST or GROUP of ANALYTES**	SPECIFICATION OR STANDARD METHOD (all SW846 unless specified)	* KEY EQUIPMENT OR TECHNOLOGY USED
Aqueous	Turbidity	SM 2130 B	Turbidimetric
Aqueous	Hardness	SM 2340 B	Calculation
Aqueous	Hardness	SM 2340C	Titrimetric
Aqueous	Specific Conductance	SM 2510 B	Probe/ Meter
Aqueous	Solids, Total	SM 2540 B	Gravimetric
Aqueous	Solids, Total Dissolved	SM 2540 C	Gravimetric
Aqueous	Solids, Total Suspended	SM 2540 D	Gravimetric
Aqueous	Ferrous Iron (Fe+2)	SM 3500-Fe B	Colorimetric
Aqueous	Phosphorus, Total Phosphate and Orthophosphate	SM 4500 P B/E	Colorimetric
Aqueous	pH	SM 4500-H+ B	Probe/ Meter
Aqueous	Chloride	SM 4500-Cl^- C	Titrimetric
Aqueous	Cyanide	SM 4500-CN E	Colorimetric
Aqueous	Carbon Dioxide	SM 4500-CO2 D	Titrimetric
Aqueous	Potassium Permanganate	SM 4500-KMnO4 B	Colorimetric
Aqueous	Ammonia (as N)	SM 4500-NH3 B/C	Titrimetric

MATRIX	SPECIFIC TEST or GROUP of ANALYTES**	SPECIFICATION OR STANDARD METHOD (all SW846 unless specified)	* KEY EQUIPMENT OR TECHNOLOGY USED
Aqueous	Ammonia, unionized (as N)	SM 4500-NH3 B/C (M)	Probe/ Meter
Aqueous	Nitrite (as N)	SM 4500-NO2 B	Colorimetric
Aqueous	Nitrate (as N)	SM 4500-NO3 E	Colorimetric
Aqueous	Biochemical Oxygen Demand (BOD)	SM 5210 B	Probe/ Meter
Aqueous	Chemical Oxygen Demand (COD)	SM 5220 D	Colorimetric
Aqueous	Total and Dissolved Organic Carbon	SM 5310 B	Combustion TOC Analyzer
Aqueous	Total and Dissolved Organic Carbon	SM 5310 D	Wet Oxidation
Aqueous	EDB and DBCP	EPA 504.1	GC-ECD
Aqueous	Volatiles	EPA 524.2	GC-MS
Aqueous	Oil & Grease	EPA 1664A	Gravimetric
Aqueous/Solids	Perchlorate	EPA 314.0	Conductometric
Aqueous/Solids	Ignitability/Flashpoint	EPA 1010A	Closed cup
Aqueous/Solids	TKN	EPA 351.3	Titrimetric
Aqueous/Solids	Metals	EPA 6010B & EPA 6010C	ICP-AES
Aqueous/Solids	Metals	EPA 6020 & EPA 6020A	ICP-MS

MATRIX	SPECIFIC TEST or GROUP of ANALYTES**	SPECIFICATION OR STANDARD METHOD (all SW846 unless specified)	* KEY EQUIPMENT OR TECHNOLOGY USED
Aqueous/Solids	Perchlorate	EPA 6850 `	LC/MS/MS
Aqueous/Solids	Hexavalent Chromium (CrVI)	EPA 7196A	Colorimetric
Aqueous/Solids	Hexavalent Chromium (CrVI)	EPA 7199	IC
Aqueous/Solids	Anions	EPA 9056A	IC
Aqueous/Solids	Particle Size	Laser ASTM D4464 (M)	Laser/PIDS
Aqueous/Solids	Cyanide	EPA 9010C/9014	Colorimetric
Aqueous/Solids	Cyanide, Reactive Sulfide, Reactive	SW 846 Sec 7.3	Distillation Reactive
Aqueous/Solids	1,4-Dioxane	8270C(M) Isotope Dilution	GC-MS
Aqueous/Solids	1,2,3-Trichloropropane	Calscience SOP M389 SRL 524M-TCP	GC-MS
Aqueous/Solids	Organic Acids	Calscience SOP M490 Organic Acids	HPLC/UV
Aqueous	NDMA	EPA 1625C	GC-MS
Aqueous/Solids	Petroleum Hydrocarbons	EPA 8015B	GC-FID
Aqueous/Solids	Organochlorine Pesticides	EPA 8081A & EPA 8081B	GC-ECD
Aqueous/Solids	PCBs	EPA 8082 & EPA 8082A	GC-ECD
Aqueous/Solids	Organophoshorus Pesticides	EPA 8141A	GC-NPD

MATRIX	SPECIFIC TEST or GROUP of ANALYTES**	SPECIFICATION OR STANDARD METHOD (all SW846 unless specified)	* KEY EQUIPMENT OR TECHNOLOGY USED
Aqueous/Solids	Herbicides	EPA 8151A	GC-ECD
Aqueous/Solids	Volatiles	EPA 8260B & EPA 8260C	GC-MS
Aqueous/Solids	Base Neutrals & Acids	EPA 8270C & EPA 8270D	GC-MS
Aqueous/Solids	PCB Congeners	EPA 8270C SIM PCB Congeners	GC-MS
Aqueous/Solids	Explosives	EPA 8330A	HPLC
Aqueous/Solids	Petroleum Hydrocarbons	NWTPH EPH	GC-FID
Aqueous/Solids	Petroleum Hydrocarbons	NWTPH VPH GC/MS	GC-MS
Aqueous/Solids	Petroleum Hydrocarbons	NWTPH-Dx	GC-FID
Aqueous/Solids	Petroleum Hydrocarbons	NWTPH-Gx	GC-FID
Aqueous/Solids	Dieldrin	Calscience SOP M447/ EPA 8270D M/ TQ	GC-MS
Aqueous	Base, Neutrals and Acids (Dieldrin)	Calscience SOP M447/ EPA 8270D M/ TQ	GC-MS
Solids	Organic Lead	CA LUFT	GFAA
Solids	pH	EPA 9045D	Probe/ Meter
Solids	Mercury	EPA 7471A & 7471B	CVAA
Aqueous	Digestion	EPA 3005A	Digestion

MATRIX	SPECIFIC TEST or GROUP of ANALYTES**	SPECIFICATION OR STANDARD METHOD (all SW846 unless specified)	* KEY EQUIPMENT OR TECHNOLOGY USED
Aqueous	Digestion	EPA 3010A	Digestion
Aqueous	Digestion	EPA 3020A	Digestion
Aqueous	Separatory Funnel Extraction	EPA 3510C	Separatory Funnel Extraction
Aqueous	Micro Extraction	EPA 3511	Micro Extraction
Aqueous	Continuous Liquid-Liquid Extraction	EPA 3520C	Continuous Liquid-Liquid Extraction
Aqueous/Solids	Prep	EPA 3630C	Silica Gel Cleanup
Aqueous/Solids	Prep	EPA 3660A	Sulfur Cleanup
Aqueous/Solids	Prep	EPA 3665A	Sulfuric Acid Cleanup
Aqueous/Solids	TCLP	EPA 1311	Leaching
Aqueous/Solids	SPLP	EPA 1312	Leaching
Aqueous/Solids	STLC	CA Title 22, Chapter 11, Article 5, Appendix II	Leaching
Solids	Acid Digestion	EPA 3050B	Prep
Solids	Alkaline Digestion	EPA 3060A	Prep
Solids	Soxhlet Extraction	EPA 3540C	Prep
Solids	Pressurized Fluid Extraction (PFE)	EPA 3545A	Prep

MATRIX	SPECIFIC TEST or GROUP of ANALYTES**	SPECIFICATION OR STANDARD METHOD (all SW846 unless specified)	* KEY EQUIPMENT OR TECHNOLOGY USED
Solids	Ultrasonic Extraction	EPA 3550C	Prep
Solids	Waste Dilution	EPA 3580A	Prep
Solids	Purge & Trap Volatile	EPA 5030C	Prep
Solids	Purge & Trap Volatile	EPA 5035A	Prep
Solids	Multi-Incremental Sampling (MIS)	ASTM D 6323-98	Gravimetric
Solids	% Moisture	ASTM D2216 (M)	Gravimetric

Notes:

1. ** = As Applicable*
2. *** = Refer to Accredited Analyte Listing for specific analytes in which the laboratory is accredited.*
3. *This scope is part of and must be included with the Certificate of Accreditation No. ADE- 1864*

Vice President

500 Montgomery St. Suite 625 | Alexandria, VA 22314 | 703-836-0025 | www.aclasscorp.com

Calscience Environmental Laboratories, Inc.												
17440 Lincoln Way												
Garden Grove, CA 92841												
Analyte	**Matrix**											
	Aqueous						**Solid**				**Air**	
Trace Metals												
Aluminum	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Antimony	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Arsenic	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Barium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Beryllium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Boron	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Cadmium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Chromium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Hexavalent Chromium	EPA 218.6	EPA 7196A	EPA 7199				EPA 7196A	EPA 7199				
Cobalt	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Copper	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Iron	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Lead	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Manganese	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Mercury	EPA 7470A						EPA 7471A	EPA 7471B				
Molybdenum	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Nickel	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Selenium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Silver	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Strontium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Thallium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Tin	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Titanium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Vanadium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Zinc	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Silica as SiO2	EPA 6010B	EPA 6010C										
Calcium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Magnesium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Potassium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Sodium	EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A			EPA 6010B	EPA 6010C	EPA 6020	EPA 6020A		
Organic Lead							DHS LUFT					
Anions												
Bromide	EPA 300.0	EPA 9056A					EPA 9056A					
Chloride	EPA 300.0	EPA 9056A					EPA 9056A					
Fluoride	EPA 300.0	EPA 9056A					EPA 9056A					
Nitrate as N	EPA 300.0	EPA 9056A					EPA 9056A					
Nitrate + Nitrite as N	EPA 300.0	EPA 9056A										
Nitrite as N	EPA 300.0	EPA 9056A										
ortho-Phosphate as P	EPA 300.0	EPA 9056A					EPA 9056A					
Sulfate	EPA 300.0	EPA 9056A					EPA 9056A					
Perchlorate												
Perchlorate	EPA 314.0	EPA 6850					EPA 314.0 (M)	EPA 6850				
General Chemistry												
Ammonia as N	EPA 350.1	SM4500-NH3 B/C (M)	SM4500-NH3 B/C									
Total Kjeldahl Nitrogen	EPA 351.3						EPA 351.3					
Ignitability/Flashpoint	EPA 1010A						EPA 1010A					
n-Hexane Extractable Material(O&G)(Grav)	EPA 1664A											
Total Hardness by Calculation	SM2340 B											
Total Hardness as CaCO3	SM2340 C											
Turbidity	SM2310 B											
Specific Conductance	SM2510 B											
Total Solids	SM2540 B											
Total Dissolved Solids	SM2540 C											
Total Suspended Solids	SM2540 D											
Ferrous Iron	SM3500-Fe B											
Cyanide, total	SM4500-CN E											
Carbon Dioxide	SM4500-CO2 D											
Potassium Permanganate	SM4500-KMnO4 B											
ortho-Phosphate as P	SM4500-P B/E											
Total Phosphorus	SM4500-P B/E											
BOD	SM5210 B											
CBOD	SM5210 B											
COD	SM5220 D											
TOC	SM5310 B	SM5310D										

Calscience Environmental Laboratories, Inc.												
17440 Lincoln Way												
Garden Grove, CA 92841												
Analyte	**Matrix**											
	Aqueous						**Solid**				**Air**	
Chloride	SM4500-Cl- C											
pH	SM4500-H+ B											
Nitrite as N	SM4500-NO2- B											
Nitrate as N	SM4500-NO3- E											
Reactive Sulfide							EPA 7.3.3.2					
Reactive Cyanide							EPA 7.3.3.2					
Amenable Cyanide							EPA 9010C / 9014					
Cyanide, total							EPA 9010C / 9014					
Corrosivity (pH)							EPA 9045 D					
% Moisture							ASTM D2216					
Petroleum Hydrocarbons												
Diesel Range Organics (DRO)	EPA 8015B	NWTPH-Dx					EPA 8015B	NWTPH-Dx DRO				
Gasoline Range Organics (GRO)	EPA 8015B	EPA 8260B	EPA 8260C	NWTPH-Gx			EPA 8015B	NWTPH-Gx GRO				
Benzene in VPH	EPA 8260B	EPA 8260C	NWTPH VPH (GC/MS)				NWTPH VPH (GC/MS)					
Ethylbenzene in VPH	EPA 8260B	EPA 8260C	NWTPH VPH (GC/MS)				NWTPH VPH (GC/MS)					
tert-Butyl methyl ether (MTBE) in VPH	EPA 8260B	EPA 8260C	NWTPH VPH (GC/MS)				NWTPH VPH (GC/MS)					
Naphthalene in VPH	EPA 8260B	EPA 8260C	NWTPH VPH (GC/MS)				NWTPH VPH (GC/MS)					
Toluene in VPH	EPA 8260B	EPA 8260C	NWTPH VPH (GC/MS)				NWTPH VPH (GC/MS)					
o-Xylene in VPH	EPA 8260B	EPA 8260C	NWTPH VPH (GC/MS)				NWTPH VPH (GC/MS)					
m&p-Xylene in VPH	EPA 8260B	EPA 8260C	NWTPH VPH (GC/MS)				NWTPH VPH (GC/MS)					
Xylenes, total in VPH	EPA 8260B	EPA 8260C	NWTPH VPH (GC/MS)				NWTPH VPH (GC/MS)					
C5-C8 Aliphatics (MA VPH)	EPA 8260B	EPA 8260C	NWTPH VPH (GC/MS)				NWTPH VPH (GC/MS)					
C5-C8 Aliphatics Unadjusted (MA VPH)	EPA 8260B	EPA 8260C	NWTPH VPH (GC/MS)				NWTPH VPH (GC/MS)					
C9-C10 Aromatics (MA VPH)	EPA 8260B	EPA 8260C	NWTPH VPH (GC/MS)				NWTPH VPH (GC/MS)					
Benzene in GRO	EPA 8260B	EPA 8260C										
Ethylbenzene in GRO	EPA 8260B	EPA 8260C										
Toluene in GRO	EPA 8260B	EPA 8260C										
Xylenes, total in GRO	EPA 8260B	EPA 8260C										
C19-C36 Aliphatics (MA EPH)	NWTPH EPH						NWTPH EPH					
C9-C18 Aliphatics (MA EPH)	NWTPH EPH						NWTPH EPH					
C11-C22 Aromatics Unadjusted (MA EPH)	NWTPH EPH						NWTPH EPH					
Pesticides												
Aldrin	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
delta-BHC	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
alpha-BHC	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
beta-BHC	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
gamma-BHC(Lindane)	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
alpha-Chlordane	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
gamma-Chlordane	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
Chlordane, technical	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
4,4'-DDD	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
4,4'-DDE	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
4,4'-DDT	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
Dieldrin	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
Endosulfan I	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
Endosulfan II	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
Endosulfan sulfate	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
Endrin aldehyde	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
Endrin ketone	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
Endrin	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
Heptachlor	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
Heptachlor epoxide (beta)	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
Methoxychlor	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
Toxaphene	EPA 8081A	EPA 8081B					EPA 8081A	EPA 8081B				
PCBs												
Aroclor 1016	EPA 8082	EPA 8082A					EPA 8082	EPA 8082A				
Aroclor 1221	EPA 8082	EPA 8082A					EPA 8082	EPA 8082A				
Aroclor 1232	EPA 8082	EPA 8082A					EPA 8082	EPA 8082A				
Aroclor 1242	EPA 8082	EPA 8082A					EPA 8082	EPA 8082A				
Aroclor 1248	EPA 8082	EPA 8082A					EPA 8082	EPA 8082A				
Aroclor 1254	EPA 8082	EPA 8082A					EPA 8082	EPA 8082A				
Aroclor 1260	EPA 8082	EPA 8082A					EPA 8082	EPA 8082A				
Organophoshorus Pesticides												
Azinphos-methyl (Guthion)	EPA 8141A						EPA 8141A					

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Analyte	**Matrix**											
	Aqueous						**Solid**				**Air**	
Chlorpyrifos	EPA 8141A						EPA 8141A					
Diazinon	EPA 8141A						EPA 8141A					
Dimethoate	EPA 8141A						EPA 8141A					
Ethion	EPA 8141A						EPA 8141A					
Ethoprop	EPA 8141A						EPA 8141A					
Famphur	EPA 8141A						EPA 8141A					
Malathion	EPA 8141A						EPA 8141A					
Methyl Parathion	EPA 8141A						EPA 8141A					
Ethyl Parathion	EPA 8141A						EPA 8141A					
Phorate	EPA 8141A						EPA 8141A					
Ronnel	EPA 8141A						EPA 8141A					
Stirophos	EPA 8141A						EPA 8141A					
Dichlorvos (DDVP)	EPA 8141A						EPA 8141A					
Disulfoton	EPA 8141A						EPA 8141A					
Hebicides												
MCPA	EPA 8151A						EPA 8151A					
MCPP	EPA 8151A						EPA 8151A					
2,4-D	EPA 8151A						EPA 8151A					
Dalapon	EPA 8151A						EPA 8151A					
2,4-DB	EPA 8151A						EPA 8151A					
Dicamba	EPA 8151A						EPA 8151A					
Dichlorprop	EPA 8151A						EPA 8151A					
Dinoseb	EPA 8151A						EPA 8151A					
2,4,5-TP (Silvex)	EPA 8151A						EPA 8151A					
2,4,5-T	EPA 8151A						EPA 8151A					
VOCs												
Acetone	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Acetonitrile												
Acrolein												
Acrylonitrile												
1,2-Dibromo-3-Chloropropane												EPA TO-17 (M)
1,1,1,2-Tetrachloroethane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				EPA TO-17 (M)
1,1,1-Trichloroethane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
1,1,2,2-Tetrachloroethane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
1,1,2-Trichloro-1,2,2-Trifluoroethane	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
1,1,2-Trichloroethane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
1,1-Dichloroethane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
1,1-Dichloroethylene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
1,1-Dichloropropene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
1,2,3-Trichlorobenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
1,2,3-Trichloropropane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				EPA TO-17 (M)
1,2,4-Trichlorobenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				EPA TO-17 (M)
1,2,3-Trichloropropane (TCP)												
1,2,4-Trichlorobenzene	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
1,2,4-Trimethylbenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
1,2-Dibromo-3-chloropropane (DBCP)												
1,2-Dibromoethane (EDB)	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
1,2-Dichlorobenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
1,2-Dichloroethane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
1,2-Dichloropropane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
1,2-Dichlorotetrafluoroethane (Freon 114)												
1,3,5-Trimethylbenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
1,3-Butadiene											EPA TO-15 GCMS	
1,3-Dichlorobenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
1,3-Dichloropropane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
1,4-Dichlorobenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
1,4-Dioxane											EPA TO-15 GCMS	
2,2-Dichloropropane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
2-Butanone (MEK)	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
2-Chloroethylvinylether												
sec-Butylbenzene												EPA TO-17 (M)
2-Chlorotoluene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
2-Hexanone	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
4-Ethyltoluene											EPA TO-15 GCMS	
4-Chlorotoluene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
4-Methyl-2-pentanone (MIBK)	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)

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Analyte	**Matrix**											
	Aqueous						**Solid**				**Air**	
Acrylonitrile	EPA 8260B	EPA 8260C										
4-Isopropyltoluene			524.2									
Benzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Benzyl Chloride											EPA TO-15 GCMS	
Bromobenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
Bromochloromethane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
Bromodichloromethane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Bromoform	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Bromomethane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Butane											EPA TO-15 GCMS	
cis-1,2-Dichloroethylene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
cis-1,3-Dichloropropylene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Carbon disulfide	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Carbon tetrachloride	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Chlorobenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Chlorodibromomethane			524.2									
Chloroethane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Chloroform	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Chloromethane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Cyclohexane											EPA TO-15 GCMS	
Dibromochloromethane	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Dibromomethane	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				EPA TO-17 (M)
Dichlorodifluoromethane (Freon 12)	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Dichlorotetrafluoroethane											EPA TO-15 GCMS	
Diisopropyl Ether (DIPE)	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Ethanol	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Ethyl Acetate											EPA TO-15 GCMS	
Ethylbenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
p-Ethyltoluene												
Ethyl-t-Butyl Ether (ETBE)	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Fluorotrichloromethane			524.2									
n-Heptane											EPA TO-15 GCMS	
Hexachloro-1,3-Butadiene	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Hexachlorobutadiene			524.2									
Hexane												
Iodomethane	EPA 8260B	EPA 8260C										
Isopropanol											EPA TO-15 GCMS	
Isopropylbenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
Methanol											EPA TO-15 GCMS	
Methylene chloride	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
tert-Butyl methyl ether (MTBE)	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Naphthalene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
n-Butylbenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
Propylene											EPA TO-15 GCMS	
n-Propylbenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
o-Xylene	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
m&p-Xylene	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Xylenes, total	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
p-Isopropyltoluene	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C				EPA TO-17 (M)
sec-Butylbenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
Styrene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
trans-1,2-Dichloroethylene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
trans-1,3-Dichloropropylene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
t-1,4-Dichloro-2-Butene	EPA 8260B	EPA 8260C										
Tert-Amyl-Methyl Ether (TAME)	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Tert-Butyl Alcohol (TBA)	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
tert-Butylbenzene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C				
Tetrachloroethylene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Tetrahydrofuran											EPA TO-15 GCMS	
Toluene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Trichloroethene	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	EPA TO-17 (M)
Trichlorotrifluoroethane (Freon 113)	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Vinyl acetate	EPA 8260B	EPA 8260C					EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Vinyl chloride	EPA 8260B	EPA 8260C	524.2				EPA 8260B	EPA 8260C			EPA TO-15 GCMS	
Air												
Methane											ASTM-1946	
Carbon Dioxide											ASTM-1946	

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Analyte	**Matrix**											
	Aqueous						**Solid**				**Air**	
Carbon Monoxide											ASTM-1946	
Oxygen + Argon											ASTM-1946	
Nitrogen											ASTM-1946	
TPH as Diesel (C10-C21)												EPA TO-17 (M)
Gasoline Range Organics (C6-C12)											TO-3M	
TPH as Gasoline											TO-3M	
Ethane											TO-3M	
Ethylene	RSK-175											
Methane	RSK-175											
Carbon Dioxide	RSK-175											
1,3-Butadiene											Calscience SOP M374 BTEX APH	
Benzene											Calscience SOP M374 BTEX APH	
C5-C8 Aliphatic Hydrocarbons											Calscience SOP M374 BTEX APH	
C9-C10 Aromatic Hydrocarbons											Calscience SOP M374 BTEX APH	
C9-C12 Aliphatic Hydrocarbons											Calscience SOP M374 BTEX APH	
Ethylbenzene											Calscience SOP M374 BTEX APH	
Methyl-t-Butyl Ether (MTBE)											Calscience SOP M374 BTEX APH	
Naphthalene											Calscience SOP M374 BTEX APH	
o-Xylene											Calscience SOP M374 BTEX APH	
p/m-Xylene											Calscience SOP M374 BTEX APH	
Toluene											Calscience SOP M374 BTEX APH	
Other VOCs												
1,2,3-Trichloropropane (TCP)	SRL 524M-TCP	EPA 8260B	EPA 8260C				EPA 8260B	EPA 8260C				
Dibromochloropropane (DBCP)	EPA 504.1						EPA 8260B	EPA 8260C				
Ethylene Dibromide (EDB)	EPA 504.1						EPA 8260B	EPA 8260C				
BTEX & MTBE												
Xylenes, total	EPA 8260B	EPA 8260C										
Benzene in water	EPA 8260B	EPA 8260C										
Ethylbenzene in Water	EPA 8260B	EPA 8260C										
tert-Butyl methyl ether (MTBE) in water	EPA 8260B	EPA 8260C										
Toluene in Water	EPA 8260B	EPA 8260C										
o-Xylene in Water	EPA 8260B	EPA 8260C										
m&p-Xylene in water	EPA 8260B	EPA 8260C										
Xylenes, total in Water	EPA 8260B	EPA 8260C										
SVOCs												
1,2-Dichlorobenzene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
1,3-Dichlorobenzene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
1,4-Dichlorobenzene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Hexachlorobutadiene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Hexachloroethane	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Naphthalene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Nitrobenzene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Pyridine	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
1,2,4-Trichlorobenzene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Acenaphthene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Acenaphthylene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Aniline	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Anthracene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Benzo(a)anthracene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Benzo(a)pyrene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Benzo(b)fluoranthene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Benzo(g,h,i)perylene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Benzidine	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				

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Analyte	**Matrix**											
	Aqueous						**Solid**				**Air**	
Benzo(k)fluoranthene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Benzoic acid	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Benzyl alcohol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
4-Bromophenyl-phenylether	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Butylbenzylphthalate	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
4-Chloro-3-methylphenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
4-Chloroaniline	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
bis(2-Chloroethoxy)methane	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
bis(2-Chloroethyl)ether	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
bis(2-Chloroisopropyl)ether	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2-Chloronaphthalene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2-Chlorophenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
4-Chlorophenyl-phenylether	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Chrysene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Dibenz(a,h)anthracene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Dibenzofuran	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Di-n-butylphthalate	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
3,3'-Dichlorobenzidine	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2,4-Dichlorophenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2,6-Dichlorophenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
bis(2-Ethylhexyl)phthalate	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Diethylphthalate	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2,4-Dimethylphenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Dimethylphthalate	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2,4-Dinitrophenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2,4-Dinitrotoluene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2,6-Dinitrotoluene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Di-n-octylphthalate	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Fluoranthene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Fluorene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Hexachlorobenzene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Hexachlorocyclopentadiene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Indeno(1,2,3-cd)pyrene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Isophorone	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
4,6-Dinitro-2-methylphenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2-Methylnaphthalene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
1-Methylnaphthalene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2-Methylphenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
4-Methylphenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
3/4-Methylphenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2-Nitroaniline	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
3-Nitroaniline	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
4-Nitroaniline	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2-Nitrophenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
4-Nitrophenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
N-Nitrosodimethylamine	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
N-Nitrosodiphenylamine	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
N-Nitroso-di-n-propylamine	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Pentachlorophenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Phenanthrene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Phenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
Pyrene	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2,4,5-Trichlorophenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
2,4,6-Trichlorophenol	EPA 8270C	EPA 8270D					EPA 8270C	EPA 8270D				
NDMA	EPA 1625C											
Isotope Dilution												
1,4-Dioxane	EPA 8270C (M) SIM Isotope Dilution						EPA 8270C (M) SIM Isotope Dilution					
Pesticides by Triple Quad												
Dieldrin	EPA 8270D (M) TQ						EPA 8270D (M) TQ					
PCB Congeners												
2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB 180)	EPA 8270C SIM						EPA 8270C SIM					
2,2',3,4,4',5'-Hexachlorobiphenyl (PCB 138)	EPA 8270C SIM						EPA 8270C SIM					
2,2',4,4',5,5'-Hexachlorobiphenyl (PCB 153)	EPA 8270C SIM						EPA 8270C SIM					

Calscience Environmental Laboratories, Inc.												
17440 Lincoln Way												
Garden Grove, CA 92841												
Analyte	**Matrix**											
	Aqueous						**Solid**				**Air**	
2,2',4,5,5'-Pentachlorobiphenyl (PCB 101)	EPA 8270C SIM						EPA 8270C SIM					
2,2',5,5'-Tetrachlorobiphenyl (PCB 52)	EPA 8270C SIM						EPA 8270C SIM					
2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB 189)	EPA 8270C SIM						EPA 8270C SIM					
2,3,3',4,4',5-Hexachlorobiphenyl (PCB 156)	EPA 8270C SIM						EPA 8270C SIM					
2,3,3',4,4',5'-Hexachlorobiphenyl (PCB 157)	EPA 8270C SIM						EPA 8270C SIM					
2,3,3',4,4'-Pentachlorobiphenyl (PCB 105)	EPA 8270C SIM						EPA 8270C SIM					
2,3',4,4',5,5'-Hexachlorobiphenyl (PCB 167)	EPA 8270C SIM						EPA 8270C SIM					
2,3,4,4',5-Pentachlorobiphenyl (PCB 114)	EPA 8270C SIM						EPA 8270C SIM					
2,3',4,4',5-Pentachlorobiphenyl (PCB 118)	EPA 8270C SIM						EPA 8270C SIM					
2,3',4,4',5'-Pentachlorobiphenyl (PCB 123)	EPA 8270C SIM						EPA 8270C SIM					
2,4,4'-Trichlorobiphenyl (PCB 28)	EPA 8270C SIM						EPA 8270C SIM					
3,3',4,4',5,5'-Hexachlorobiphenyl (PCB 169)	EPA 8270C SIM						EPA 8270C SIM					
3,3',4,4',5-Pentachlorobiphenyl (PCB 126)	EPA 8270C SIM						EPA 8270C SIM					
3,3',4,4'-Tetrachlorobiphenyl (PCB 77)	EPA 8270C SIM						EPA 8270C SIM					
3,4,4',5-Tetrachlorobiphenyl (PCB 81)	EPA 8270C SIM						EPA 8270C SIM					
PCBs, total	EPA 8270C SIM						EPA 8270C SIM					
Nitroaromatic and Nitroamines												
Nitrobenzene	EPA 8330A						EPA 8330A					
1,3-Dinitrobenzene	EPA 8330A						EPA 8330A					
2,4-Dinitrotoluene	EPA 8330A						EPA 8330A					
2,6-Dinitrotoluene	EPA 8330A						EPA 8330A					
Tetryl	EPA 8330A						EPA 8330A					
1,3,5-Trinitrobenzene	EPA 8330A						EPA 8330A					
2-Amino-4,6-dinitrotoluene	EPA 8330A						EPA 8330A					
4-Amino-2,6-dinitrotoluene	EPA 8330A						EPA 8330A					
RDX	EPA 8330A						EPA 8330A					
2-Nitrotoluene	EPA 8330A						EPA 8330A					
3-Nitrotoluene	EPA 8330A						EPA 8330A					
4-Nitrotoluene	EPA 8330A						EPA 8330A					
HMX	EPA 8330A						EPA 8330A					
2,4,6-Trinitrotoluene	EPA 8330A						EPA 8330A					
Organic Acids												
Acetic Acid	Calscience SOP M490 Organic Acids						Calscience SOP M490 Organic Acids					
Butyric Acid	Calscience SOP M490 Organic Acids						Calscience SOP M490 Organic Acids					
Lactic Acid	Calscience SOP M490 Organic Acids						Calscience SOP M490 Organic Acids					
Propionic Acid	Calscience SOP M490 Organic Acids						Calscience SOP M490 Organic Acids					
Pyruvic Acid	Calscience SOP M490 Organic Acids						Calscience SOP M490 Organic Acids					
Particle Size												
Particle Size	Laser ASTM D4464 (M)						Laser ASTM D4464 (M)					

CALIFORNIA STATE
ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM
Accredited Fields of Testing

Eurofins Calscience, Inc.

7440 Lincoln Way
Garden Grove, CA 92841-1427
Phone: (714) 895-5494

Certificate No.: 2944
Renew Date: 9/30/2015
INTERIM

Field of Testing: 102 - Inorganic Chemistry of Drinking Water

102.015	001	Hydrogen Ion (pH)	EPA 150.1
102.020	001	Turbidity	EPA 180.1
102.026	001	Calcium	EPA 200.7
102.026	002	Magnesium	EPA 200.7
102.026	003	Potassium	EPA 200.7
102.026	004	Silica	EPA 200.7
102.026	005	Sodium	EPA 200.7
102.026	006	Hardness (calculation)	EPA 200.7
102.030	001	Bromide	EPA 300.0
102.030	002	Chlorate	EPA 300.0
102.030	003	Chloride	EPA 300.0
102.030	005	Fluoride	EPA 300.0
102.030	006	Nitrate	EPA 300.0
102.030	007	Nitrite	EPA 300.0
102.030	008	Phosphate, Ortho	EPA 300.0
102.030	009	Sulfate	EPA 300.0
102.040	001	Bromide	EPA 300.1
102.040	002	Chlorite	EPA 300.1
102.040	003	Chlorate	EPA 300.1
102.040	004	Bromate	EPA 300.1
102.045	001	Perchlorate	EPA 314.0
102.047	001	Perchlorate	EPA 331.0
102.060	001	Nitrate (as N) (Calculation)	EPA 353.2
102.061	001	Nitrite	EPA 353.2
102.070	001	Phosphate, Ortho	EPA 365.1
102.095	001	Turbidity	SM2130B-2001
102.100	001	Alkalinity	SM2320B-1997
102.120	001	Hardness (calculation)	SM2340B-1997
102.121	001	Hardness	SM2340C-1997
102.130	001	Conductivity	SM2510B-1997
102.140	001	Residue, Filterable TDS	SM2540C-1997
102.148	001	Calcium	SM3500-Ca B-1997
102.174	001	Chlorine, Free	SM4500-Cl F-2000
102.174	002	Chlorine, Total Residual	SM4500-Cl F-2000
102.190	001	Cyanide, Total	SM4500-CN E
102.192	001	Cyanide, amenable	SM4500-CN G
102.200	001	Fluoride	SM4500-F B,C-1997
102.203	001	Hydrogen Ion (pH)	SM4500-H+ B-2000
102.220	001	Nitrite	SM4500-NO2- B-2000

As of 9/30/2014 , this list supersedes all previous lists for this certificate number.
Customers: Please verify the current accreditation standing with the State.

102.232	002	Nitrate	SM4500-NO3- E-2000
102.240	001	Phosphate, Ortho	SM4500-P E
102.260	001	Total Organic Carbon	SM5310B
102.261	001	Organic carbon-Dissolved DOC	SM5310B
102.264	001	Total Organic Carbon	SM5310D
102.265	001	Organic carbon-Dissolved DOC	SM5310D

Field of Testing: 103 - Toxic Chemical Elements of Drinking Water

103.130	001	Aluminum	EPA 200.7
103.130	003	Barium	EPA 200.7
103.130	004	Beryllium	EPA 200.7
103.130	005	Cadmium	EPA 200.7
103.130	007	Chromium	EPA 200.7
103.130	008	Copper	EPA 200.7
103.130	009	Iron	EPA 200.7
103.130	011	Manganese	EPA 200.7
103.130	012	Nickel	EPA 200.7
103.130	015	Silver	EPA 200.7
103.130	017	Zinc	EPA 200.7
103.130	018	Boron	EPA 200.7
103.140	001	Aluminum	EPA 200.8
103.140	002	Antimony	EPA 200.8
103.140	003	Arsenic	EPA 200.8
103.140	004	Barium	EPA 200.8
103.140	005	Beryllium	EPA 200.8
103.140	006	Cadmium	EPA 200.8
103.140	007	Chromium	EPA 200.8
103.140	008	Copper	EPA 200.8
103.140	009	Lead	EPA 200.8
103.140	010	Manganese	EPA 200.8
103.140	012	Nickel	EPA 200.8
103.140	013	Selenium	EPA 200.8
103.140	014	Silver	EPA 200.8
103.140	015	Thallium	EPA 200.8
103.140	016	Zinc	EPA 200.8
103.140	017	Boron	EPA 200.8
103.140	018	Vanadium	EPA 200.8
103.160	001	Mercury	EPA 245.1
103.310	001	Chromium (VI)	EPA 218.6

Field of Testing: 104 - Volatile Organic Chemistry of Drinking Water

104.030	001	1,2-Dibromoethane	EPA 504.1
104.030	002	1,2-Dibromo-3-chloropropane	EPA 504.1
104.035	001	1,2,3-Trichloropropane	SRL 524M-TCP
104.040	000	Volatile Organic Compounds	EPA 524.2
104.040	001	Benzene	EPA 524.2
104.040	002	Bromobenzene	EPA 524.2
104.040	003	Bromochloromethane	EPA 524.2
104.040	006	Bromomethane	EPA 524.2

104.040	007	n-Butylbenzene	EPA 524.2
104.040	008	sec-Butylbenzene	EPA 524.2
104.040	009	tert-Butylbenzene	EPA 524.2
104.040	010	Carbon Tetrachloride	EPA 524.2
104.040	011	Chlorobenzene	EPA 524.2
104.040	012	Chloroethane	EPA 524.2
104.040	014	Chloromethane	EPA 524.2
104.040	015	2-Chlorotoluene	EPA 524.2
104.040	016	4-Chlorotoluene	EPA 524.2
104.040	018	Dibromomethane	EPA 524.2
104.040	019	1,3-Dichlorobenzene	EPA 524.2
104.040	020	1,2-Dichlorobenzene	EPA 524.2
104.040	021	1,4-Dichlorobenzene	EPA 524.2
104.040	022	Dichlorodifluoromethane	EPA 524.2
104.040	023	1,1-Dichloroethane	EPA 524.2
104.040	024	1,2-Dichloroethane	EPA 524.2
104.040	025	1,1-Dichloroethene	EPA 524.2
104.040	026	cis-1,2-Dichloroethene	EPA 524.2
104.040	027	trans-1,2-Dichloroethene	EPA 524.2
104.040	028	Dichloromethane	EPA 524.2
104.040	029	1,2-Dichloropropane	EPA 524.2
104.040	030	1,3-Dichloropropane	EPA 524.2
104.040	031	2,2-Dichloropropane	EPA 524.2
104.040	032	1,1-Dichloropropene	EPA 524.2
104.040	033	cis-1,3-Dichloropropene	EPA 524.2
104.040	034	trans-1,3-Dichloropropene	EPA 524.2
104.040	035	Ethylbenzene	EPA 524.2
104.040	036	Hexachlorobutadiene	EPA 524.2
104.040	037	Isopropylbenzene	EPA 524.2
104.040	038	4-Isopropyltoluene	EPA 524.2
104.040	039	Naphthalene	EPA 524.2
104.040	041	N-propylbenzene	EPA 524.2
104.040	042	Styrene	EPA 524.2
104.040	043	1,1,1,2-Tetrachloroethane	EPA 524.2
104.040	044	1,1,2,2-Tetrachloroethane	EPA 524.2
104.040	045	Tetrachloroethene	EPA 524.2
104.040	046	Toluene	EPA 524.2
104.040	047	1,2,3-Trichlorobenzene	EPA 524.2
104.040	048	1,2,4-Trichlorobenzene	EPA 524.2
104.040	049	1,1,1-Trichloroethane	EPA 524.2
104.040	050	1,1,2-Trichloroethane	EPA 524.2
104.040	051	Trichloroethene	EPA 524.2
104.040	052	Trichlorofluoromethane	EPA 524.2
104.040	053	1,2,3-Trichloropropane	EPA 524.2
104.040	054	1,2,4-Trimethylbenzene	EPA 524.2
104.040	055	1,3,5-Trimethylbenzene	EPA 524.2
104.040	056	Vinyl Chloride	EPA 524.2
104.040	057	Xylenes, Total	EPA 524.2

104.045	000	Trihalomethanes, Total	EPA 524.2
104.045	001	Bromodichloromethane	EPA 524.2
104.045	002	Bromoform	EPA 524.2
104.045	003	Chloroform	EPA 524.2
104.045	004	Dibromochloromethane	EPA 524.2
104.050	002	Methyl tert-butyl Ether (MTBE)	EPA 524.2
104.050	004	tert-Amyl Methyl Ether (TAME)	EPA 524.2
104.050	005	Ethyl tert-butyl Ether (ETBE)	EPA 524.2
104.050	006	Trichlorotrifluoroethane	EPA 524.2

Field of Testing: 107 - Microbiology of Wastewater

107.010	001	Heterotrophic Bacteria	SM9215B
107.020	002	Total Coliform	SM9221B-2006
107.030	002	Total Coliform with Chlorine Present	SM9221B-2006
107.040	002	Fecal Coliform	SM9221C,E-2006
107.050	002	Fecal Coliform with Chlorine Present	SM9221C,E-2006
107.100	002	Enterococci	SM9230B
107.100	002	Fecal Streptococci	SM9230B-2007
107.242	001	Enterococci	Enterolert
107.245	002	E. coli	SM9223B-2004

Field of Testing: 108 - Inorganic Chemistry of Wastewater

108.020	001	Conductivity	EPA 120.1
108.030	001	Hardness	EPA 130.1
108.090	001	Residue, Volatile	EPA 160.4
108.110	001	Turbidity	EPA 180.1
108.112	001	Boron	EPA 200.7
108.112	002	Calcium	EPA 200.7
108.112	004	Magnesium	EPA 200.7
108.112	005	Potassium	EPA 200.7
108.112	006	Silica	EPA 200.7
108.112	007	Sodium	EPA 200.7
108.112	008	Phosphorus, Total	EPA 200.7
108.113	001	Boron	EPA 200.8
108.113	002	Calcium	EPA 200.8
108.113	003	Magnesium	EPA 200.8
108.113	004	Potassium	EPA 200.8
108.113	005	Silica	EPA 200.8
108.113	006	Sodium	EPA 200.8
108.120	001	Bromide	EPA 300.0
108.120	002	Chloride	EPA 300.0
108.120	003	Fluoride	EPA 300.0
108.120	008	Sulfate	EPA 300.0
108.120	012	Nitrate (as N)	EPA 300.0
108.120	013	Nitrate-Nitrite (as N)	EPA 300.0
108.120	014	Nitrite as N	EPA 300.0
108.120	015	Phosphate, Ortho (as P)	EPA 300.0
108.141	001	Alkalinity	EPA 310.2
108.183	001	Cyanide, Total	EPA 335.4

108.209	001	Ammonia	EPA 350.1
108.209	001	Ammonia (as N)	EPA 350.1
108.211	002	Kjeldahl Nitrogen, Total (as N)	EPA 351.2
108.260	001	Phosphate, Ortho	EPA 365.1
108.261	001	Phosphorus, Total	EPA 365.1
108.264	001	Phosphate, Ortho	EPA 365.3
108.265	001	Phosphorus, Total	EPA 365.3
108.266	001	Phosphorus, Total	EPA 365.4
108.267	001	Phosphorus, Total	EPA 200.7
108.323	001	Chemical Oxygen Demand	EPA 410.4
108.350	001	Total Recoverable Petroleum Hydrocarbons	EPA 418.1
108.360	001	Phenols, Total	EPA 420.1
108.381	001	Oil and Grease	EPA 1664A
108.385	001	Color	SM2120B-2001
108.390	001	Turbidity	SM2130B-2001
108.400	001	Acidity	SM2310B-1997
108.410	001	Alkalinity	SM2320B-1997
108.420	001	Hardness (calculation)	SM2340B-1997
108.421	001	Hardness	SM2340C-1997
108.430	001	Conductivity	SM2510B-1997
108.439	001	Residue, Volatile	SM2540E-1997
108.440	001	Residue, Total	SM2540B-1997
108.441	001	Residue, Filterable TDS	SM2540C-1997
108.442	001	Residue, Non-filterable TSS	SM2540D-1997
108.443	001	Residue, Settleable	SM2540F-1997
108.449	001	Calcium	SM3500-Ca B-1997
108.451	001	Chloride	SM4500-Chloride C-1997
108.464	001	Chlorine, Total	SM4500-Cl F-2000
108.464	002	Chlorine, Free	SM4500-Cl F-2000
108.472	001	Cyanide, Total	SM4500-CN C,E-1999
108.473	001	Cyanide, amenable	SM4500-CN G-1999
108.480	001	Fluoride	SM4500-F B,C-1997
108.490	001	Hydrogen Ion (pH)	SM4500-H+ B-2000
108.500	001	Ammonia	SM4500-NH3 C
108.501	001	Kjeldahl Nitrogen	SM4500-NH3 C
108.502	001	Ammonia	SM4500-NH3 E
108.502	002	Ammonia (as N)	SM4500-NH3 E-1997
108.511	001	Kjeldahl Nitrogen, Total (as N)	SM4500-Norg B- 1997
108.513	001	Kjeldahl Nitrogen, Total (as N)	SM4500-Norg D-1997
108.514	001	Nitrite as N	SM4500-NO2- B-2000
108.528	001	Nitrate-Nitrite (as N)	SM4500-NO3- E-2000
108.528	002	Nitrite as N	SM4500-NO3- E-2000
108.536	001	Oxygen, dissolved	SM4500-O G-2001
108.540	001	Phosphate, Ortho	SM4500-P E-1999
108.560	001	Sulfite	SM4500-SO3 B
108.572	001	Sulfate	SM4500-SO4 E
108.584	001	Sulfide (as S)	SM4500-S= D-2000
108.592	001	Biochemical Oxygen Demand	SM5210B-2001

108.592	002	Carbonaceous BOD	SM5210B-2001
108.595	001	Chemical Oxygen Demand	SM5220D-1997
108.596	001	Organic Carbon-Total (TOC)	SM5310B-2000
108.598	001	Organic Carbon-Total (TOC)	SM5310D-2000
108.603	001	Oil & Grease Total	SM5520B-2001
108.605	001	Surfactants	SM5540C-2000

Field of Testing: 109 - Toxic Chemical Elements of Wastewater

109.010	001	Aluminum	EPA 200.7
109.010	002	Antimony	EPA 200.7
109.010	003	Arsenic	EPA 200.7
109.010	004	Barium	EPA 200.7
109.010	005	Beryllium	EPA 200.7
109.010	006	Boron	EPA 200.7
109.010	007	Cadmium	EPA 200.7
109.010	009	Chromium	EPA 200.7
109.010	010	Cobalt	EPA 200.7
109.010	011	Copper	EPA 200.7
109.010	012	Iron	EPA 200.7
109.010	013	Lead	EPA 200.7
109.010	015	Manganese	EPA 200.7
109.010	016	Molybdenum	EPA 200.7
109.010	017	Nickel	EPA 200.7
109.010	019	Selenium	EPA 200.7
109.010	021	Silver	EPA 200.7
109.010	023	Thallium	EPA 200.7
109.010	024	Tin	EPA 200.7
109.010	025	Titanium	EPA 200.7
109.010	026	Vanadium	EPA 200.7
109.010	027	Zinc	EPA 200.7
109.020	001	Aluminum	EPA 200.8
109.020	002	Antimony	EPA 200.8
109.020	003	Arsenic	EPA 200.8
109.020	004	Barium	EPA 200.8
109.020	005	Beryllium	EPA 200.8
109.020	006	Cadmium	EPA 200.8
109.020	007	Chromium	EPA 200.8
109.020	008	Cobalt	EPA 200.8
109.020	009	Copper	EPA 200.8
109.020	010	Lead	EPA 200.8
109.020	011	Manganese	EPA 200.8
109.020	012	Molybdenum	EPA 200.8
109.020	013	Nickel	EPA 200.8
109.020	014	Selenium	EPA 200.8
109.020	015	Silver	EPA 200.8
109.020	016	Thallium	EPA 200.8
109.020	017	Vanadium	EPA 200.8
109.020	018	Zinc	EPA 200.8
109.020	020	Gold	EPA 200.8

109.020	021	Iron	EPA 200.8
109.020	022	Tin	EPA 200.8
109.020	023	Titanium	EPA 200.8
109.104	001	Chromium (VI)	EPA 218.6
109.190	001	Mercury	EPA 245.1
109.361	001	Mercury	EPA 1631E

Field of Testing: 110 - Volatile Organic Chemistry of Wastewater

110.020	000	Aromatic Volatiles	EPA 602
110.040	000	Purgeable Organic Compounds	EPA 624

Field of Testing: 111 - Semi-volatile Organic Chemistry of Wastewater

111.060	000	Polynuclear Aromatics	EPA 610
111.100	000	Base/Neutral & Acid Organics	EPA 625
111.120	000	Semi-volatile Organics	EPA 1625
111.170	000	Organochlorine Pesticides & PCBs	EPA 608

Field of Testing: 114 - Inorganic Chemistry of Hazardous Waste

114.010	001	Antimony	EPA 6010B
114.010	002	Arsenic	EPA 6010B
114.010	003	Barium	EPA 6010B
114.010	004	Beryllium	EPA 6010B
114.010	005	Cadmium	EPA 6010B
114.010	006	Chromium	EPA 6010B
114.010	007	Cobalt	EPA 6010B
114.010	008	Copper	EPA 6010B
114.010	009	Lead	EPA 6010B
114.010	010	Molybdenum	EPA 6010B
114.010	011	Nickel	EPA 6010B
114.010	012	Selenium	EPA 6010B
114.010	013	Silver	EPA 6010B
114.010	014	Thallium	EPA 6010B
114.010	015	Vanadium	EPA 6010B
114.010	016	Zinc	EPA 6010B
114.020	001	Antimony	EPA 6020
114.020	002	Arsenic	EPA 6020
114.020	003	Barium	EPA 6020
114.020	004	Beryllium	EPA 6020
114.020	005	Cadmium	EPA 6020
114.020	006	Chromium	EPA 6020
114.020	007	Cobalt	EPA 6020
114.020	008	Copper	EPA 6020
114.020	009	Lead	EPA 6020
114.020	010	Molybdenum	EPA 6020
114.020	011	Nickel	EPA 6020
114.020	012	Selenium	EPA 6020
114.020	013	Silver	EPA 6020
114.020	014	Thallium	EPA 6020
114.020	015	Vanadium	EPA 6020
114.020	016	Zinc	EPA 6020

114.103	001	Chromium (VI)	EPA 7196A
114.106	001	Chromium (VI)	EPA 7199
114.130	001	Lead	EPA 7420
114.140	001	Mercury	EPA 7470A
114.141	001	Mercury	EPA 7471A
114.222	001	Cyanide	EPA 9014
114.230	001	Sulfides, Total	EPA 9034
114.240	001	Corrosivity - pH Determination	EPA 9040B
114.241	001	Corrosivity - pH Determination	EPA 9045C
114.250	001	Fluoride	EPA 9056

Field of Testing: 115 - Extraction Test of Hazardous Waste

115.020	001	Toxicity Characteristic Leaching Procedure (TCLP)	EPA 1311
115.021	001	TCLP Inorganics	EPA 1311
115.022	001	TCLP Extractables	EPA 1311
115.023	001	TCLP Volatiles	EPA 1311
115.030	001	Waste Extraction Test (WET)	CCR Chapter11, Article 5, Appendix II
115.040	001	Synthetic Precipitation Leaching Procedure (SPLP)	EPA 1312

Field of Testing: 116 - Volatile Organic Chemistry of Hazardous Waste

116.020	031	Ethanol and Methanol	EPA 8015B
116.030	001	Gasoline-range Organics	EPA 8015B
116.040	023	1,2-Dichlorobenzene	EPA 8021B
116.040	024	1,3-Dichlorobenzene	EPA 8021B
116.040	025	1,4-Dichlorobenzene	EPA 8021B
116.040	041	Methyl tert-butyl Ether (MTBE)	EPA 8021B
116.040	062	BTEX	EPA 8021B
116.080	000	Volatile Organic Compounds	EPA 8260B
116.080	120	Oxygenates	EPA 8260B
116.100	001	Total Petroleum Hydrocarbons - Gasoline	LUFT GC/MS
116.100	010	BTEX and MTBE	LUFT GC/MS
116.110	001	Total Petroleum Hydrocarbons - Gasoline	LUFT

Field of Testing: 117 - Semi-volatile Organic Chemistry of Hazardous Waste

117.010	001	Diesel-range Total Petroleum Hydrocarbons	EPA 8015B
117.016	001	Diesel-range Total Petroleum Hydrocarbons	LUFT
117.017	001	TRPH Screening	EPA 418.1
117.110	000	Extractable Organics	EPA 8270C
117.111	073	Polynuclear Aromatic Hydrocarbons	EPA 8270C
117.111	076	Other Extractables	EPA 8270C
117.140	000	Polynuclear Aromatic Hydrocarbons	EPA 8310
117.150	000	Carbonyl Compounds	EPA 8315A
117.170	000	Nitroaromatics and Nitramines	EPA 8330
117.170	009	2-Nitrotoluene	EPA 8330
117.170	010	3-Nitrotoluene	EPA 8330
117.170	011	4-Nitrotoluene	EPA 8330
117.170	012	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	EPA 8330
117.170	013	1,3,5-Trinitrobenzene	EPA 8330
117.170	014	2,4,6-Trinitrotoluene	EPA 8330
117.171	000	Nitroaromatics and Nitramines	EPA 8330A

117.171	005	2,6-Dinitrotoluene	EPA 8330A
117.171	006	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	EPA 8330A
117.171	007	Methyl-2,4,6-trinitrophenylnitramine	EPA 8330A
117.171	008	Nitrobenzene	EPA 8330A
117.171	009	2-Nitrotoluene	EPA 8330A
117.171	010	3-Nitrotoluene	EPA 8330A
117.171	011	4-Nitrotoluene	EPA 8330A
117.171	012	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	EPA 8330A
117.171	013	1,3,5-Trinitrobenzene	EPA 8330A
117.171	014	2,4,6-Trinitrotoluene	EPA 8330A
117.210	000	Organochlorine Pesticides	EPA 8081A
117.220	000	PCBs	EPA 8082
117.240	000	Organophosphorus Pesticides	EPA 8141A
117.250	000	Chlorinated Herbicides	EPA 8151A

Field of Testing: 119 - Toxicity Bioassay of Hazardous Waste

119.010	001	Fathead Minnow (P. promelas)	Polisini & Miller (CDFG 1988)

Field of Testing: 120 - Physical Properties of Hazardous Waste

120.010	001	Ignitability	EPA 1010
120.022	001	Ignitability	EPA 1030
120.040	001	Reactive Cyanide	Section 7.3 SW-846
120.050	001	Reactive Sulfide	Section 7.3 SW-846
120.070	001	Corrosivity - pH Determination	EPA 9040B
120.080	001	Corrosivity - pH Determination	EPA 9045C

PERRY JOHNSON LABORATORY ACCREDITATION, INC.

Certificate of Accreditation

Perry Johnson Laboratory Accreditation, Inc. has assessed the Laboratory of:

Maxxam Analytics International Corp. O/A

6740 Campobello Road, Mississauga, ON L5N 2L8, Canada

(Hereinafter called the Organization) and hereby declares that Organization has met the requirements of ISO/IEC 17025:2005 "General Requirements for the competence of Testing and Calibration Laboratories" and the DoD Quality Systems Manual for Environmental Laboratories Version 5.0 July 2013 and is accredited is accordance with the:

United States Department of Defense Environmental Laboratory Accreditation Program (DoD-ELAP)

This accreditation demonstrates technical competence for the defined scope:

Environmental Testing

(As detailed in the supplement)

Accreditation claims for such testing and/or calibration services shall only be made from addresses referenced within this certificate. This Accreditation is granted subject to the system rules governing the Accreditation referred to above, and the Organization hereby covenants with the Accreditation body's duty to observe and comply with the said rules.

For PJLA:

Initial Accreditation Date:	*Issue Date:*	*Revision Date:*
September 29, 2011	April 18, 2015	May 31, 2017

Accreditation No.:	*Certificate No.:*
66912	L15-127

Tracy Szerszen
President/Operations Manager

Perry Johnson Laboratory Accreditation, Inc. (PJLA)
755 W. Big Beaver, Suite 1325
Troy, Michigan 48084

The validity of this certificate is maintained through ongoing assessments based on a continuous accreditation cycle. The validity of this certificate should be confirmed through the PJLA website: www.pjlabs.com

Certificate of Accreditation: Supplement

ISO/IEC 17025:2005 and DoD-ELAP

PJLA

Maxxam Analytics International Corp. O/A
6740 Campobello Road, Mississauga, ON L5N 2L8, Canada
Contact: Salima Haniff Phone: 905-817-5700

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Drinking Water	EPA 331 MOD/Mississauga CAM SOP 00451	LCMSMS	Perchlorate
Aqueous/Solids	EPA 8270/EPA 625 MOD/Mississauga BRL SOP 00217	GCMS	1,4-Dioxane
Aqueous/Solids	EPA 1625C MOD/Mississauga BRL SOP 00400	HRGC HRMS	N-Nitrosodiethylamine
Aqueous/Solids	EPA 1625C MOD/Mississauga BRL SOP 00400	HRGC HRMS	N-Nitrosodimethylamine
Aqueous/Solids	EPA 1625C MOD/Mississauga BRL SOP 00400	HRGC HRMS	N-Nitroso-di-n-butylamine
Aqueous/Solids	EPA 1625C MOD/Mississauga BRL SOP 00400	HRGC HRMS	N-Nitroso-di-n-propylamine
Aqueous/Solids	EPA 1625C MOD/Mississauga BRL SOP 00400	HRGC HRMS	N-Nitrosoethylmethylamine
Aqueous/Solids	EPA 1625C MOD/Mississauga BRL SOP 00400	HRGC HRMS	N-Nitrosomorpholine
Aqueous/Solids	EPA 1625C MOD/Mississauga BRL SOP 00400	HRGC HRMS	N-Nitrosopiperidine
Aqueous/Solids	EPA 1625C MOD/Mississauga BRL SOP 00400	HRGC HRMS	N-Nitrosopyrrolidine
Aqueous/Solids	EPA 537 MOD/Mississauga CAM SOP 00894	LCMSMS	Perfluorinated Compounds
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl (PCB-209)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (PCB-206)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,4',5,5'-Octachlorobiphenyl(PCB-194)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl(PCB-207)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,4',5,6-Octachlorobiphenyl(PCB-195)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,4',5,6'-Octachlorobiphenyl(PCB-196)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,4',5-Heptachlorobiphenyl (PCB-170)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,4',6,6'-Octachlorobiphenyl(PCB-197)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,4',6-Heptachlorobiphenyl(PCB-171)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,4'-Hexachlorobiphenyl(PCB-128)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl (PCB-208)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,5,5',6-Octachlorobiphenyl(PCB-198)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,5,5',6'-Octachlorobiphenyl(PCB-199)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,5,5'-Heptachlorobiphenyl(PCB-172)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,5,6,6'-Octachlorobiphenyl(PCB-200)

Certificate of Accreditation: Supplement

ISO/IEC 17025:2005 and DoD-ELAP

Maxxam Analytics International Corp. O/A
6740 Campobello Road, Mississauga, ON L5N 2L8, Canada
Contact: Salima Haniff Phone: 905-817-5700

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,5',6,6'-Octachlorobiphenyl(PCB-201)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,5,6-Heptachlorobiphenyl(PCB-173)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,5,6'-Heptachlorobiphenyl(PCB-174)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,5',6-Heptachlorobiphenyl(PCB-175)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,5',6'-Heptachlorobiphenyl(PCB-177)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,5-Hexachlorobiphenyl (PCB-129)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,5'-Hexachlorobiphenyl(PCB-130)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,6,6'-Heptachlorobiphenyl(PCB-176)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,6-Hexachlorobiphenyl (PCB-131)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4,6'-Hexachlorobiphenyl (PCB-132)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',4-Pentachlorobiphenyl(PCB-82)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',5,5',6,6'-Octachlorobiphenyl (PCB-202)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',5,5',6-Heptachlorobiphenyl(PCB-178)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',5,5'-Hexachlorobiphenyl (PCB-133)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',5,6,6'-Heptachlorobiphenyl(PCB-179)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',5,6-Hexachlorobiphenyl(PCB-134)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',5,6'-Hexachlorobiphenyl (PCB-135)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',5-Pentachlorobiphenyl (PCB-83)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',6,6'-Hexachlorobiphenyl (PCB-136)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3',6-Pentachlorobiphenyl (PCB-84)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,3'-Tetrachlorobiphenyl (PCB-40)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,4',5,5',6-Octachlorobiphenyl (PCB-203)

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PJLA

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Contact: Salima Haniff Phone: 905-817-5700

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB-180)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,4',5,6,6'-Octachlorobiphenyl (PCB-204)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,4',5,6-Heptachlorobiphenyl (PCB-181)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,4',5,6'-Heptachlorobiphenyl (PCB-182)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,4',5',6-Heptachlorobiphenyl (PCB-183)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,4',5-Hexachlorobiphenyl (PCB-137)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,4',5'-Hexachlorobiphenyl (PCB-138)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,4',6,6'-Heptachlorobiphenyl (PCB-184)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,4',6-Hexachlorobiphenyl (PCB-139)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,4',6'-Hexachlorobiphenyl (PCB-140)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,4'-Pentachlorobiphenyl (PCB-85)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,5,5',6-Heptachlorobiphenyl (PCB-185)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4',5,5',6-Heptachlorobiphenyl (PCB-187)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,5,5'-Hexachlorobiphenyl (PCB-141)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4',5,5'-Hexachlorobiphenyl (PCB-146)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4',5,6,6'-Heptachlorobiphenyl (PCB-188)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,5,6,6'-Heptachlorobiphenyl (PCB-186)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,5,6-Hexachlorobiphenyl (PCB-142)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,5,6'-Hexachlorobiphenyl (PCB-143)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,5',6-Hexachlorobiphenyl (PCB-144)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4',5,6-Hexachlorobiphenyl (PCB-147)

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Contact: Salima Haniff Phone: 905-817-5700

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4',5,6'-Hexachlorobiphenyl (PCB-148)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4',5',6-Hexachlorobiphenyl (PCB-149)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,5-Pentachlorobiphenyl (PCB-86)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,5'-Pentachlorobiphenyl (PCB-87)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4',5-Pentachlorobiphenyl (PCB-90)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4',5'-Pentachlorobiphenyl (PCB-97)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,6,6'-Hexachlorobiphenyl (PCB-145)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4',6,6'-Hexachlorobiphenyl (PCB-150)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,6-Pentachlorobiphenyl (PCB-88)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4,6'-Pentachlorobiphenyl (PCB-89)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4',6-Pentachlorobiphenyl (PCB-91)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4',6'-Pentachlorobiphenyl (PCB-98)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4-Tetrachlorobiphenyl (PCB-41)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,4'-Tetrachlorobiphenyl(PCB-42)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,5,5',6-Hexachlorobiphenyl (PCB-151)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,5,5'-Pentachlorobiphenyl (PCB-92)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,5,6,6'-Hexachlorobiphenyl (PCB-152)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,5,6-Pentachlorobiphenyl (PCB-93)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,5,6'-Pentachlorobiphenyl (PCB-94)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,5',6-Pentachlorobiphenyl (PCB-95)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,5-Tetrachlorobiphenyl (PCB-43)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,5'-Tetrachlorobiphenyl (PCB-44)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,6,6'-Pentachlorobiphenyl (PCB-96)

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Contact: Salima Haniff Phone: 905-817-5700

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Matrix	Standard/Method	Technology	Analyte
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,6-Tetrachlorobiphenyl (PCB-45)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3,6'-Tetrachlorobiphenyl (PCB-46)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',3-Trichlorobiphenyl (PCB-16)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,4',5,5'-Hexachlorobiphenyl (PCB-153)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,4',5,6'-Hexachlorobiphenyl (PCB-154)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,4',5-Pentachlorobiphenyl (PCB-99)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,4',6,6'-Hexachlorobiphenyl (PCB-155)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,4',6-Pentachlorobiphenyl (PCB-100)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,4'-Tetrachlorobiphenyl (PCB-47)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,5,5'-Pentachlorobiphenyl (PCB-101)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,5,6'-Pentachlorobiphenyl (PCB-102)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,5',6-Pentachlorobiphenyl (PCB-103)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,5-Tetrachlorobiphenyl (PCB-48)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,5'-Tetrachlorobiphenyl (PCB-49)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,6,6'-Pentachlorobiphenyl (PCB-104)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,6-Tetrachlorobiphenyl (PCB-50)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4,6'-Tetrachlorobiphenyl (PCB-51)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',4-Trichlorobiphenyl (PCB-17)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',5,5'-Tetrachlorobiphenyl (PCB-52)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',5-Trichlorobiphenyl (PCB-18)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',6,6'-Tetrachlorobiphenyl (PCB-54)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2',6-Trichlorobiphenyl (PCB-19)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,2'-Dichlorobiphenyl (PCB-4)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,4',5,5',6-Octachlorobiphenyl (PCB-205)

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PJLA

Maxxam Analytics International Corp. O/A

6740 Campobello Road, Mississauga, ON L5N 2L8, Canada
Contact: Salima Haniff Phone: 905-817-5700

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB-189)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,4',5,6-Heptachlorobiphenyl (PCB-190)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,4',5',6-Heptachlorobiphenyl (PCB-191)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,4',5-Hexachlorobiphenyl (PCB-156)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,4',5'-Hexachlorobiphenyl (PCB-157)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,4',6-Hexachlorobiphenyl (PCB-158)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,4'-Pentachlorobiphenyl (PCB-105)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4',5,5',6-Heptachlorobiphenyl (PCB-193)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,5,5',6-Heptachlorobiphenyl (PCB-192)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,5,5'-Hexachlorobiphenyl (PCB-159)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4',5,5'-Hexachlorobiphenyl (PCB-162)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,5,6-Hexachlorobiphenyl (PCB-160)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,5',6-Hexachlorobiphenyl (PCB-161)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4',5,6-Hexachlorobipheny l(PCB-163)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4',5',6-Hexachlorobiphenyl (PCB-164)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,5-Pentachlorobiphenyl (PCB-106)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4',5-Pentachlorobiphenyl (PCB-107)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,5'-Pentachlorobiphenyl (PCB-108)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4',5'-Pentachlorobipheny l(PCB-122)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4,6-Pentachlorobiphenyl (PCB-109)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4',6-Pentachlorobiphenyl (PCB-110)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4-Tetrachlorobiphenyl (PCB-55)

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PJLA

Maxxam Analytics International Corp. O/A
6740 Campobello Road, Mississauga, ON L5N 2L8, Canada
Contact: Salima Haniff Phone: 905-817-5700

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',4'-Tetrachlorobiphenyl (PCB-56)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',5,5',6-Hexachlorobiphenyl (PCB-165)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',5,5'-Pentachlorobiphenyl (PCB-111)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',5,6-Pentachlorobiphenyl (PCB-112)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',5',6-Pentachlorobiphenyl (PCB-113)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',5-Tetrachlorobiphenyl (PCB-57)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',5'-Tetrachlorobiphenyl (PCB-58)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3',6-Tetrachlorobiphenyl (PCB-59)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,3'-Trichlorobiphenyl (PCB-20)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4,4',5,5'-Hexachlorobiphenyl (PCB-167)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,4,4',5,6-Hexachlorobiphenyl (PCB-166)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4,4',5',6-Hexachlorobiphenyl (PCB-168)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,4,4',5-Pentachlorobiphenyl (PCB-114)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4,4',5-Pentachlorobiphenyl (PCB-118)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4,4',5'-Pentachlorobiphenyl (PCB-123)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,4,4',6-Pentachlorobiphenyl (PCB-115)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4,4',6-Pentachlorobiphenyl (PCB-119)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,4,4'-Tetrachlorobiphenyl (PCB-60)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4,4'-Tetrachlorobiphenyl (PCB-66)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4,5,5'-Pentachlorobiphenyl (PCB-120)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4',5,5'-Pentachlorobiphenyl (PCB-124)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,4,5,6-Pentachlorobiphenyl (PCB-116)

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6740 Campobello Road, Mississauga, ON L5N 2L8, Canada
Contact: Salima Haniff Phone: 905-817-5700

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,4',5,6-Pentachlorobiphenyl (PCB-117)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4,5',6-Pentachlorobiphenyl (PCB-121)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4',5',6-Pentachlorobiphenyl (PCB-125)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,4,5-Tetrachlorobiphenyl (PCB-61)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,4',5-Tetrachlorobiphenyl (PCB-63)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4,5-Tetrachlorobiphenyl (PCB-67)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4,5'-Tetrachlorobipheny l(PCB-68)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4',5-Tetrachlorobiphenyl (PCB-70)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4',5'-Tetrachlorobiphenyl (PCB-76)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,4,6-Tetrachlorobiphenyl (PCB-62)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,4',6-Tetrachlorobiphenyl (PCB-64)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4,6-Tetrachlorobiphenyl (PCB-69)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4',6-Tetrachlorobiphenyl (PCB-71)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,4-Trichlorobiphenyl (PCB-21)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,4'-Trichlorobiphenyl (PCB-22)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4-Trichlorobiphenyl (PCB-25)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',4'-Trichlorobiphenyl (PCB-33)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',5,5'-Tetrachlorobiphenyl (PCB-72)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,5,6-Tetrachlorobiphenyl (PCB-65)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',5',6-Tetrachlorobiphenyl (PCB-73)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,5-Trichlorobiphenyl (PCB-23)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',5-Trichlorobipheny l(PCB-26)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',5'-Trichlorobiphenyl (PCB-34)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3,6-Trichlorobiphenyl (PCB-24)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3',6-Trichlorobiphenyl (PCB-27)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3-Dichlorobiphenyl (PCB-5)

Certificate of Accreditation: Supplement

ISO/IEC 17025:2005 and DoD-ELAP

PJLA

Maxxam Analytics International Corp. O/A
6740 Campobello Road, Mississauga, ON L5N 2L8, Canada
Contact: Salima Haniff Phone: 905-817-5700

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,3'-Dichlorobiphenyl (PCB-6)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,4,4',5-Tetrachlorobipheny l(PCB-74)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,4,4',6-Tetrachlorobiphenyl (PCB-75)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,4,4'-Trichlorobiphenyl(PCB-28)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,4,5-Trichlorobiphenyl(PCB-29)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,4',5-Trichlorobiphenyl(PCB-31)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,4,6-Trichlorobiphenyl(PCB-30)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,4',6-Trichlorobiphenyl(PCB-32)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,4-Dichlorobiphenyl (PCB-7)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,4'-Dichlorobiphenyl(PCB-8)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,5-Dichlorobiphenyl(PCB-9)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2,6-Dichlorobiphenyl(PCB-10)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	2-Monochlorobiphenyl (PCB-1)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,3',4,4',5,5'-Hexachlorobiphenyl (PCB-169)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,3',4,4',5-Pentachlorobiphenyl (PCB-126)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,3',4,4'-Tetrachlorobiphenyl (PCB-77)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,3',4,5,5'-Pentachlorobiphenyl (PCB-127)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,3',4,5-Tetrachlorobiphenyl (PCB-78)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,3',4,5'-Tetrachlorobiphenyl (PCB-79)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,3',4-Trichlorobiphenyl(PCB-35)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,3',5,5'-Tetrachlorobiphenyl(PCB-80)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,3',5-Trichlorobiphenyl(PCB-36)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,3'-Dichlorobiphenyl(PCB-11)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,4,4',5-Tetrachlorobiphenyl (PCB-81)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,4,4'-Trichlorobiphenyl (PCB-37)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,4,5-Trichlorobiphenyl(PCB-38)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,4',5-Trichlorobiphenyl(PCB-39)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,4-Dichlorobiphenyl(PCB-12)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,4'-Dichlorobiphenyl(PCB-13)

Certificate of Accreditation: Supplement

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Maxxam Analytics International Corp. O/A
6740 Campobello Road, Mississauga, ON L5N 2L8, Canada
Contact: Salima Haniff Phone: 905-817-5700

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3,5-Dichlorobiphenyl(PCB-14)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	3-Monochlorobiphenyl (PCB-2)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	4,4'-Dichlorobiphenyl (PCB-15)
Aqueous/Solids	EPA 1668A/B MOD/Mississauga BRL SOP 00408	HRGC HRMS	4-Monochlorobiphenyl (PCB-3)
Aqueous/Solids	EPA 6850 MOD/Mississauga CAM SOP 00451	LCMSMS	Perchlorate
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,4,6,7,8,9-Octachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,4,6,7,8-Heptachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,4,7,8,9-Heptachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,4,7,8-Hexachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,6,7,8-Hexachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,7,8,9-Hexachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,7,8-Pentachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	1,2,3,7,8-Pentachlorodibenzo-p-dioxin
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	2,3,4,6,7,8-Hexachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	2,3,4,7,8-Pentachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	2,3,7,8-Tetrachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	2,3,7,8-Tetrachlorodibenzo-p-dioxin
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	Total Heptachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	Total Heptachlorodibenzo-p-dioxin
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	Total Hexachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	Total Hexachlorodibenzo-p-dioxin
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	Total Pentachlorodibenzofuran

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Contact: Salima Haniff Phone: 905-817-5700

Accreditation is granted to the facility to perform the following testing:

Matrix	Method	Technology	Analyte
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	Total Pentachlorodibenzo-p-dioxin
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	Total Tetrachlorodibenzofuran
Aqueous/Solids	EPA 8290A MOD/Mississauga BRL SOP 00406	HRGC HRMS	Total Tetrachlorodibenzo-p-dioxin
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,4,6,7,8,9-Octachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,4,6,7,8-Heptachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,4,7,8,9-Heptachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,4,7,8-Hexachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,6,7,8-Hexachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,7,8,9-Hexachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,7,8-Pentachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	1,2,3,7,8-Pentachlorodibenzo-p-dioxin
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	2,3,4,6,7,8-Hexachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	2,3,4,7,8-Pentachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	2,3,7,8-Tetrachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	2,3,7,8-Tetrachlorodibenzo-p-dioxin
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	Total Heptachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	Total Heptachlorodibenzo-p-dioxin
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	Total Hexachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	Total Hexachlorodibenzo-p-dioxin

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PJLA

Maxxam Analytics International Corp. O/A
6740 Campobello Road, Mississauga, ON L5N 2L8, Canada
Contact: Salima Haniff Phone: 905-817-5700

Accreditation is granted to the facility to perform the following testing:

Matrix	Method	Technology	Analyte
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	Total Pentachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	Total Pentachlorodibenzo-p-dioxin
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	Total Tetrachlorodibenzofuran
Aqueous/Drinking Water/Solids	EPA 1613B MOD/Mississauga BRL SOP 00410	HRGC HRMS	Total Tetrachlorodibenzo-p-dioxin

Certificate of Accreditation: Supplement

ISO/IEC 17025:2005 and DoD-ELAP

PJLA

Maxxam Analytics International Corp. O/A
6740 Campobello Road, Mississauga, ON L5N 2L8, Canada
Contact: Salima Haniff Phone: 905-817-5700

Accreditation is granted to the facility to perform the following testing:

Matrix	Method	Technology	Analyte
Aqueous	SW-846 3510C MOD/Mississauga BRL SOP 00005	Liq-Liq Extraction	Semivolatile Organics
Solids	SW-846 3540C MOD/Mississauga BRL SOP 00004	Soxhlet Extraction	Semivolatile Organics
Solids	SW-846 3545A MOD/Mississauga BRL SOP 00005	PFE	Semivolatile Organics
Solids	SW-846 3640A MOD/Mississauga BRL SOP 00003	GPC	Semivolatile Organics
Aqueous/Solids	SW-846 3620C MOD/Mississauga BRL SOP 00409	Cleanup-Florisil	Semivolatile Organics
Aqueous/Solids	SW-846 3610B MOD/ Mississauga BRL SOP 00405	Cleanup-Alumina	Semivolatile Organics
Aqueous/Solids	EPA 1613B MOD EPA 8290A MOD	DF Cleanup Method, Alumina; Florisil & GPC	Dioxins and Furans
Aqueous/Solids	EPA 1613B MOD EPA 8290A MOD	DF Extraction, Liquid-Liquid & Soxhlet extraction	Dioxins and Furans
Aqueous/Solids	EPA 1668A	PC Cleanup, GPC, & Soxhlet Extraction	PCB Congeners

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

CALIFORNIA STATE

ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM

CERTIFICATE OF ENVIRONMENTAL ACCREDITATION

Is hereby granted to

Maxxam Analytics International Corporation

6740 Campobello Road

Mississauga, Ontario, Canada L5N 2L8 Canada

Scope of the certificate is limited to the
"Fields of Testing"
which accompany this Certificate.

Continued accredited status depends on successful completion of on-site inspection, proficiency testing studies, and payment of applicable fees.

This Certificate is granted in accordance with provisions of Section 100825, et seq. of the Health and Safety Code.

Certificate No.: **2923**

Expiration Date: **3/31/2016**

Effective Date: **4/1/2014**

Sacramento, California
subject to forfeiture or revocation

Christine Sotelo, Chief
Environmental Laboratory Accreditation Program

CALIFORNIA Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

CALIFORNIA STATE
ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM
Accredited Fields of Testing

Maxxam Analytics International Corporation

6740 Campobello Road
Mississauga, Ontario, CN L5N 2L8 Canada
Phone: 905-817-5700

Certificate No.: 2923
Renew Date: 3/31/2016

Field of Testing: 105 - Semi-volatile Organic Chemistry of Drinking Water

105.230	001	2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	EPA 1613

Field of Testing: 111 - Semi-volatile Organic Chemistry of Wastewater

111.111	000	Dioxins and Dibenzofurans	EPA 1613B

Field of Testing: 117 - Semi-volatile Organic Chemistry of Hazardous Waste

117.110	000	Extractable Organics	EPA 8270C
117.130	000	Dioxins and Dibenzofurans	EPA 8290
117.150	000	Carbonyl Compounds	EPA 8315A

As of 3/30/2015 , this list supersedes all previous lists for this certificate number.
Customers: Please verify the current accreditation standing with the State.

ATTACHMENT A-3

DOD QUALITY SYSTEMS MANUAL (ver 4.2)
QUALITY CONTROL LIMITS

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Appendix G – SW-846 LCS Control Limits

DoD conducted a study to establish control limits for laboratory control samples (LCS) using data collected from DoD-approved environmental laboratories. LCS recoveries for all the analytes on the target analyte lists were pooled, and statistical analyses (such as outlier tests and analysis of variance) were performed on the data before generating the final LCS control limits (LCS-CLs). A complete description of the methodology and findings for Method 8270 can be found in the Laboratory Control Sample Pilot Study (DoD, 2000).

Environmental testing laboratories that perform work for DoD must utilize the DoD-specified LCS-CLs when assessing batch acceptance whenever they are available. This appendix presents the control limits generated by the LCS study and the methodology for applying the limits to LCS data. All analytes spiked in the LCS shall meet the DoD-generated LCS control limits. As described in Section D.1.1.2.1.e of NELAC Appendix D, a number of sporadic marginal exceedances are allowed. Depending on the length of the list of analytes, a specified small number of analytes may exceed the generated control limit. Upper and lower marginal exceedance (ME) limits, calculated at 4 standard deviations around the mean, are established to mark the boundaries of marginal exceedances. If more analytes exceed the LCS-CLs than are allowed, or if any one analyte exceeds the ME limits, then the LCS has failed.

DoD LCS Control Limits Policy

- The laboratory shall use project-specific control limits based on data quality objectives (DQOs), if available. If not, DoD-generated LCS-CLs shall be used, if available. Otherwise, the laboratory's own in-house control limits shall be used.
- The LCS-CLs are based on the promulgated versions of SW-846 methods at the time of the study (2000). They should be used as a benchmark to evaluate acceptability even as methods are updated or alternative methods for the same class of compounds become available.
- The fact that the LCS-CLs are based on certain SW-846 methods should not limit the use of alternative analytical methods, if appropriate. If an alternative method is used, however, it should be capable of producing LCS recoveries that are at least as good as the DoD-generated LCS-CLs, unless project-specific DQOs allow less stringent criteria.
- The LCS study shows that preparatory methods may have a significant influence on a laboratory's ability to achieve certain LCS-CLs. If a laboratory is unable to achieve the LCS-CLs presented in this appendix, it should investigate the use of alternative preparatory methods as a means to improve precision and accuracy.

G.1 Generated LCS Control Limits

As mentioned above, DoD compiled LCS data from multiple laboratories, performing statistical analyses on the data sets before generating control limits. The control limits were set at 3 standard deviations around the mean for all methods except 8151 (see below for further explanation). Limits were then rounded to the nearest 5 for ease of use. The ME limits were set at 4 standard deviations around the mean. The lower ME limit was then raised to 10% for those analytes in which 4 standard deviations falls below that level. Tables G -4 through G -19 at the end of this appendix present the mean or median, standard deviation, lower control limit, upper control limit, lower ME limit, and upper ME limit, as applicable, for each analyte in Methods 8260, 8270, 8151, 8310, 8330, 8081, 8082, 6010, and 7470/7471, for the water and solid matrices. The lower and upper ME limits are not presented for Methods 8151, 8082, and 7470/7471, since those methods have fewer than 11 analytes and are not capable of utilizing the sporadic marginal exceedance allowance. The analytes for Method 8270 are grouped by compound class.

The control limits for explosives Method 8330 in the water matrix were generated using data that were extracted with solid phase extraction (SPE) using acetonitrile only. Analysis of the data received from the LCS study showed that the extraction method produced recoveries with higher means and lower

standard deviations than the salting out extraction method. This results in significantly narrower control limits. Since SPE/acetonitrile is less expensive, cumbersome, and time and labor intensive, the LCS control limits for Method 8330 in water were set with data using only that method. A limited amount of data were received that used SPE/acetonitrile, therefore, no outliers were removed during the statistical analysis. This ensures that a representative data set was used to generate the control limits (see Table G -12).

Note: Laboratories may use any extraction method they feel is appropriate; however, the LCS recoveries must fall within the LCS-CLs presented in Table G-12.

Control limits for chlorinated herbicides Method 8151 were generated using a non-parametric statistical approach. This is a different approach than for the other methods in the LCS study due to the large amount of intralaboratory variability in recoveries for all analytes in the method. The control limits for Method 8151, both solid and water matrices, were set at the 5th and 95th percentile of all data received in the study (no outliers were removed). Tables G -8 and G -9 present the median, lower control limit, and upper control limit for each analyte. LCS failure is assessed and corrective action applied the same way for all methods with control limits in this appendix (see Sections G.3 and G.4).

Note: These data represent the current capability of the SW-846 analytical and preparatory methods. Use of alternative preparatory procedures and/or improvements through PBMS is encouraged. Project-specific control limits can supersede these DoD limits.

If limits are not available for a project-specific analyte, the laboratory shall discuss with the client appropriate limits considering the project-specific DQOs.

Control limits for metals Method 6010, and mercury Method 7470/7471 were set at 80 – 120% even though generated limits were within these numbers. This reflects the allowable uncertainty in the calibration of the instrument. In one case the generated limit (silver in solid) was outside 80 – 120%, and therefore the generated limit was used.

G.2 Marginal Exceedance

As described in Section D.1.1.2.1.e of NELAC Appendix D, a number of sporadic marginal exceedances of the LCS-CLs will be allowed. The number of exceedances is based on the total number of analytes spiked in the LCS. As the number of analytes in the LCS increases, more marginal exceedances are allowed. Table G-1 presents the allowable number of marginal exceedances for a given number of analytes in the LCS (as presented in NELAC Appendix D).

Table G-1. Number of Marginal Exceedances

Number of Analytes in LCS	Allowable Number of Marginal Exceedances of LCS-CLs
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

A *marginal* exceedance is defined as beyond the LCS-CL but still within the marginal exceedance limits (set at 4 standard deviations around the mean). This outside boundary prevents a grossly out-of-control LCS from passing.

NELAC requires that the marginal exceedances be sporadic, i.e., random. As defined by DoD, if the same analyte exceeds the LCS-CLs repeatedly (e.g., two out of three consecutive LCS), that is an indication that the problem is systematic and something is wrong with the measurement system. The source of error should be located and the appropriate corrective action taken. Laboratories must monitor the application of the sporadic marginal exceedance allowance to the LCS results through QA

channels to ensure random behavior. Effective implementation of the marginal exceedance allowance requires cooperation from the laboratory. If the laboratory fails to implement the policy properly, the privilege of using the marginal exceedance option will be revoked. Oversight and appropriate corrective action will be a focus of DoD laboratory assessments in the future.

G.3 LCS Failure

Each LCS must be evaluated against the appropriate control limits and ME limits before being accepted. The laboratory shall use project-specific control limits, if available. If not, DoD generated LCS-CLs shall be used, if available (see Tables G-4 through G-19). Otherwise, the laboratory's own in-house control limits shall be used. First, the recoveries for the analytes spiked in the LCS should be compared with the LCS control limits. If a recovery is less than the lower control limit or greater than the upper control limit, that is an exceedance. The laboratory should note which analytes exceeded the control limits and make a comparison to the list of project-specific analytes of concern. **If a project-specific analyte of concern exceeds its LCS-CLs, the LCS has failed.** Next, the laboratory should add up the total number of exceedances for the LCS. Based on the number of analytes spiked in the LCS, the total number of exceedances should be compared with the allowable number from Table G-1. (The allowable number of marginal exceedances depends on the total number of analytes spiked in the LCS, even if DoD-generated control limits are not available for all analytes.) **If a LCS has more than the allowable number of marginal exceedances, the LCS has failed.** Finally, the recoveries for those analytes that exceeded the LCS-CLs should be compared with the ME limits from Tables G-4 to G-7, G-10 to G-15, or G-18 to G-19. **If a single analyte exceeds its marginal exceedance limit, the LCS has failed.** (This applies only to methods with greater than 10 analytes.)

In summary, failure of the LCS can occur several ways:

- Exceedance of a LCS-CL by any project-specific analyte of concern
- Marginal exceedance of the LCS-CLs by more than the allowable number of analytes
- Exceedance of the ME limits by one or more analytes

Once a LCS has failed, corrective action is required, see section D.4.

G.4 Corrective Action

If a sample fails based on any of the criteria in section G.3, corrective action is required. The corrective action requirement applies to all analytes that exceeded the LCS-CLs, even if one specific analyte's exceedance was not the trigger of LCS failure (see example below). **All exceedances of the LCS-CLs, marginal or otherwise, are subject to corrective action.**

Example of Applying Corrective Action

- In a single LCS, anthracene has a recovery of 30%.
- The lower ME limit for anthracene is 45, therefore the LCS has failed.
- In the same LCS three other analytes exceeded their LCS-CLs but were within their ME limits.
- The LCS was spiked with 74 analytes; therefore, according to Table G-1, four marginal exceedances are allowed.
- The four total exceedances (anthracene plus the three other analytes) are within the allowable number for that analyte list size.

Corrective action is triggered for the LCS because the anthracene recovery exceeded its ME limit, but it is required for all four analytes that exceeded the LCS-CLs.

If a LCS fails, an attempt must be made to determine the source of error and find a solution. All the findings and corrective action should be documented. DoD requires that the analytes subject to corrective action in the LCS and all the samples in the batch be reprepped and reanalyzed or the batch rerun with a new LCS. The corrective action applied shall be based on professional judgment in the review of other QC measures (i.e., surrogates). If an analyte falls outside the LCS-CLs a second time or

if there is not sufficient sample material available to be reanalyzed, then all the results in the associated batch for that analyte must be flagged with a Q (see DoD Gray Box 47). The recoveries of those analytes subject to corrective action must be documented in the case narrative, whether flagging is needed or not.

G.5 Poor Performing Analytes

On the basis of results from the LCS study, DoD identified certain compounds that do not perform well with specific methods. These compounds produce low mean recoveries and high standard deviations, resulting in wide LCS control limits with particularly low lower control limits (sometimes negative values). The performance of these compounds reflects routine implementation of the method in many laboratories. DoD has defined a poor performing analyte as having a lower control limit of 10% or less. DoD does not feel it is appropriate to control batch acceptance on these compounds because there is a high level of uncertainty in their recovery. The data may be used; however, routine performance of the method on these compounds can result in being able to identify only a small percentage of the analyte.

The laboratory should include all target analytes in the calibration standard, including the poor performing analytes. If one of the poor performing analytes identified below is a project-specific analyte of concern *or* if it is detected in the project samples, the laboratory should contact the client (DoD), who will then work with the laboratory on an appropriate course of action. Ideally DoD and the laboratory would use an alternative method to test for the analyte (one that is known to produce higher recoveries) or else modify the original method to optimize conditions for the poor performing analyte.

Poor performing analytes were only identified in SW-846 Methods 8270, 8151, and 8330. These analytes, along with the mean, standard deviation, lower control limit, upper control limit, lower ME limit, and upper ME limit (as generated by the LCS study) are presented in Table G-2.

Table G-2. Poor Performing Analytes[1]

Analyte	Mean/ Median	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
8270 Water:						
4-Nitrophenol	54	23	0	125	0	145
Benzoic acid	54	24	0	125	0	150
Phenol	55	19	0	115	0	135
Phenol-d_5/d_6 (surrogate)	62	18	10	115	0	135
8270 Solid:						
3,3'Dichlorobenzidine	68	19	10	130	0	145
4-Chloroaniline	51	14	10	100	0	110
Benzoic acid	55	18	0	110	0	130
8151 Solid:						
Dinoseb	72		5	130		
8330 and 8330A Solid:						
Methyl-2,4,6-trinitrophenylnitramine (Tetryl)	80	23	10	150	0	172

Note: Lower limits calculated as negative values were raised to zero.

The LCS control limits generated by the study for the poor performing analytes are provided as a benchmark against which laboratories can measure the effectiveness of alternative methods or modifications to the current methods. Batch acceptance should not be evaluated using these limits. When choosing alternative or modified methods, laboratories should strive to raise the mean recoveries and lower the standard deviations in comparison with the performance of the analytes

[1]Control limits for Method 8151 were generated using non-parametric statistics; therefore, the median is presented without standard deviation (see section G.1 for further explanation). ME limits are not used for Method 8151 since the target analyte list has fewer than 11 analytes.

presented in Table G-2. The lower control limit generated for alternative or modified methods must be greater than 10% to be considered acceptable.

G.6 Surrogates

The surrogate compounds for each method are added to all samples, standards, and blanks to assess the ability of the method to recover specific non-target analytes from a given matrix and to monitor sample-specific recovery. Control limits for these compounds were calculated in the same study as the other analytes on the target analyte lists. Below are the limits for some of the surrogates of Methods 8260, 8270, 8081, and 8082, based on 3 standard deviations around the mean (Table G-3). Sufficient data were not received for those analytes during the LCS study to perform statistically significant analyses. No ME limits are presented as marginal exceedances are not acceptable for surrogate spikes.

Note: DoD prefers the use of those surrogates not identified as poor performing analytes in Table G-2 above.

Table G-3. Surrogates

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
8260 Water:				
1,2-Dichloroethane-d_4	95	8	70	120
4-Bromofluorobenzene	98	7	75	120
Dibromofluoromethane	100	5	85	115
Toluene-d_8	102	6	85	120
8260 Solid:				
4-Bromofluorobenzene	101	6	85	120
Toluene-d_8	100	5	85	115
8270 Water:				
2-Fluorobiphenyl	79	10	50	110
Terphenyl-d_{14}	92	14	50	135
2,4,6-Tribromophenol	82	13	40	125
2-Fluorophenol	63	14	20	110
Nitrobenzene-d_5	76	11	40	110
8270 Solid:				
2-Fluorobiphenyl	72	10	45	105
Terphenyl-d_{14}	78	15	30	125
2,4,6-Tribromophenol	80	15	35	125
2-Fluorophenol	70	11	35	105
Phenol-d_5/d_6	71	10	40	100
Nitrobenzene-d_5	69	10	35	100
8081 Water:				
Decachlorobiphenyl	83	17	30	135
TCMX	81	19	25	140
8081 Solid:				
Decachlorobiphenyl	94	13	55	130
TCMX	97	9	70	125
8082 Water:				
Decachlorobiphenyl	88	15	40	135
8082 Solid:				
Decachlorobiphenyl	91	11	60	125

G.7 In-House LCS Control Limits

The acceptability of LCS results within any preparatory batch shall be based on project-specified limits or the following DoD-specified LCS control limits, if project-specific limits are not available. If DoD limits are not available, the laboratory must use its in-house limits for batch acceptance.

DoD strongly believes that it is important for laboratories to maintain their own in-house LCS limits. These in-house limits must be consistent with (i.e., within) the DoD limits (project-specific, if available; otherwise the following LCS-CLs). The laboratory in-house limits shall be calculated from the laboratory's historical LCS data in accordance with a documented procedure (e.g., SOP) that is consistent with good laboratory practice. That document must describe the process for establishing and maintaining LCS limits and the use of control charts.

The laboratory in-house limits are to be used for several purposes:

- Laboratories are expected to utilize their in-house limits as part of their quality control system, and to evaluate trends and monitor and improve performance.
- When a laboratory's in-house limits are outside the DoD control limits (upper and/or lower), they must report their in-house limits in the laboratory report (see Appendix E) even if the LCS associated with the batch fell within the DoD limits. Using this information, DoD will be able to determine how laboratory performance affects the quality of the environmental data.
- DoD may review the laboratory in-house limits and associated trends, as reflected in control charts, to determine whether the laboratory's overall performance is acceptable. If deemed unacceptable, this can allow DoD to decide not to use the laboratory again until substantial improvement has occurred.

Table G-4. LCS Control Limits for Volatile Organic Compounds SW-846 Method 8260 Water Matrix[2]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
1,1,1,2-Tetrachloroethane	105	8	80	130	75	135
1,1,1-Trichloroethane	100	11	65	130	55	145
1,1,2,2-Tetrachloroethane	96	11	65	130	55	140
1,1,2-Trichloroethane	100	8	75	125	65	135
1,1-Dichloroethane	101	11	70	135	60	145
1,1-Dichloroethene	99	10	70	130	55	140
1,1-Dichloropropene	102	10	75	130	65	140
1,2,3-Trichlorobenzene	99	14	55	140	45	155
1,2,3-Trichloropropane	98	9	75	125	65	130
1,2,4-Trichlorobenzene	100	11	65	135	55	145
1,2,4-Trimethylbenzene	103	10	75	130	65	140
1,2-Dibromo-3-chloropropane	91	14	50	130	35	145
1,2-Dibromoethane	100	7	80	120	75	125
1,2-Dichlorobenzene	96	9	70	120	60	130
1,2-Dichloroethane	100	10	70	130	60	140
1,2-Dichloropropane	100	8	75	125	65	135
1,3,5-Trimethylbenzene	102	10	75	130	65	140
1,3-Dichlorobenzene	100	8	75	125	65	130
1,3-Dichloropropane	100	9	75	125	65	135
1,4-Dichlorobenzene	99	8	75	125	65	130
2,2-Dichloropropane	103	11	70	135	60	150
2-Butanone	91	20	30	150	10	170

[2] A number of sporadic marginal exceedances of the control limits are allowed, depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits. LCS control limits are not available for Total Xylene. Xylene may be reported on a project-specific basis as a total number; however, for the purposes of the DoD QSM, it will be analyzed and reported as m,p-Xylene and o-Xylene. Additional limits for poor performing compounds can be found in section G.5 and for surrogate compounds in section G.6.

Table G-4. LCS Control Limits for Volatile Organic Compounds SW-846 Method 8260 Water Matrix[2] (continued)

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
2-Chlorotoluene	100	9	75	125	65	135
2-Hexanone	92	12	55	130	45	140
4-Chlorotoluene	101	9	75	130	65	135
4-Methyl-2-pentanone	96	13	60	135	45	145
Acetone	91	17	40	140	20	160
Benzene	102	7	80	120	75	130
Bromobenzene	100	8	75	125	70	130
Bromochloromethane	97	11	65	130	55	140
Bromodichloromethane	98	8	75	120	70	130
Bromoform	99	10	70	130	60	140
Bromomethane	88	19	30	145	10	165
Carbon disulfide	100	21	35	160	15	185
Carbon tetrachloride	102	12	65	140	55	150
Chlorobenzene	102	7	80	120	75	130
Chlorodibromomethane	96	13	60	135	45	145
Chloroethane	99	12	60	135	50	145
Chloroform	100	12	65	135	50	150
Chloromethane	83	15	40	125	25	140
cis-1,2-Dichloroethene	99	9	70	125	60	135
cis-1,3-Dichloropropene	100	10	70	130	60	140
Dibromomethane	101	8	75	125	65	135
Dichlorodifluoromethane	93	21	30	155	10	175
Ethylbenzene	100	9	75	125	65	135
Hexachlorobutadiene	97	15	50	140	35	160
Isopropylbenzene	101	9	75	125	65	135
m,p-Xylene	102	9	75	130	65	135
Methyl tert-butyl ether	94	10	65	125	55	135
Methylene chloride	96	14	55	140	40	155
Naphthalene	96	14	55	140	40	150
n-Butylbenzene	103	11	70	135	55	150
n-Propylbenzene	101	9	70	130	65	140
o-Xylene	100	7	80	120	75	130
p-Isopropyltoluene	102	10	75	130	65	140
sec-Butylbenzene	100	9	70	125	65	135
Styrene	100	11	65	135	55	145
tert-Butylbenzene	99	10	70	130	60	140
Tetrachloroethene	96	18	45	150	25	165
Toluene	100	7	75	120	70	130
trans-1,2-Dichloroethene	99	13	60	140	45	150
trans-1,3-Dichloropropene	98	15	55	140	40	155
Trichloroethene	99	9	70	125	60	135
Trichlorofluoromethane	103	15	60	145	45	160
Vinyl chloride	99	16	50	145	35	165

Table G-5. LCS Control Limits for Volatile Organic Compounds SW-846 Method 8260 Solid Matrix[3]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
1,1,1,2-Tetrachloroethane	100	9	75	125	65	135
1,1,1-Trichloroethane	101	11	70	135	55	145
1,1,2,2-Tetrachloroethane	93	13	55	130	40	145
1,1,2-Trichloroethane	95	11	60	125	50	140
1,1-Dichloroethane	99	9	75	125	65	135
1,1-Dichloroethene	100	12	65	135	55	150
1,1-Dichloropropene	102	11	70	135	60	145
1,2,3-Trichlorobenzene	97	12	60	135	50	145
1,2,3-Trichloropropane	97	11	65	130	50	140
1,2,4-Trichlorobenzene	98	11	65	130	55	140
1,2,4-Trimethylbenzene	100	12	65	135	55	145
1,2-Dibromo-3-chloropropane	87	16	40	135	25	150
1,2-Dibromoethane	97	9	70	125	60	135
1,2-Dichlorobenzene	97	7	75	120	65	125
1,2-Dichloroethane	104	11	70	135	60	145
1,2-Dichloropropane	95	8	70	120	65	125
1,3,5-Trimethylbenzene	99	11	65	135	55	145
1,3-Dichlorobenzene	98	9	70	125	65	135
1,3-Dichloropropane	100	8	75	125	70	130
1,4-Dichlorobenzene	98	9	70	125	65	135
2,2-Dichloropropane	101	11	65	135	55	145
2-Butanone	94	22	30	160	10	180
2-Chlorotoluene	98	10	70	130	60	140
2-Hexanone	97	16	45	145	30	160
4-Chlorotoluene	100	9	75	125	65	135
4-Methyl-2-pentanone	97	17	45	145	30	165
Acetone	88	23	20	160	10	180
Benzene	99	9	75	125	65	135
Bromobenzene[4]	93	9	65	120	55	130
Bromochloromethane	99	9	70	125	60	135
Bromodichloromethane	100	9	70	130	60	135
Bromoform	96	13	55	135	45	150
Bromomethane	95	21	30	160	10	180
Carbon disulfide	103	19	45	160	30	180
Carbon tetrachloride	100	11	65	135	55	145
Chlorobenzene	99	8	75	125	65	130
Chlorodibromomethane	98	11	65	130	55	140
Chloroethane	98	20	40	155	20	175

[3] A number of sporadic marginal exceedances of the control limits are allowed, depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits. LCS control limits are not available for Methyl tert-butyl ether and Total Xylene. Sufficient data to perform statistically significant analyses were not received for MTBE during the LCS study. Xylene may be reported on a project-specific basis as a total number; however, for the purposes of the DoD QSM, it will be analyzed and reported as m,p-Xylene and o-Xylene. Additional limits for poor performing compounds can be found in section G.5 and for surrogate compounds in section G.6.

[4] Provisional limits – outlier analyses during the LCS study resulted in LCS-CLs generated with data from fewer than four laboratories. Limits may be adjusted in the future as additional data become available.

Table G-5. LCS Control Limits for Volatile Organic Compounds SW-846 Method 8260 Solid Matrix[3] (continued)

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Chloroform	98	9	70	125	65	135
Chloromethane	90	13	50	130	40	140
cis-1,2-Dichloroethene	96	10	65	125	55	135
cis-1,3-Dichloropropene	99	9	70	125	65	135
Dibromomethane	100	9	75	130	65	135
Dichlorodifluoromethane[4]	85	17	35	135	15	155
Ethylbenzene	101	9	75	125	65	135
Hexachlorobutadiene	98	15	55	140	40	155
Isopropylbenzene	103	9	75	130	70	140
m,p-Xylene	102	8	80	125	70	135
Methylene chloride	97	14	55	140	40	155
Naphthalene	84	14	40	125	25	140
n-Butylbenzene	101	12	65	140	50	150
n-Propylbenzene	99	12	65	135	50	145
o-Xylene	101	8	75	125	70	135
p-Isopropyltoluene	104	10	75	135	65	140
sec-Butylbenzene	97	11	65	130	50	145
Styrene	101	9	75	125	65	135
tert-Butylbenzene	99	11	65	130	55	145
Tetrachloroethene	103	12	65	140	55	150
Toluene	99	9	70	125	60	135
trans-1,2-Dichloroethene	100	11	65	135	55	145
trans-1,3-Dichloropropene	96	10	65	125	55	140
Trichloroethene	101	8	75	125	70	130
Trichlorofluoromethane	106	27	25	185	10	215
Vinyl chloride	92	11	60	125	45	140

Table G-6. LCS Control Limits for Semivolatile Organic Compounds SW-846 Method 8270 Water Matrix[5]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Polynuclear Aromatics						
2-Methylnaphthalene	75.0	9.5	45	105	35	115
Acenaphthene	77.6	10.1	45	110	35	120
Acenaphthylene	78.5	9.4	50	105	40	115
Anthracene	83.0	9.7	55	110	45	120
Benz[a]anthracene	82.7	8.9	55	110	45	120
Benzo[a]pyrene	81.3	9.5	55	110	45	120

[5] A number of sporadic marginal exceedances of the control limits are allowed depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits. LCS control limits are not available for Benzidine, 2,6-Dichlorophenol, and N-nitrosopyrrolidine. Sufficient data to perform statistically significant analyses were not received for those analytes during the LCS study. Additional limits for poor performing compounds can be found in section G.5.

Table G-6. LCS Control Limits for Semivolatile Organic Compounds SW-846 Method 8270 Water Matrix[5] (continued)

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Benzo[b]fluoranthene	81.8	12.1	45	120	35	130
Benzo[k]fluoranthene	84.6	13.2	45	125	30	135
Benzo[g,h,i]perylene	80.5	14.1	40	125	25	135
Chrysene	82.1	8.9	55	110	45	120
Dibenz[a,h]anthracene	84.7	14.1	40	125	30	140
Fluoranthene	85.2	10.4	55	115	45	125
Fluorene	80.6	10.3	50	110	40	120
Indeno[1,2,3-cd]pyrene	84.3	13.6	45	125	30	140
Naphthalene	70.8	10.5	40	100	30	115
Phenanthrene	84.0	11.0	50	115	40	130
Pyrene	88.6	13.2	50	130	35	140
Phenolic/Acidic						
2,4,5-Trichlorophenol	79.7	10.3	50	110	40	120
2,4,6-Trichlorophenol	80.7	10.7	50	115	40	125
2,4-Dichlorophenol	76.3	9.6	50	105	40	115
2,4-Dimethylphenol	68.8	13.5	30	110	15	125
2,4-Dinitrophenol	75.8	20.6	15	140	10	160
2-Chlorophenol	71.3	11.4	35	105	25	115
2-Methylphenol	73.3	11.7	40	110	25	120
2-Nitrophenol	75.8	12.4	40	115	25	125
3-Methylphenol/4-Methylphenol	71.3	13.0	30	110	20	125
4,6-Dinitro-2-methylphenol	84.9	15.0	40	130	25	145
4-Chloro-3-methylphenol	78.6	10.7	45	110	35	120
Pentachlorophenol	77.6	13.3	40	115	25	130
Basic						
3,3'-Dichlorobenzidine	65.2	15.3	20	110	10	125
4-Chloroaniline	62.2	15.6	15	110	10	125
Phthalate Esters						
Bis(2-ethylhexyl) phthalate	84.2	14.0	40	125	30	140
Butyl benzyl phthalate	81.1	11.7	45	115	35	130
Di-n-butyl phthalate	84.8	10.3	55	115	45	125
Di-n-octyl phthalate	87.4	16.6	35	135	20	155
Diethyl phthalate	79.2	12.9	40	120	30	130
Dimethyl phthalate	75.9	16.9	25	125	10	145
Nitrosoamines						
N-Nitrosodi-n-propylamine	80.9	15.7	35	130	20	145
N-Nitrosodimethylamine	67.9	14.1	25	110	10	125
N-Nitrosodiphenylamine	79.6	10.6	50	110	35	120
Chlorinated Aliphatics						
Bis(2-chlorethoxy)methane	76.2	10.2	45	105	35	115
Bis(2-chloroethyl) ether	73.3	12.3	35	110	25	120
Bis(2-chloroisopropyl) ether	78.2	17.5	25	130	10	150
Hexachlorobutadiene	65.2	12.6	25	105	15	115
Hexachloroethane	60.9	11.1	30	100	15	105

Table G-6. LCS Control Limits for Semivolatile Organic Compounds SW-846 Method 8270 Water Matrix[5] (continued)

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Halogenated Aromatics						
1,2,4-Trichlorobenzene	71.7	11.6	35	105	25	120
1,2-Dichlorobenzene	67.3	11.4	35	100	20	115
1,3-Dichlorobenzene	64.8	10.9	30	100	20	110
1,4-Dichlorobenzene	64.8	10.9	30	100	20	110
2-Chloronaphthalene	76.5	9.3	50	105	40	115
4-Bromophenyl phenyl ether	82.9	10.2	50	115	40	125
4-Chlorophenyl phenyl ether	80.6	10.3	50	110	40	120
Hexachlorobenzene	82.3	10.0	50	110	40	120
Nitroaromatics						
2,4-Dinitrotoluene	84.3	11.2	50	120	40	130
2,6-Dinitrotoluene	82.7	11.3	50	115	35	130
2-Nitroaniline	81.8	11.2	50	115	35	125
3-Nitroaniline	72.6	17.7	20	125	10	145
4-Nitroaniline	77.2	13.7	35	120	20	130
Nitrobenzene	76.8	10.8	45	110	35	120
Neutral Aromatics						
Carbazole	82.5	11.4	50	115	35	130
Dibenzofuran	80.3	8.8	55	105	45	115
Others						
1,2-Diphenylhydrazine	84.8	9.4	55	115	45	120
Benzyl alcohol	71.0	13.8	30	110	15	125
Isophorone	81.0	10.5	50	110	40	125

Table G-7. LCS Control Limits for Semivolatile Organic Compounds SW-846 Method 8270 Solid Matrix[6]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Polynuclear Aromatics						
2-Methylnaphthalene	77.3	10.0	45	105	35	115
Acenaphthene	77.3	10.3	45	110	35	120
Acenaphthylene	75.7	10.4	45	105	35	115
Anthracene	79.9	9.0	55	105	45	115
Benz[a]anthracene	81.6	9.8	50	110	40	120
Benzo[a]pyrene	80.7	10.3	50	110	40	120
Benzo[b]fluoranthene	79.7	11.4	45	115	35	125
Benzo[k]fluoranthene	83.8	12.9	45	125	30	135
Benzo[g,h,i]perylene	81.8	14.7	40	125	25	140
Chrysene	82.6	9.9	55	110	45	120

[6] A number of sporadic marginal exceedances (ME) of the control limits are allowed, depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits. LCS control limits are not available for Benzidine, 2,6-Dichlorophenol, 1,2-Diphenylhydrazine, and N-nitrosopyrrolidine. Sufficient data to perform statistically significant analyses were not received for those analytes during the LCS study. Additional limits for poor performing compounds can be found in section G.5.

Table G-7. LCS Control Limits for Semivolatile Organic Compounds SW-846 Method 8270 Solid Matrix[6] (continued)

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Dibenz[a,h]anthracene	82.9	13.9	40	125	25	140
Fluoranthene	83.9	10.1	55	115	45	125
Fluorene	78.3	9.8	50	110	40	115
Indeno[1,2,3-cd]pyrene	79.7	13.8	40	120	25	135
Naphthalene	73.4	11.1	40	105	30	120
Phenanthrene	80.1	10.0	50	110	40	120
Pyrene	84.4	12.8	45	125	35	135
Phenolic/Acidic						
2,4,5-Trichlorophenol	80.1	10.4	50	110	40	120
2,4,6-Trichlorophenol	76.3	11.0	45	110	30	120
2,4-Dichlorophenol	77.2	10.9	45	110	35	120
2,4-Dimethylphenol	67.3	11.9	30	105	20	115
2,4-Dinitrophenol	72.6	20.0	15	130	10	150
2-Chlorophenol	74.7	10.3	45	105	35	115
2-Methylphenol	71.7	10.6	40	105	30	115
2-Nitrophenol	76.2	11.5	40	110	30	120
3-Methylphenol/4-Methylphenol	73.9	10.9	40	105	30	120
4,6-Dinitro-2-methylphenol	83.1	18.0	30	135	10	155
4-Chloro-3-methylphenol	79.5	11.1	45	115	35	125
4-Nitrophenol	77.0	20.2	15	140	10	160
Pentachlorophenol	71.9	15.6	25	120	10	135
Phenol	69.7	10.2	40	100	30	110
Phthalate Esters						
Bis(2-ethylhexyl) phthalate	87.4	13.3	45	125	35	140
Butyl benzyl phthalate	86.4	12.3	50	125	35	135
Di-n-butyl phthalate	83.2	9.1	55	110	45	120
Di-n-octyl phthalate	86.4	15.2	40	130	25	145
Diethyl phthalate	82.2	10.6	50	115	40	125
Dimethyl phthalate	79.6	10.2	50	110	40	120
Nitrosoamines						
N-Nitrosodi-n-propylamine	76.8	12.3	40	115	30	125
N-Nitrosodimethylamine	66.1	15.9	20	115	10	130
N-Nitrosodiphenylamine	82.4	11.1	50	115	40	125
Chlorinated Aliphatics						
Bis(2-chlorethoxy)methane	75.5	10.9	45	110	30	120
Bis(2-chloroethyl) ether	71.1	11.2	40	105	25	115
Bis(2-chloroisopropyl) ether	68.4	15.7	20	115	10	130
Hexachlorobutadiene	78.2	12.9	40	115	25	130
Hexachloroethane	71.9	12.6	35	110	20	120
Halogenated Aromatics						
1,2,4-Trichlorobenzene	77.4	11.2	45	110	30	120
1,2-Dichlorobenzene	70.9	8.7	45	100	35	105
1,3-Dichlorobenzene	69.7	10.3	40	100	30	110
1,4-Dichlorobenzene	69.0	11.4	35	105	25	115

Table G-7. LCS Control Limits for Semivolatile Organic Compounds SW-846 Method 8270 Solid Matrix (continued)

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
2-Chloronaphthalene	75.2	9.9	45	105	35	115
4-Bromophenyl phenyl ether	81.7	11.8	45	115	35	130
4-Chlorophenyl phenyl ether	79.6	10.7	45	110	35	120
Hexachlorobenzene	82.5	11.7	45	120	35	130
Nitroaromatics						
2,4-Dinitrotoluene	82.0	11.4	50	115	35	130
2,6-Dinitrotoluene	80.2	10.7	50	110	35	125
2-Nitroaniline	81.0	12.2	45	120	30	130
3-Nitroaniline	68.8	13.8	25	110	15	125
4-Nitroaniline	73.6	13.1	35	115	20	125
Nitrobenzene	77.2	11.9	40	115	30	125
Neutral Aromatics						
Carbazole	80.4	12.3	45	115	30	130
Dibenzofuran	77.1	8.8	50	105	40	110
Others						
Benzyl alcohol	70.9	17.4	20	125	10	140
Isophorone	77.0	11.4	45	110	30	125

Table G-8. LCS Control Limits for Chlorinated Herbicides SW-846 Method 8151 Water Matrix[7]

Analyte	Median	Lower Control Limit	Upper Control Limit
2,4-D	88	35	115
2,4-DB	99	45	130
2,4,5-T	83	35	110
2,4,5-TP (Silvex)	87	50	115
Dalapon	62	40	110
Dicamba	86	60	110
Dichloroprop	91	70	120
Dinoseb	65	20	100
MCPA	93	60	145

[7] LCS control limits were generated using non-parametric statistics (see section G.1 for further explanation). LCS control limits are not available for MCPP. Sufficient data to perform statistically significant analyses were not received for the analyte during the LCS study.

Table G-9. LCS Control Limits for Chlorinated Herbicides SW-846 Method 8151 Solid Matrix[8]

Analyte	Median	Lower Control Limit	Upper Control Limit
2,4-D	88	35	145
2,4-DB	108	50	155
2,4,5-T	86	45	135
2,4,5-TP (Silvex)	90	45	125
Dicamba	90	55	110
Dichloroprop	99	75	140

Table G-10. LCS Control Limits for Polynuclear Aromatic Hydrocarbons SW-846 Method 8310 Water Matrix[9]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Acenaphthene	70	11	35	105	25	115
Acenaphthylene	74	13	35	115	20	125
Anthracene	77	12	40	110	30	125
Benz[a]anthracene	81	11	50	110	40	125
Benzo[a]pyrene	79	11	45	115	35	125
Benzo[b]fluoranthene	82	10	50	110	40	125
Benzo[k]fluoranthene	79	10	50	110	40	120
Benzo[g,h,i]perylene	77	14	35	120	20	135
Chrysene	83	11	50	115	40	125
Dibenz[a,h]anthracene	64	15	20	110	10	125
Fluoranthene	82	11	50	115	35	125
Fluorene	69	11	35	105	25	115
Indeno[1,2,3-cd]pyrene	80	11	45	110	35	125
Naphthalene	68	12	35	105	20	115
Phenanthrene	80	13	40	120	25	135
Pyrene	80	9	50	110	45	115

[8] LCS control limits were generated using non-parametric statistics (see section G.1 for further explanation). LCS control limits are not available for Dalapon, MCPA, and MCPP. Sufficient data to perform statistically significant analyses were not received for those analytes during the LCS study. Additional limits for poor performing compounds can be found in section G.5.

[9] A number of sporadic marginal exceedances of the control limits are allowed, depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits.

Table G-11. LCS Control Limits for Polynuclear Aromatic Hydrocarbons SW-846 Method 8310 Solid Matrix[10]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Acenaphthene	71	12	35	110	20	120
Acenaphthylene	73	13	35	115	20	125
Anthracene	86	13	45	125	35	140
Benz[a]anthracene	78	9	50	105	40	115
Benzo[a]pyrene	86	15	40	135	25	150
Benzo[b]fluoranthene	89	11	55	120	45	130
Benzo[k]fluoranthene	84	12	50	120	35	135
Benzo[g,h,i]perylene[11]	85	10	55	115	45	125
Chrysene	87	11	55	120	45	130
Dibenz[a,h]anthracene	81	11	45	115	35	125
Fluoranthene	88	16	40	135	25	150
Fluorene	76	10	45	105	35	115
Indeno[1,2,3-cd]pyrene	95	13	55	135	45	145
Naphthalene	80	11	50	110	40	120
Phenanthrene	91	12	55	125	45	135
Pyrene	82	11	50	115	40	125

Table G-12. LCS Control Limits for Explosives SW-846 Methods 8330 and 8330A Water Matrix[12]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
1,3,5-Trinitrobenzene	102	13	65	140	50	150
1,3-Dinitrobenzene	103	18	45	160	30	175
2,4-Dinitrotoluene	98	12	60	135	50	145
2,6-Dinitrotoluene	99	13	60	135	50	150
2,4,6-Trinitrotoluene (TNT)	98	15	50	145	35	160
2-Amino-4,6-dinitrotoluene[13]	101	17	50	155	35	170
2-Nitrotoluene	88	15	45	135	30	150
3-Nitrotoluene	90	14	50	130	35	145
4-Amino-2,6-dinitrotoluene[13]	104	16	55	155	40	170
4-Nitrotoluene	90	14	50	130	35	145
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	106	18	50	160	35	180
Methyl-2,4,6-trinitrophenylnitramine (Tetryl)[13]	98	25	20	175	10	200
Nitrobenzene	94	15	50	140	35	155
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	99	6	80	115	75	120

[10] A number of sporadic marginal exceedances of the control limits are allowed, depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits.

[11] Provisional limits – outlier analyses during the LCS study resulted in LCS-CLs generated with data from fewer than four laboratories. Limits may be adjusted in the future as additional data become available.

[12] A number of sporadic marginal exceedances of the control limits are allowed, depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits. LCS control limits were generated using solid phase extraction with acetonitrile only, without removing outliers from the data set (see section G.1 for further explanation).

[13] Provisional limits – outlier analyses during the LCS study resulted in LCS-CLs generated with data from fewer than four laboratories. Limits may be adjusted in the future as additional data become available.

Table G-13. LCS Control Limits for Explosives SW-846 Methods 8330 and 8330A Solid Matrix[14]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
1,3,5-Trinitrobenzene	99	9	75	125	65	135
1,3-Dinitrobenzene	102	8	80	125	70	135
2,4-Dinitrotoluene	102	7	80	125	75	130
2,6-Dinitrotoluene	100	7	80	120	70	130
2,4,6-Trinitrotoluene (TNT)	99	14	55	140	45	155
2-Amino-4,6-dinitrotoluene	102	7	80	125	75	130
2-Nitrotoluene	101	7	80	125	70	130
3-Nitrotoluene	100	7	75	120	70	130
4-Amino-2,6-dinitrotoluene	101	7	80	125	75	130
4-Nitrotoluene	101	8	75	125	70	135
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	103	10	70	135	65	145
Nitrobenzene	100	8	75	125	70	130
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	100	9	75	125	65	135

Table G-14. LCS Control Limits for Organochlorine Pesticides SW-846 Method 8081 Water Matrix[15]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
4,4'-DDD	88	20	25	150	10	170
4,4'-DDE	87	18	35	140	15	160
4,4'-DDT	92	15	45	140	30	155
Aldrin	83	19	25	140	10	155
alpha-BHC	94	11	60	130	50	140
alpha-Chlordane	93	10	65	125	55	135
beta-BHC	96	10	65	125	55	135
delta-BHC	91	15	45	135	30	150
Dieldrin	95	11	60	130	50	140
Endosulfan I[16]	80	10	50	110	40	120
Endosulfan II	79	17	30	130	10	150
Endosulfan sulfate	96	14	55	135	40	150
Endrin	95	13	55	135	45	145
Endrin aldehyde	96	14	55	135	40	150
Endrin ketone	102	8	75	125	70	135
gamma-BHC	82	18	25	135	10	155
gamma-Chlordane	94	11	60	125	50	135
Heptachlor	87	15	40	130	30	145
Heptachlor epoxide	96	11	60	130	50	140
Methoxychlor	103	16	55	150	40	165

[14] A number of sporadic marginal exceedances of the control limits are allowed, depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits. Additional limits for poor performing compounds can be found in section G.5.

[15] A number of sporadic marginal exceedances of the control limits are allowed, depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits. LCS control limits are not available for Hexachlorobenzene and Toxaphane. Sufficient data to perform statistically significant analyses were not received for those analytes during the LCS study. Additional limits for surrogate compounds can be found in section G.6.

[16] Provisional limits – outlier analyses during the LCS study resulted in LCS-CLs generated with data from fewer than four laboratories. Limits may be adjusted in the future as additional data becomes available.

Table G-15. LCS Control Limits for Organochlorine Pesticides SW-846 Method 8081 Solid Matrix [17]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
4,4'-DDD	81	18	30	135	10	155
4,4'-DDE	97	10	70	125	60	135
4,4'-DDT	92	16	45	140	30	155
Aldrin	93	16	45	140	30	155
alpha-BHC	93	10	60	125	50	135
alpha-Chlordane	92	10	65	120	55	130
beta-BHC	95	11	60	125	50	135
delta-BHC	94	12	55	130	45	145
Dieldrin	96	10	65	125	55	135
Endosulfan I	74	20	15	135	10	155
Endosulfan II	89	17	35	140	20	160
Endosulfan sulfate	99	12	60	135	50	145
Endrin	97	12	60	135	50	145
Endrin aldehyde	92	18	35	145	20	165
Endrin ketone	100	11	65	135	55	145
gamma-BHC	91	11	60	125	50	135
gamma-Chlordane	96	10	65	125	55	135
Heptachlor	96	15	50	140	35	155
Heptachlor epoxide	98	11	65	130	55	140
Methoxychlor	100	14	55	145	45	155

Table G-16. LCS Control Limits for Polychlorinated Biphenyls SW-846 Method 8082 Water Matrix[18]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
Aroclor 1016	85	20	25	145
Aroclor 1260	87	19	30	145

Table G-17. LCS Control Limits for Polychlorinated Biphenyls SW-846 Method 8082 Solid Matrix[18]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
Aroclor 1016	90	16	40	140
Aroclor 1260	96	12	60	130

[17] A number of sporadic marginal exceedances of the control limits are allowed, depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits. LCS control limits are not available for Hexachlorobenzene, Hexachlorocyclopentadiene, and Toxaphane. Sufficient data to perform statistically significant analyses were not received for those analytes during the LCS study. Additional limits for surrogate compounds can be found in section G.6.

[18] LCS control limits are not available for Aroclors 1221, 1232, 1242, 1248, 1262, and 1268. Sufficient data to perform statistically significant analyses were not received for those analytes during the LCS study. Additional limits for surrogate compounds can be found in section G.6.

Table G-18. LCS Control Limits for Metals SW-846 Methods 6010 and 7470 Water Matrix[19]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Aluminum	97	5	80	120	80	120
Antimony	98	4	80	120	80	120
Arsenic	98	4	80	120	80	120
Barium	99	4	80	120	80	120
Beryllium	99	4	80	120	80	120
Cadmium	100	4	80	120	80	120
Calcium	98	4	80	120	80	120
Chromium	100	4	80	120	80	120
Cobalt	99	3	80	120	80	120
Copper	99	3	80	120	80	120
Iron	102	4	80	120	80	120
Lead	99	4	80	120	80	120
Magnesium	98	4	80	120	80	120
Manganese	100	4	80	120	80	120
Mercury	100	5	80	120	No ME	No ME
Molybdenum	95	5	80	120	75	120
Nickel	100	4	80	120	80	120
Potassium	98	4	80	120	80	120
Selenium	98	6	80	120	75	120
Silver	97	5	80	120	75	120
Sodium	99	4	80	120	80	120
Thallium	97	4	80	120	80	120
Vanadium	99	4	80	120	80	120
Zinc	100	4	80	120	80	120

[19] The as-generated limits have been adjusted to reflect Method requirements and acceptable calibration uncertainty. A number of sporadic marginal exceedances of the control limits are allowed for Method 6010, depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits.

Table G-19. LCS Control Limits for Metals SW-846 Methods 6010 and 7471 Solid Matrix [20]

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Aluminum	95	5	80	120	75	120
Antimony	96	5	80	120	75	120
Arsenic	95	4	80	120	80	120
Barium	98	3	80	120	80	120
Beryllium	99	4	80	120	80	120
Cadmium	97	4	80	120	80	120
Calcium	97	4	80	120	80	120
Chromium	99	5	80	120	80	120
Cobalt	98	4	80	120	80	120
Copper	97	3	80	120	80	120
Iron	100	4	80	120	80	120
Lead	95	4	80	120	80	120
Magnesium	96	3	80	120	80	120
Manganese	97	4	80	120	80	120
Mercury	100	6	80	120	No ME	No ME
Molybdenum	96	5	80	120	75	120
Nickel	97	4	80	120	80	120
Potassium	96	4	80	120	80	120
Selenium	93	4	80	120	75	120
Silver	96	7	75	120	70	125
Sodium	96	4	80	120	80	120
Thallium	94	4	80	120	80	120
Vanadium	99	3	80	120	80	120
Zinc	95	5	80	120	75	120

[20] The as-generated limits have been adjusted to reflect Method requirements and acceptable calibration uncertainty. A number of sporadic marginal exceedances of the control limits are allowed for Method 6010, depending on the number of analytes spiked in the LCS. Refer to section G.2 and Table G-1 for guidance on the appropriate application of control and ME limits.

ATTACHMENT A-4

LABORATORY STANDARD OPERATING PROCEDURES

(PROVIDED ON CD-ROM)

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Title : **EPA METHOD 3510C, SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION**

Document No. : SOP-M200
Revision No. : 2.6
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APPROVED FOR RELEASE BY: _____ 11/20/12
MANAGEMENT **DATE**

_____ 11-20-12
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 3510C, Separatory Funnel Liquid-Liquid Extraction.

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous matrices.

3. DETECTION LIMITS

3.1. Refer to the determinative (analytical) method for detection limits.

4. SCOPE AND APPLICATION

4.1. EPA Method 3510C describes the procedures for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods including, but not limited to, EPA Methods 8081B, 8082A, 8141A, 8270D, and 8310.

4.2. This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organic compounds in preparation for a variety of chromatographic procedures.

4.3. This method is restricted to use by or under the supervision of analysts/technicians experienced in the use of the equipments and apparatus required to execute the procedure.

5. METHOD SUMMARY

5.1. A measured volume of sample, usually one liter, at a specified pH (see Appendix A), is serially extracted with methylene chloride using a 2-L separatory funnel. The extract is dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be employed. Refer to Appendix A for specifics.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined

matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. ***Limit of Detection (LOD) is defined as the smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99 %). At the LOD, the false negative rate (Type II error) is 1 %.***

6.13. ***Limit of Quantitation (LOQ) is at the lowest concentration that produces a quantitative result within specified limits of precision and bias***

6.14. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an

independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.15. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.16. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.17. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.18. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.19. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.20. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.21. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.22. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.23. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.24. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.26. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.27. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.28. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary.

7.2. Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to the current revisions of SOP-M233, "EPA Method 3640A Gel-Permeation Cleanup" and SOP-M234, "EPA Method 3600C(M) Cleanup" for guidance on cleanup procedures.

7.3. Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

7.4. Glassware contaminated with surfactants can cause analyte degradation. Specifically, aldrin, heptachlor, and most organophosphorus pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., K-D flask, etc.). These items should be hand-rinsed very carefully to avoid this problem.

7.5. Boiling stones with acidic or basic characteristics can interfere with base/neutral or acid analysis. Care should be taken when selecting boiling stones so that they are not a factor in the loss of base/neutral or acid analytes.

7.6. The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with

increasing pH, and are decreased by shorter reaction times available in EPA Method 3510C. Hence, EPA Method 3510C is preferred over EPA Method 3520C for the analysis of these classes of compounds. However, the recovery of phenols may be optimized by using EPA Method 3520C, and performing the initial extraction at the acid pH.

7.7. Refer to the determinative method for other potential interferences.

8. SAFETY

8.1. Methylene chloride creates excessive pressure very rapidly. Extreme care must be taken when methylene chloride is added to the sample bottle and to the separatory funnel. Initial venting should be done immediately after the sample bottle or separatory funnel has been sealed and shaken once. Vent often into a fume hood to avoid exposure to solvent vapors.

8.2. Extraction must be performed in a fume hood vented to the exterior of the laboratory.

8.3. For the safety of the analyst, cracked or broken glassware should be immediately discarded into a broken glassware receptacle. Broken glassware shall not be used in any step of the extraction.

8.4. To ensure the safety of the analyst during any possible emergency situation, it is recommended that chemists do not perform extractions alone. Another chemist should be present during any extraction process.

8.5. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

8.7. Many compounds covered by this method have been tentatively classified as known or suspected human carcinogens. A NIOSH/MESA approved toxic gas respirator should be worn when extracting high concentration samples.

9. EQUIPMENT AND SUPPLIES

9.1. Separatory funnels, 2-L, pear-shaped, borosilicate glass or transparent polytetrafluoroethylene (PTFE), with PTFE stopcock and PTFE stopper or screw cap, Kimax Squibb Separatory Funnel, Nalgene Squibb Transparent FEP Separatory Funnel, or equivalent.

9.2. VOA vials, 28-mm × 95-mm (40-mL capacity), screw top, clear or amber glass, with Teflon- or aluminum foil-lined open top or closed top screw caps and Teflon-lined septa, EPA VOA Vial or equivalent.

9.3. Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

9.4. Autoinjector/Autosampler vials, 12-mm × 32-mm (2-mL capacity), crimp top, clear glass, with aluminum crimp caps and Teflon-lined septa, disposable.

9.5. Vial inserts, 300−µL, clear glass, with conical bottom and spring.

9.6. Graduated cylinders, 100-mL, 1000-mL, 2000-mL, or other capacity, glass, Class A.

9.7. Erlenmeyer flasks, 500-mL or other capacity, glass.

9.8. Pipets, Pasteur, glass, disposable.

9.9. pH indicator paper, wide range. pH range should include the desired extraction pH (see Appendix A).

9.10. Glass wool, borosilicate glass fiber without binder resin, Pyrex® or equivalent.

9.11. Filtration apparatus:

9.11.1. Hirsch funnel, short-stemmed, glass.

9.11.2. Filter paper, untreated or silicone-treated, 150-mm or 185-mm diameter, Whatman 1PS Phase Separator or equivalent.

9.11.2.1. Rinse silicone-treated filter paper with 5−10 mL of the extraction solvent prior to filtering sample extract. Discard the rinsate in the appropriate waste stream.

9.12. Kuderna-Danish (K-D) apparatus:

9.12.1. Concentrator tube, 10-mL, 19/22 joint size, graduated, without hooks, borosilicate glass, Kimble Kontes 570051-1025 or equivalent.

9.12.2. Evaporation flask, 250-mL or 500-mL, 24/40 top joint size, 19/22 bottom joint size, borosilicate glass, Kimble Kontes 570011-0250, Kimble Kontes 570037-0500, or equivalent.

9.12.2.1. Attach evaporation flask to concentrator tube with clamps.

9.12.3. Snyder column, three-ball macro, 24/40 joint size, without hooks, borosilicate glass, Kimble Kontes 503000-0121 or equivalent.

9.12.4. Snyder column, two-ball micro, 19/22 joint size, without hooks, borosilicate glass, Kimble Kontes 569011-0219 or equivalent.

9.12.5. Clamps, fitting 19/22 joint size, polyacetal, Kimble Kontes 675300-0019 or equivalent.

9.12.6. Stopper, pennyhead, fitting 19/22 joint size, ground glass, Kimble Kontes 850500-1922 or equivalent.

9.12.6.1. Use ground-glass stopper to prevent evaporation of extract after concentration.

9.13. Boiling stones, Teflon.

9.14. Water bath, heated, capable of temperature control within ± 5°C.

9.14.1. Place water bath in a fume hood.

9.15. Beakers, 2000-mL or other capacity, glass.

9.16. Thermometer, calibrated.

9.17. Hot plate.

9.18. Gloves, heat resistant.

9.19. Nitrogen, N_2, 99.998%, compressed, Praxair 4.8 grade or higher.

9.20. Balance, top loading, capable of weighing to the nearest 0.01 g.

9.21. Dispensers, 1–10-mL, 2.5–25-mL, and 5–50-mL, analog display, adjustable volume.

9.22. Shaker, 40–400-rpm variable speed, 0–60-min mechanical timer, Thermo Scientific Lab-Line MaxQ 3000 Open-Air Shaker Model SHKA3000 or equivalent.

9.23. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certification.

9.24. Refer to the specific SOPs of the determinative methods for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free.

10.1.2. Sodium sulfate, Na_2SO_4, anhydrous, white powder, reagent grade or equivalent.

10.1.2.1. Purify sodium sulfate by heating at 400°C for 4 hours in a shallow tray, or by pre-cleaning with methylene chloride. If sodium sulfate is pre-cleaned with methylene chloride, use method blank to demonstrate that the drying agent is free of interferences.

10.1.3. Sodium hydroxide, NaOH, white pellets and granules, reagent grade or equivalent.

10.1.4. Sodium hydroxide, NaOH, 10-N.

10.1.4.1. Prepare the 10-N NaOH solution by dissolving 400 g of NaOH in reagent water, cool and dilute to 1000 mL with additional reagent water.

10.1.5. Sulfuric acid, H_2SO_4, 90–98% (v/v), concentrated, colorless liquid, reagent grade or equivalent.

10.1.6. Sulfuric acid, H_2SO_4, 1:1 (v/v).

10.1.6.1. Prepare the 1:1 H_2SO_4 solution by slowly adding 500 mL of concentrated H_2SO_4 to 500 mL of reagent water.

10.1.7. Methylene chloride, CH_2Cl_2, clear colorless liquid, boiling point 39.8°C, pesticide grade or equivalent.

10.1.8. Hexane, C_6H_{14}, clear colorless liquid, boiling point 68.7°C, pesticide grade or equivalent.

10.1.9. Acetonitrile, CH_3CN, clear colorless liquid, boiling point 81.6°C, pesticide grade or equivalent.

10.1.10. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Refer to the specific SOPs of the determinative methods for standards.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Refer to the specific SOPs of the mobility extraction and determinative methods for sample collection, preservation, containers and holding times.

12. QUALITY CONTROL

12.1. Event Based Quality Control (LCS/LCSDs and MBs)

12.1.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.1.2. One LCS consisting of the specified compounds spiked into clean reagent water is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. The LCSD is handled identically to the LCS.

12.1.3. One MB consisting of clean reagent water is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

12.1.4. The MB/LCS/LCSD is processed concurrently with the associated samples. In the processing of the MB/LCS/LCSD, reagents and procedures identical to those for actual samples are used (e.g., surrogates, internal standards, etc.).

12.2. Matrix Based Quality Control (Surrogates and MS/MSDs)

12.2.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and surrogates added to each sample.

12.2.2. One MS consisting of the actual sample matrix spiked with known concentrations of specific target analytes is required for every batch of 20 samples per matrix or portion thereof processed concurrently. The MSD is handled identically to the MS.

12.2.3. The sample which is spiked for the MS/MSD is processed concurrently with the associated samples. In the processing of the MS/MSD, reagents and procedures identical to those for actual samples are used (e.g., surrogates, internal standards, etc.).

12.3. A variety of problems can occur during the course of the extraction process and can drastically affect the integrity of the data produced.

12.3.1. If the extract is inadvertently concentrated to dryness, the sample can be irrevocably altered. A portion of the analyte content can be lost to the atmosphere. In this case, if there is sufficient sample, the best solution is to re-extract the sample. If there is insufficient sample, first let the extractor cool and allow the vapor to condense to see how much solvent can be recovered. Then add fresh solvent to the desired final volume (see Appendix A). If the latter is the only option, a notation must be made of the error. In addition, the analyst and the client must be made aware of the error. Low surrogate recoveries are indicative of the possible loss of target analytes. To avoid this problem, extracts should never be left unattended during concentration.

12.3.2. If the Snyder column floods, special care must be taken to correct the problem without losing any of the sample. In case of flooding, gently remove the Snyder column from the concentrator. Once it has cooled sufficiently, and the vapors have condensed, gently shake the column and allow the solvent to drain back into the concentrator. If the column is shaken while it is still hot and attached to the concentrator, the pressure build-up can force vapor out of the column and into the atmosphere, irrevocably altering the sample.

12.4. Refer to the specific SOPs of the determinative methods for additional information on quality control.

13. CALIBRATION AND STANDARDIZATION

13.1. Top Loading Balance

13.1.1. Calibrate the top loading balance at 100 g, 1000 g, and 2000 g using Class 2 weights.

13.1.2. Calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If the values are not within these limits, recalibrate the balance.

13.2. Thermometer

13.2.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T042, "Thermometer Calibration."

13.3. Dispenser

13.3.1. Calibrate the dispenser according to the procedure outlined in the Dispenser Calibration Check Logbook.

14. PROCEDURE

14.1. Aqueous Sample Preparation

14.1.1. The amount of sample required for analytical determination is established by the determinative method or the project's Quality Assurance Project Plan (QAPP).

14.1.1.1. The amount of sample generally required is 1000 mL nominal.

14.1.2. Mark the level of an aqueous sample on the outside of the sample bottle with a sharpie.

14.1.2.1. Alternatively, zero a top loading balance, and weigh the aqueous sample including the sample bottle. Record the mass to the nearest 1 g.

14.1.3. Check the pH by transferring a few drops of the aqueous sample onto a wide-range pH paper.

14.1.4. Quantitatively transfer the whole aqueous sample from the sample bottle into a clean separatory funnel.

14.1.4.1. For MB/LCS/LCSD, measure exactly 1000 mL of clean reagent water.

14.1.4.2. For MS/MSD, measure exactly 1000 mL of aqueous sample in each analytical batch selected for spiking.

14.1.5. Add the appropriate volume(s) of the surrogate standard solution(s) listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks.

14.1.5.1. If EPA Method 3640A, "Gel-Permeation Cleanup," is to be employed, add four times the volume of surrogate standard solution since only one quarter of the extract is processed by the GPC apparatus.

14.1.6. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spikes and laboratory control samples.

14.1.6.1. If EPA Method 3640A, "Gel-Permeation Cleanup," is to be employed, add four times the volume of spike standard solution since only one quarter of the extract is processed by the GPC apparatus.

14.1.7. Proceed to Section 14.3. for primary extraction procedure.

14.1.8. At the completion of the extraction step, measure the volume of the aqueous sample used by filling the sample bottle to the marked line with

tap water, and then transfer the tap water into a 1000-mL or 2000-mL graduated cylinder. Record the volume to the nearest 10 mL or the smallest graduation of the graduated cylinder.

14.1.8.1. Alternatively, zero the same top loading balance, and weigh the sample bottle. Record the mass to the nearest 1 g.

14.1.8.2. Calculate the volume of the aqueous sample used. The formula for calculating volume is listed in Section 15.1. Record the volume to the nearest 10 mL.

14.2. Mobility-Procedure Extract Preparation

14.2.1. Check the pH by transferring a few drops of a mobility-procedure extract onto a wide-range pH paper.

14.2.2. Measure exactly 100 mL of the mobility-procedure extract into a clean separatory funnel. Record the volume to the nearest 1 mL.

14.2.2.1. For MB/LCS/LCSD, measure exactly 100 mL of mobility-procedure extract designated as MB/LCS/LCSD. Refer to the mobility extraction method for information.

14.2.2.2. For MS/MSD, measure exactly 100 mL of mobility-procedure extract designated as MS/MSD. Refer to the mobility extraction method for information.

14.2.3. Add the appropriate volume(s) of the surrogate standard solution(s) listed in the determinative method to all sample, matrix spike, laboratory control sample, and method blank mobility-procedure extracts.

14.2.4. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spike and laboratory control sample mobility-procedure extracts.

14.2.5. Add exactly 900 mL of reagent water to the mobility-procedure extract.

14.2.6. Proceed to Section 14.3. for primary extraction procedure.

14.3. Primary Extraction

14.3.1. Adjust the pH of the aqueous sample or mobility-procedure extract with 1:1 H_2SO_4 or 10-N NaOH solution to the desired pH indicated in Appendix A for the specific determinative method that will be employed.

14.3.1.1. Adjust the pH of each associated QC sample or mobility-procedure extract with 1:1 H_2SO_4 or 10-N NaOH solution to the same pH.

14.3.2. Add 60 mL of methylene chloride to the sample bottle. Seal and shake the sample bottle vigorously with periodic venting to rinse the sample bottle. Transfer this rinse solvent to the separatory funnel.

14.3.3. Seal and shake the separatory funnel vigorously for 1−2 minutes with periodic venting to release excess pressure.

14.3.3.1. If an open-air shaker is to be utilized, seal and shake the separatory funnel vigorously for a few seconds with periodic venting to release excess pressure. Hold the separatory funnel in place with the clamps on the open-air shaker, and agitate the aqueous sample at 200 rpm for 2 minutes.

14.3.4. Allow the organic solvent layer to separate from the aqueous phase for a minimum of 10 minutes.

14.3.4.1. If the emulsion interface between layers is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the phase separation.

14.3.4.2. Break the emulsion or separate the phases of the emulsion by stirring, filtering the emulsion through glass wool, or centrifuging.

14.3.4.3. If the emulsion cannot be broken, transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in EPA Method 3520C, "Continuous Liquid-Liquid Extraction."

14.3.5. Collect the solvent extract in an Erlenmeyer flask.

14.3.6. Repeat the extraction two more times using 60 mL of fresh methylene chloride each time (Sections 14.3.2. through 14.3.5.).

14.3.6.1. Methylene chloride may be added directly to the separatory funnel without using the sample bottle.

14.3.7. Collect and combine the three solvent extracts in the same Erlenmeyer flask. Label the combined extract appropriately.

14.3.8. Proceed to Section 14.5. for concentration procedure.

14.3.8.1. If further pH adjustment and extraction are required (as indicated in Appendix A), proceed to Section 14.4. for secondary extraction procedure.

14.4. Secondary Extraction

14.4.1. Adjust the pH of the aqueous phase with 1:1 H_2SO_4 or 10-N NaOH solution to the desired pH indicated in Appendix A for the specific determinative method that will be employed.

14.4.1.1. Adjust the pH of the aqueous phase of each associated QC sample or mobility-procedure extract with 1:1 H_2SO_4 or 10-N NaOH solution to the same pH.

14.4.2. Serially extract three times with 60 mL of fresh methylene chloride each time (Sections 14.3.2. through 14.3.5.).

14.4.2.1. Methylene chloride may be added directly to the separatory funnel without using the sample bottle.

14.4.3. Collect and combine the three solvent extracts in the same Erlenmeyer flask. Label the combined extract appropriately.

14.4.4. If performing GC/MS analysis, the acid and base/neutral extracts (Sections 14.3.7. and 14.4.3.) may be combined prior to concentration.

14.4.4.1. If the presence or absence of specific acid or base/neutral compounds at low concentrations must be determined, separate extract analyses may be preferable.

14.4.5. Proceed to Section 14.5. for concentration procedure.

14.5. Assemble a Kuderna-Danish (K-D) apparatus by attaching a 10-mL concentrator tube to a 250-mL or 500-mL evaporation flask.

14.6. Dry the extract by passing it through a glass funnel containing silicone-treated filter paper (or anhydrous sodium sulfate on untreated filter paper). Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask thoroughly with methylene chloride, and add it to the funnel to complete the quantitative transfer.

14.7. Add one or two clean boiling stones to the evaporation flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15–20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10–20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

14.8. If a solvent exchange is required (as indicated in Appendix A), momentarily remove the Snyder column, add 50 mL of the exchange solvent (see Appendix A), a new boiling stone, and reattach the Snyder column. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath. Concentrate the extract, as per Section 14.7., raising the temperature of the water bath, if necessary, to maintain proper distillation.

14.9. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1–2 mL of methylene chloride or exchange solvent. It is possible that white sulfur crystals can appear in the extract during the concentration phase. If sulfur crystals appear, clean up the extract as outlined in the current revision of SOP-M234. The extract may be further concentrated by using the technique outlined in Section 14.10. or adjusted to the desired final volume (see Appendix A) with the solvent last used.

14.10. If further concentration is indicated in Appendix A, either the micro Snyder column technique or nitrogen blowdown technique can be used to adjust the extract to the final volume required.

14.10.1. If micro Snyder column technique is used, add another clean boiling stone to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water

bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5–10 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches about one half of the final volume, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or exchange solvent, and adjust to the desired final volume (see Appendix A) with the solvent last used.

14.10.2. If nitrogen blowdown technique is used, place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to the desired final volume (see Appendix A) by blowing a gentle stream of high-purity nitrogen above the extract. The internal wall of the concentrator tube must be rinsed several times with methylene chloride or exchange solvent during the operation. Position the concentrator tube to avoid water condensation (i.e. the solvent level should be below the level of the water bath). Do not allow the extract to become dry.

14.10.2.1. If a water bath is not to be utilized, transfer the extract to a screw-top storage vial, and apply the nitrogen blowdown technique to adjust the extract volume.

14.10.2.2. Semi-volatile analytes may be lost if the extract is reduced to below 1 mL.

14.11. Transfer the extract obtained from either Section 14.9. or 14.10. to a crimp-top autoinjector/autosampler vial or a screw-top storage vial and label appropriately. The extract may now be analyzed using the appropriate determinative method.

14.11.1. If necessary, perform the appropriate cleanup methods on the sample extracts prior to sample analysis. Refer to the current revision of SOP-M233 or SOP-M234 for cleanup.

14.11.2. Add the internal standard solution if required in the determinative method to all sample extracts including the QC extracts at the completion of the concentration step, or the cleanup step if applicable.

14.11.3. If the analysis will not be performed immediately, store the sample extracts under dark and refrigerated (0–6°C) conditions.

14.12. Thoroughly document all aspects of the extraction in an extraction logbook. This logbook includes, but is not limited to:

14.12.1. Extraction date, start time, and end time.

14.12.2. pH adjustment date, time, and reagent lot (or identification) number.

14.12.3. Sample matrix, initial volume, and final volume.

14.12.4. Solvent lot (or identification) number and volume.

14.12.5. Standard lot (or identification) number, concentration, and volume added.

14.12.6. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

15. CALCULATIONS

15.1. The volume of an aqueous sample used for separatory funnel liquid-liquid extraction is calculated as follows:

15.1.1. If the whole aqueous sample is used for separatory funnel liquid-liquid extraction, the volume is calculated as follows:

$$V_A = (M_2 - M_0) \times \rho$$

where: V_A = volume of aqueous sample used for separatory funnel liquid-liquid extraction in mL.
M_2 = mass of sample bottle with the whole aqueous sample in g.
M_0 = mass of sample bottle in g.
ρ = density of aqueous sample in mL/g. Assume $\rho = 1$.

15.1.2. If only a portion of the aqueous sample is used for separatory funnel liquid-liquid extraction, the volume is calculated as follows:

$$V_A = (M_2 - M_1) \times \rho$$

where: V_A = volume of aqueous sample used for separatory funnel liquid-liquid extraction in mL.
M_2 = mass of sample bottle with the whole aqueous sample in g.
M_1 = mass of sample bottle with the remaining aqueous sample in g.
ρ = density of aqueous sample in mL/g. Assume $\rho = 1$.

15.2. The dilution factor is calculated as follows:

$$D = \frac{V_f}{V_i}$$

where: D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.
V_f = volume of extract after dilution in mL.
V_i = volume of extract before dilution in mL.

15.3. Refer to the mobility extraction and determinative methods for additional calculations.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Refer to the determinative method for data assessment and acceptance criteria.

18.2. Additional information regarding internal quality control checks is provided in SOP-T020.

18.3. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Refer to the determinative method for contingencies for out-of-control or unacceptable data.

20.2. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Separatory Funnel Liquid-Liquid Extraction*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 3510C, USEPA, Revision 3, December 1996. http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3510c.pdf

22.2. *Organic Extraction and Sample Preparation*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 3500C, USEPA, Revision 3, February 2007.

22.3. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.4. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.5. *Organic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, February 2007.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: EPA Method 3510C Extraction Table.

23.2. Appendix B: Modified Procedure for Total Petroleum Hydrocarbons as Diesel Extraction.

23.3. Appendix C: Modified Procedure for Aliphatic and Aromatic Petroleum Hydrocarbons Extraction.

23.4. Appendix D: Additional Quality Control Criteria for Department of Defense Project.

23.5. Appendix E: Additional Quality Control Criteria for BP Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 3510C are noted.

24.1.1. Equipment and Supplies

24.1.1.1. The apparatus for drying extract is modified.

24.1.2. Procedure

24.1.2.1. The volume of spike standard solution added to a solid sample with an extract that will undergo EPA Method 3640A cleanup procedure is modified.

24.1.2.2. The volume of surrogate standard solution added to a solid sample with an extract that will undergo EPA Method 3640A cleanup procedure is modified.

25. REVISION HISTORY

Revision	Description	Author(s)	Effective Date
2.6	SOP reviewed	Y. Patel	12/03/12

Appendix A

EPA METHOD 3510C EXTRACTION TABLE

Calscience Environmental Laboratories, Inc.

Appendix A

EPA Method 3510C Extraction Table

Analytical Method	Primary Extraction pH	Secondary Extraction pH	Extraction Solvent Name	Extraction Solvent Volume (mL)	Exchange Solvent Name	Exchange Solvent Volume (mL)	Final Extract Volume (mL)
EPA 8081B	5-9	N/A	Methylene Chloride	60 / Each*	Hexane	10	10
EPA 8082A	5-9	N/A	Methylene Chloride	60 / Each*	Hexane	10	10
EPA 8141B	As Received	N/A	Methylene Chloride	60 / Each*	Hexane	10	10
EPA 8270D	< 2	> 11	Methylene Chloride	60 / Each*	N/A	N/A	2
EPA 8310	As Received	N/A	Methylene Chloride	60 / Each*	Acetonitrile	5	1

* Need 3 (three) times of separatory funnel liquid-liquid extractions.

Appendix B

MODIFIED PROCEDURE FOR TOTAL PETROLEUM HYDROCARBONS AS DIESEL EXTRACTION

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 3510C(M), Separatory Funnel Liquid-Liquid Extraction – Modified Procedure for Total Petroleum Hydrocarbons as Diesel Extraction.

2. SCOPE AND APPLICATION

2.1. The procedure described herein either supersedes or is in addition to the standard procedure.

3. EQUIPMENT AND SUPPLIES

3.1. Separatory funnels, 1-L, pear-shaped, transparent polytetrafluoroethylene (PTFE), with PTFE stopcock and PTFE screw cap, Nalgene Squibb Transparent FEP Separatory Funnel, or equivalent.

3.2. Spatula, stainless steel.

3.3. Nitrogen evaporation system:

3.3.1. Evaporator, Caliper Life Sciences TurboVap® LV Concentration Workstation or equivalent.

3.4. Refer to the specific SOPs of the determinative methods for additional equipment and supplies.

4. REAGENTS AND STANDARDS

4.1. Reagents

4.1.1. Silica gel, SiO_2, 60–200-mesh (nominal), white powder, reagent grade 62 or equivalent.

4.1.2. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

4.2. Standards

4.2.1. Refer to the specific SOPs of the determinative methods for standards.

5. PROCEDURE

5.1. Aqueous Sample Preparation

5.1.1. The amount of sample required for analytical determination is established by the determinative method or the project's Quality Assurance Project Plan (QAPP).

5.1.1.1. The amount of sample generally required is 500 mL nominal.

5.1.2. Mark the level of an aqueous sample on the outside of the sample bottle with a sharpie.

5.1.2.1. Alternatively, zero a top loading balance, and weigh the aqueous sample including the sample bottle. Record the mass to the nearest 0.1 g.

5.1.3. Quantitatively transfer the whole aqueous sample from the sample bottle into a clean separatory funnel.

5.1.3.1. For MB/LCS/LCSD, measure exactly 500 mL of clean reagent water.

5.1.3.2. For MS/MSD, measure exactly 500 mL of aqueous sample in each analytical batch selected for spiking.

5.1.4. Add the appropriate volume of the surrogate standard solution listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks.

5.1.5. Add the appropriate volume of the spike standard solution listed in the determinative method to all matrix spikes and laboratory control samples.

5.1.6. Proceed to Section 5.3. of this appendix for extraction procedure.

5.1.7. At the completion of the extraction step, measure the volume of the aqueous sample used by filling the sample bottle to the marked line with tap water, and then transfer the tap water into a 500-mL or 1000-mL graduated cylinder. Record the volume to the nearest 10 mL or the smallest graduation of the graduated cylinder.

5.1.7.1. Alternatively, zero the same top loading balance, and weigh the sample bottle. Record the mass to the nearest 0.1 g.

5.1.7.2. Calculate the volume of the aqueous sample used. Record the volume to the nearest 1 mL.

5.2. Mobility-Procedure Extract Preparation

5.2.1. Mark the level of a mobility-procedure extract on the outside of the extract bottle with a sharpie.

5.2.1.1. Alternatively, zero a top loading balance, and weigh the mobility-procedure extract including the extract bottle. Record the mass to the nearest 0.1 g.

5.2.2. Quantitatively transfer the whole mobility-procedure extract from the extract bottle into a clean separatory funnel.

5.2.2.1. For MB/LCS/LCSD, measure exactly 500 mL of mobility-procedure extract designated as MB/LCS/LCSD. Refer to the mobility extraction method for information.

5.2.2.2. For MS/MSD, measure exactly 500 mL of mobility-procedure extract designated as MS/MSD. Refer to the mobility extraction method for information.

5.2.3. Add the appropriate volume of the surrogate standard solution listed in the determinative method to all sample, matrix spike, laboratory control sample, and method blank mobility-procedure extracts.

5.2.4. Add the appropriate volume of the spike standard solution listed in the determinative method to all matrix spike and laboratory control sample mobility-procedure extracts.

5.2.5. Proceed to Section 5.3. of this appendix for extraction procedure.

5.2.6. At the completion of the extraction procedure, measure the volume of the mobility-procedure extract used by filling the extract bottle to the marked line with tap water, and then transfer the tap water into a 500-mL or 1000-mL graduated cylinder. Record the volume to the nearest 10 mL or the smallest graduation of the graduated cylinder.

5.2.6.1. Alternatively, zero the same top loading balance, and weigh the extract bottle. Record the mass to the nearest 0.1 g.

5.2.6.2. Calculate the volume of the mobility-procedure extract used. Record the volume to the nearest 1 mL.

5.3. Extraction

5.3.1. Add 30 mL of methylene chloride to the sample bottle. Seal and shake the sample bottle vigorously with periodic venting to rinse the sample bottle. Transfer this rinse solvent to the separatory funnel.

5.3.2. Seal and shake the separatory funnel vigorously for 1−2 minutes with periodic venting to release excess pressure.

5.3.2.1. If an open-air shaker is to be utilized, seal and shake the separatory funnel vigorously for a few seconds with periodic venting to release excess pressure. Hold the separatory funnel in place with the clamps on the open-air shaker, and agitate the aqueous sample at 200 rpm for 2 minutes.

5.3.3. Allow the organic solvent layer to separate from the aqueous phase for a minimum of 10 minutes.

5.3.4. Collect the solvent extract in a VOA vial.

5.3.5. Repeat the extraction two more times using 30 mL of fresh methylene chloride each time (Sections 5.3.1. through 5.3.4. of this appendix).

5.3.5.1. Methylene chloride may be added directly to the separatory funnel without using the sample bottle.

5.3.6. Collect each solvent extract in a VOA vial. Label the three extracts appropriately.

5.3.7. Proceed to Section 5.4. of this appendix for concentration procedure.

5.4. Dry the extracts by adding sufficient amount of sodium sulfate to the extracts.

5.4.1. Sodium sulfate clumps in the presence of water. Continue adding sodium sulfate until it remains dispersed along the bottom of the VOA vial without clumping.

5.5. Remove sodium sulfate by transferring each dried extract to a clean VOA vial.

5.6. Place the three VOA vials in the evaporator containing a warm water bath (44°C) so that the VOA vials are partially immersed in the warm water. Adjust the nitrogen gas pressure (~5 psi) to complete the concentration. When the apparent volume of liquid reaches the desired volume, combine the three solvent extracts in the same VOA vial. Label the combined extract appropriately and continue concentration.

5.7. When the apparent volume of the combined extract reaches the desired final volume, remove the VOA vial from the water bath and allow it to cool.

5.8. If the desired final volume is 2.5 mL, transfer the extract to a screw-top storage vial and label appropriately.

5.9. Use the nitrogen blowdown technique to adjust the final volume of the extract to 2.5 mL or 25 mL based on the project specific requirement.

5.9.1. If required by the project, add 0.2–2.0 g of silica gel to remove polar, non-hydrocarbon oil and grease.

5.10. Transfer the extract to a crimp-top autoinjector vial and label appropriately. The extract may now be analyzed using the appropriate determinative method.

5.10.1. If the analysis will not be performed immediately, store the sample extracts under dark and refrigerated (0–6°C) conditions.

5.11. Thoroughly document all aspects of the extraction in an extraction logbook. This logbook includes, but is not limited to:

5.11.1. Extraction date, start time, and end time.

5.11.2. Sample matrix, initial volume, and final volume.

5.11.3. Solvent lot (or identification) number and volume.

5.11.4. Standard lot (or identification) number, concentration, and volume added.

5.11.5. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

Appendix C

MODIFIED PROCEDURE FOR ALIPHATIC AND AROMATIC PETROLEUM HYDROCARBONS EXTRACTION

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 3510C(M), Separatory Funnel Liquid-Liquid Extraction – Modified Procedure for Aliphatic and Aromatic Petroleum Hydrocarbons Extraction.

2. SCOPE AND APPLICATION

2.1. The procedure described herein either supersedes or is in addition to the standard procedure.

3. INTERFERENCES

3.1. Unsealed SPE cartridges should be stored in a dessicator to avoid inadvertent adsorption of ambient moisture.

3.1.1. Silica gel that has been exposed to moisture may perform erratically resulting in poor performance.

3.1.2. Air drying SPE cartridges may affect silica gel fractionation efficiency.

3.2. The leaching of plasticizers and other compounds has been observed from the SPE cartridges. Phthalate esters and other contaminants shall be monitored continuously by analyzing method blank.

3.3. Insufficient hexane during the fractionation procedure may cause low recoveries of the aliphatic hydrocarbons. Excess hexane may result in significant elution of lighter aromatic hydrocarbons (e.g., naphthalene and substituted naphthalenes) into the aliphatic hydrocarbon extract.

3.4. Slight changes in the volumes of eluting solvents, fractionation equipment, and/or fractionation techniques during the silica gel cleanup and fractionation procedure can drastically impact the proportion of hydrocarbons segregated in either the aliphatic or aromatic extract.

4. EQUIPMENT AND SUPPLIES

4.1. Separatory funnels, 1-L, pear-shaped, transparent polytetrafluoroethylene (PTFE), with PTFE stopcock and PTFE screw cap, Nalgene Squibb Transparent FEP Separatory Funnel, or equivalent.

4.2. pH indicator paper, narrow range (0.0–3.0).

4.3. Spatula, stainless steel.

4.4. Nitrogen evaporation system:

4.4.1. Evaporator, Caliper Life Sciences TurboVap® LV Concentration Workstation or equivalent.

4.5. Cartridges, solid-phase extraction (SPE), 20-mL/5-g, silica gel packing, Restek Resprep™ Massachusetts EPH SPE Cartridge or equivalent, equipped with the following components:

4.5.1. Tubes, 20-mL, polypropylene.

4.5.2. Frits, 20-µm port size, 2.0-cm diameter, polyethylene.

4.6. Vacuum manifold, 12-port, , Restek Resprep™ 12-port SPE Manifold or equivalent equipped with the following components:

4.6.1. Valves (stopcocks), flow control, polypropylene.

4.6.2. Valve attachments, polypropylene.

4.6.3. Lid, polypropylene.

4.6.4. Needle attachments, polypropylene.

4.6.5. Sample guides, polypropylene.

4.6.6. Vacuum chamber, glass, with vacuum regulator.

4.7. Refer to the specific SOPs of the determinative methods for additional equipment and supplies.

5. STANDARDS

5.1. Refer to the specific SOPs of the determinative methods for standards.

6. PROCEDURE

6.1. Aqueous Sample Preparation

6.1.1. The amount of sample required for analytical determination is established by the determinative method or the project's Quality Assurance Project Plan (QAPP).

6.1.1.1. The amount of sample generally required is 500 mL nominal.

6.1.2. Mark the level of an aqueous sample on the outside of the sample bottle with a sharpie.

6.1.2.1. Alternatively, zero a top loading balance, and weigh the aqueous sample including the sample bottle. Record the mass to the nearest 0.1 g.

6.1.3. Check the pH by transferring a few drops of the aqueous sample onto a narrow-range pH paper. The pH must be < 2.

6.1.3.1. If necessary, adjust the pH of the aqueous sample with 1:1 H_2SO_4 to < 2.

6.1.4. Quantitatively transfer the whole aqueous sample from the sample bottle into a clean separatory funnel.

6.1.4.1. For MB/LCS/LCSD, measure exactly 500 mL of clean reagent water.

6.1.4.2. For MS/MSD, measure exactly 500 mL of aqueous sample in each analytical batch selected for spiking.

6.1.5. Add the appropriate volume of the surrogate standard solution listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks.

6.1.6. Add the appropriate volume of the spike standard solution listed in the determinative method to all matrix spikes and laboratory control samples.

6.1.7. Proceed to Section 6.3. of this appendix for extraction procedure.

6.1.8. At the completion of the extraction step, measure the volume of the aqueous sample used by filling the sample bottle to the marked line with tap water, and then transfer the tap water into a 500-mL or 1000-mL graduated cylinder. Record the volume to the nearest 10 mL or the smallest graduation of the graduated cylinder.

6.1.8.1. Alternatively, zero the same top loading balance, and weigh the sample bottle. Record the mass to the nearest 0.1 g.

6.1.8.2. Calculate the volume of the aqueous sample used. Record the volume to the nearest 1 mL.

6.2. Mobility-Procedure Extract Preparation

6.2.1. Mark the level of a mobility-procedure extract on the outside of the extract bottle with a sharpie.

6.2.1.1. Alternatively, zero a top loading balance, and weigh the mobility-procedure extract including the extract bottle. Record the mass to the nearest 0.1 g.

6.2.2. Check the pH by transferring a few drops of a mobility-procedure extract onto a wide-range pH paper. The pH must be < 2.

6.2.2.1. If necessary, adjust the pH of the aqueous sample with 1:1 H_2SO_4 to < 2.

6.2.3. Quantitatively transfer the whole mobility-procedure extract from the extract bottle into a clean separatory funnel.

6.2.3.1. For MB/LCS/LCSD, measure exactly 500 mL of mobility-procedure extract designated as MB/LCS/LCSD. Refer to the mobility extraction method for information.

6.2.3.2. For MS/MSD, measure exactly 500 mL of mobility-procedure extract designated as MS/MSD. Refer to the mobility extraction method for information.

6.2.4. Add the appropriate volume of the surrogate standard solution listed in the determinative method to all sample, matrix spike, laboratory control sample, and method blank mobility-procedure extracts.

6.2.5. Add the appropriate volume of the spike standard solution listed in the determinative method to all matrix spike and laboratory control sample mobility-procedure extracts.

6.2.6. Proceed to Section 6.3. of this appendix for extraction procedure.

6.2.7. At the completion of the extraction procedure, measure the volume of the mobility-procedure extract used by filling the extract bottle to the marked line with tap water, and then transfer the tap water into a 500-mL or 1000-mL graduated cylinder. Record the volume to the nearest 10 mL or the smallest graduation of the graduated cylinder.

6.2.7.1. Alternatively, zero the same top loading balance, and weigh the extract bottle. Record the mass to the nearest 0.1 g.

6.2.7.2. Calculate the volume of the mobility-procedure extract used. Record the volume to the nearest 1 mL.

6.3. Extraction

6.3.1. Add 30 mL of methylene chloride to the sample bottle. Seal and shake the sample bottle vigorously with periodic venting to rinse the sample bottle. Transfer this rinse solvent to the separatory funnel.

6.3.2. Seal and shake the separatory funnel vigorously for 1–2 minutes with periodic venting to release excess pressure.

6.3.2.1. If an open-air shaker is to be utilized, seal and shake the separatory funnel vigorously for a few seconds with periodic venting to release excess pressure. Hold the separatory funnel in place with the clamps on the open-air shaker, and agitate the aqueous sample at 200 rpm for 2 minutes.

6.3.3. Allow the organic solvent layer to separate from the aqueous phase for a minimum of 10 minutes.

6.3.4. Collect the solvent extract in a VOA vial.

6.3.5. Repeat the extraction two more times using 30 mL of fresh methylene chloride each time (Sections 6.3.1. through 6.3.4. of this appendix).

6.3.5.1. Methylene chloride may be added directly to the separatory funnel without using the sample bottle.

6.3.6. Collect each solvent extract in a VOA vial. Label the three extracts appropriately.

6.3.7. Proceed to Section 6.4. of this appendix for concentration procedure.

6.4. Dry the extracts by adding sufficient amount of sodium sulfate to the extracts.

6.4.1. Sodium sulfate clumps in the presence of water. Continue adding sodium sulfate until it remains dispersed along the bottom of the VOA vial without clumping.

6.5. Remove sodium sulfate by transferring each dried extract to a clean VOA vial.

6.6. Place the three VOA vials in the evaporator containing a warm water bath (44°C) so that the VOA vials are partially immersed in the warm water. Adjust the nitrogen gas pressure (~5 psi) to complete the concentration. When the apparent volume of liquid reaches the desired volume, combine the three solvent extracts in the same VOA vial. Label the combined extract appropriately and continue concentration.

6.7. When the apparent volume of liquid reaches 2 mL, exchange the solvent by adding 5 mL of hexane to the extract, and continue concentration.

6.8. When the apparent volume of liquid reaches 2 mL, remove the VOA vial from the water bath and allow it to cool.

6.9. Transfer the extract to a screw-top storage vial and label appropriately.

6.10. Use the nitrogen blowdown technique to adjust the volume of the extract to 1.0 mL.

6.10.1. The C_9 through C_{12} analytes may be lost if the extract is reduced to below 1 mL.

6.11. Assemble the vacuum manifold according to the manufacturer's instructions.

6.12. Unseal an SPE cartridge and attach it to the valve of the vacuum manifold.

6.13. Place a waste container below the sample guide. Open the valve and rinse the cartridge tube with 30 mL of hexane.

6.14. Allow the hexane to flow through the silica gel column until the meniscus of the solvent is just above the frit. Close the valve to stop solvent flow, and discard the collected hexane.

6.14.1. The frit is located on the top of the silica gel column.

6.15. Label a clean VOA vial and place it below the sample guide.

6.16. Transfer the entire extract into the cartridge tube.

6.17. Open the valve and start collecting the aliphatic fraction of the extract.

6.18. When the meniscus of the extract is just above the frit, add 18 mL of hexane in 1–2 mL increment or dropwise using a Pasteur pipet.

6.18.1. Add each increment or drops of hexane when the meniscus of the solvent is just above the frit. Do not expose the frit to air.

6.18.2. Monitor the silica gel during elution. If any channeling, streaking, or change in silica gel is observed, replace the SPE cartridge and re-extract the sample.

6.19. Allow the final hexane to flow through the silica gel column until the meniscus of the solvent is just above the frit. Close the valve to stop solvent flow.

6.19.1. The eluted hexane extract is the aliphatic hydrocarbon extract.

6.20. Label a clean VOA vial and place it below the sample guide.

6.21. Add 2 mL of methylene chloride to the cartridge tube.

6.22. Open the valve and start collecting the aromatic fraction of the extract.

6.23. When the meniscus of the extract is just above the frit, add 18 mL of methylene chloride in 1−2 mL increment or dropwise using a Pasteur pipet.

6.23.1. Add each increment or drops of methylene chloride when the meniscus of the solvent is just above the frit. Do not expose the frit to air.

6.23.2. Monitor the silica gel during elution. If any channeling, streaking, or change in silica gel is observed, replace the SPE cartridge and re-extract the sample.

6.24. Allow the final methylene chloride to flow through the silica gel column until the meniscus of the solvent is just above the frit. Close the valve to stop solvent flow.

6.24.1. The eluted methylene chloride extract is the aromatic hydrocarbon extract.

6.25. Use the nitrogen blowdown technique to adjust the final volume of each extract to 1.0 mL.

6.25.1. The extract may be transferred to a screw-top storage vial for further concentration.

6.25.2. The C_9 through C_{12} analytes may be lost if the extract is reduced to below 1 mL.

6.26. Transfer each extract to a crimp-top autoinjector vial and label appropriately. The extracts may now be analyzed using the appropriate determinative method.

6.26.1. If the analysis will not be performed immediately, store the sample extracts under dark and refrigerated (0−6°C) conditions.

6.27. Thoroughly document all aspects of the extraction in an extraction logbook. This logbook includes, but is not limited to:

6.27.1. Extraction date, start time, and end time.

6.27.2. Sample matrix, initial volume, and final volume.

6.27.3. Solvent lot (or identification) number and volume.

6.27.4. Standard lot (or identification) number, concentration, and volume added.

6.27.5. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

7. REFERENCES

7.1. *Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)*, Massachusetts Department of Environmental Protection, Division of Environmental Analysis, Revision 1.1, May 2004.

7.2. *Evaluating Human Health Risks from Total Petroleum Hydrocarbons (TPH)*, Interim Guidance, California Department of Toxic Substances Control, June 16, 2009.

8. MODIFICATIONS

8.1. The following modifications from Massachusetts Method for the Determination of EPH are noted.

8.1.1. Equipment and Supplies

8.1.1.1. The apparatus and equipment for extraction, extract drying, and concentration are modified.

8.1.2. Procedure

8.1.2.1. The volume of exchange solvent is modified.

8.1.2.2. The volume of hexane used for fractionation is modified.

8.1.2.3. Fractionation surrogate standard solution is not used to monitor the fractionation process for naphthalene and substituted naphthalene breakthrough.

8.1.2.4. Fractionation check solution is not used to monitor the fractionation efficiency of the silica gel column.

Appendix D

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 3510C, Separatory Funnel Liquid-Liquid Extraction – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The spike standard solutions shall contain all anticipated target analytes.

3.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

4. QUALITY CONTROL

4.1. Matrix Based Quality Control (MS/MSDs)

4.1.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

5. REFERENCES

5.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 2010.

Appendix E

ADDITIONAL QUALITY CONTROL CRITERIA FOR BP PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 3510C, Separatory Funnel Liquid-Liquid Extraction – Additional Quality Control Criteria for BP Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The use of a standard from a second lot as the second source standard is acceptable if written warranties demonstrating that the standards from two different lots are not prepared from the same reference materials are obtained from the manufacturer. "Manufacturer" refers to the producer of the standard, not the vendor.

4. ►QUALITY CONTROL

4.1. Event Based Quality Control (LCS/LCSDs and MBs)

4.1.1. One LCS consisting of the specified compounds spiked into clean reagent water is required every day ***preparatory methods (i.e., extractions, cleanups, etc.)*** are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation event. The LCSD is handled identically to the LCS.

4.1.2. One MB consisting of clean reagent water is required every day ***preparatory methods (i.e., extractions, cleanups, etc.)*** are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation event.

4.2. Matrix Based Quality Control (MS/MSDs)

4.2.1. One MS consisting of the actual sample matrix spiked with known concentrations of specific target analytes is required for every batch of 20 samples per matrix or portion thereof ***processed*** concurrently within an 8-hour preparation event. The MSD is handled identically to the MS.

4.2.2. The sample selected for spiking must be one of the samples collected for the specific BP project. If 10 or less BP samples are received, and no MS is designated, then a non-BP sample may be used.

4.2.3. Samples identified as trip or field blanks cannot be used for MS/MSD.

5. PROCEDURE

5.1. Organic extracts must be stored in the same type of vials (amber glass or clear glass) as the associated standards at the appropriate storage temperature.

6. REFERENCES

6.1. Technical Requirements for Environmental Laboratory Analytical Services, BP Laboratory Management Program (LaMP), Revision 09, July 30, 2007.

Title : **EPA METHOD 3545, PRESSURIZED FLUID EXTRACTION (PFE)**

Document No. : SOP-M204
Revision No. : 1.4
Supersedes : 1.3

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Revision 1.4 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 11/07/12
MANAGEMENT **DATE**

_____ 11-06-12
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 3545, Pressurized Fluid Extraction (PFE).

2. APPLICABLE MATRICES

2.1. This method is applicable to soils, clays, sediments, sludges and waste solids.

3. DETECTION LIMITS

3.1. Refer to the determinative method for detection limit data.

4. SCOPE AND APPLICATION

4.1. EPA Method 3545 describes the procedures for extracting water insoluble or slightly water soluble organic compounds. The method uses elevated temperature (100–180°C) and pressure (1500–2000 psi) to achieve analyte recoveries equivalent to those from Soxhlet extraction, using less solvent and taking significantly less time than the Soxhlet procedure.

4.2. This method is applicable to the extraction and concentration of semivolatile organic compounds, organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides, and PCBs, in preparation for a variety of chromatographic procedures.

4.3. This method has been validated for solid matrices containing 250–12500 µg/kg of semivolatile organic compounds, 250–2500 µg/kg of organophosphorus pesticides, 5–250 µg/kg of organochlorine pesticides, 50–5000 µg/kg of chlorinated herbicides, and 1–1400 µg/kg of PCBs. The method may be applied to samples containing higher concentrations of these analytes only after adequate performance has been demonstrated for the concentrations of interest.

4.4. This method is applicable to solid samples only. It is most effective on dry materials with small particle sizes. Hence, waste samples must undergo phase separation and only the solid phase material is to be extracted by this procedure. If possible, soil/sediment samples may be air-dried and ground to a fine powder prior to extraction. If the loss of analytes during drying is a concern, soil/sediment samples may be mixed with anhydrous sodium sulfate or pelletized diatomaceous earth.

4.5. The total mass of material to be prepared depends on the specifications of the determinative method and the sensitivity required for the analysis; however, 10–30 g of material are usually necessary and can be accommodated by this extraction procedure.

4.6. This method is restricted to use by or under the supervision of analysts experienced in the use of the instruments and apparatus required to execute the procedure.

5. METHOD SUMMARY

5.1. Samples are prepared for extraction by mixing the sample with anhydrous sodium sulfate or pelletized diatomaceous earth. The sample is then ground and loaded into the extraction cell.

5.2. The extraction cell containing the sample is heated to the extraction temperature, pressurized with the appropriate solvent system, and extracted for 5 minutes (or as recommended by the instrument manufacturer).

5.3. The solvent is collected from the heated extraction vessel and allowed to cool.

5.4. The extract may be concentrated, if necessary, and, as needed, exchanged into a solvent compatible with the cleanup or determinative method being employed.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. ***Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.***

6.13. ***Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.***

6.14. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.15. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.16. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.17. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.18. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.19. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.20. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.21. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.22. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.23. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.24. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.26. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.27. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.28. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by

analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

7.2. Interferences co-extracted from the samples will vary considerably from sample to sample. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to EPA Method 3600C, "Cleanup."

7.2.1. If necessary, Florisil cleanup (EPA Method 3620C) and/or sulfur cleanup (EPA Method 3660B) procedures may be employed.

7.3. Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

7.4. Glassware contamination with surfactants can cause analyte degradation. Specifically, aldrin, heptachlor, and most organophosphorus pesticides will degrade in this situation. This problem is specially pronounced with glassware that may be difficult to rinse (i.e., K-D flask, etc.). These items should be hand-rinsed very carefully to avoid this problem. This is especially important when the determinative method to be used is EPA Method 8141A.

7.5. Boiling stones with acidic or basic characteristics can interfere with base/neutral and acid analysis. Care should be taken when selecting boiling stones so that they are not a factor in the loss of base or acid analytes.

8. SAFETY

8.1. The following provides safety information concerning the use of pressurized fluid extraction instrument:

8.1.1. Exercise caution when the cell tray and vial/bottle tray are in motion to avoid personal injury.

8.1.2. Instrument equipped with flammable vapor sensors should be operated with all covers in place and doors closed to ensure proper operation of the sensors.

8.1.3. Do not obstruct or pressurize the vent outlet. Make sure the vent tubing(s) are installed per manufacturer's instructions to allow proper venting of solvent vapors without contaminating the laboratory atmosphere during the gas purge step.

8.1.4. Extraction cells are extremely hot after an extraction. Allow the cells to cool for at least 15 minutes before handling. Use insulated gloves or tongs to remove the cells from the cell tray. Be especially cautious with cells that have been heated over 50°C.

8.2. For the safety of the analyst, cracked or broken glassware should be immediately discarded into a broken glassware receptacle. Broken glassware shall not be used in any step of the extraction.

8.3. To ensure the safety of the analyst during any possible emergency situation, chemists shall not perform extractions alone. Another chemist must be present during any extraction process.

8.4. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.5. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

8.6. Many compounds covered by this method have been tentatively classified as known or suspected human carcinogens. A NIOSH/MESA approved toxic gas respirator should be worn when extracting high concentration samples.

9. EQUIPMENT AND SUPPLIES

9.1. Pressurized Fluid Extraction Instrument: Dionex ASE 200 Accelerated Solvent Extractor or equivalent configured with oven, solvent reservoir compartment, needle mechanism, extraction cell tray, rinse tubes, collection vial tray, and control panel.

9.1.1. Extraction cell body, 33-mL capacity, stainless steel, capable of withstanding 2000+ psi pressure requirement, Dionex P/N 048822 or equivalent.

9.1.2. Extraction cell cap, consisting of a snap ring (Dionex P/N 049456 or equivalent), a cap insert, a PEEK seal (Dionex P/N 049454 or equivalent), a stainless steel frit (Dionex P/N 049453 or equivalent), and a Teflon external O-ring (Dionex P/N 049457 or equivalent) for standard applications or a Viton O-ring (Dionex P/N 056325 or equivalent) for high temperature applications, Dionex P/N 049450 or equivalent.

9.1.3. Filter disk, cellulose, 19.8-mm diameter, type D28, disposable, Dionex P/N 049458 or equivalent.

9.1.4. Collection vial, 60-mL, clear glass, pre-cleaned, consisting of an open top screw-cap (Dionex P/N 049463 or equivalent), and a Teflon-lined silicone low-bleed septum (Dionex P/N 055395 or equivalent), Dionex P/N 048784 or equivalent.

9.1.5. Tool kit, containing a small flathead screwdriver, a snap ring tool (Dionex P/N 049493 or equivalent), an O-ring insertion tool (Dionex P/N 049660 or equivalent), a filter insertion tool (Dionex P/N 049495 or equivalent), and other maintenance tools, Dionex P/N 049009 or equivalent.

9.2. Pressurized Fluid Extraction Instrument: Dionex ASE 300 Accelerated Solvent Extractor or equivalent configured with oven, solvent reservoir compartment, needle mechanism, extraction cell tray, rinse tubes, collection bottle tray, and control panel.

9.2.1. Extraction cell body, 66-mL capacity, stainless steel, capable of withstanding 1500+ psi pressure requirement, Dionex P/N 056693 or equivalent.

9.2.2. Extraction cell cap, consisting of a snap ring (Dionex P/N 056778 or equivalent), a cap insert, a PEEK seal (Dionex P/N 056776 or equivalent), a stainless steel frit (Dionex P/N 056775 or equivalent), and a Teflon external O-ring (Dionex P/N 049457 or equivalent) for standard applications or a Viton O-ring (Dionex P/N 056325 or equivalent) for high temperature applications, Dionex P/N 056921 or equivalent.

9.2.3. Filter disk, cellulose, 30-mm diameter, type D28, disposable, Dionex 056780 or equivalent.

9.2.4. Collection bottle, 250-mL, clear glass, pre-cleaned, consisting of an open top screw-cap (Dionex P/N 049463 or equivalent), and a Teflon-lined silicone low-bleed septum (Dionex P/N 055395 or equivalent), Dionex P/N 056284 or equivalent.

9.2.5. Tool kit, containing a small flathead screwdriver, a snap ring tool (Dionex P/N 056684 or equivalent), an O-ring insertion tool (Dionex P/N 049660 or equivalent), a filter insertion tool (Dionex P/N 056929 or equivalent), and other maintenance tools, Dionex P/N 056667 or equivalent.

9.3. Purge gas, high purity nitrogen.

9.4. Dry weight determination apparatus:

9.4.1. Weighing dish, aluminum, disposable.

9.4.2. Drying oven, thermostatically controlled, forced draft, capable of maintaining 104 ± 1°C.

9.4.3. Desiccator, containing indicating-type desiccant.

9.4.4. Spatula, stainless steel.

9.4.5. Forceps, stainless steel.

9.5. Filtration apparatus:

9.5.1. Funnel, short-stemmed, glass.

9.5.2. Filter paper, untreated or silicone-treated, 150-mm or 185-mm diameter.

9.6. Kuderna-Danish (K-D) apparatus:

9.6.1. Concentrator tube, 10-mL, graduated, Kontes K-570050-1025 or equivalent.

9.6.1.1. Use ground-glass stopper to prevent evaporation of extracts.

9.6.2. Evaporation flask, 250-mL or 500-mL, Kontes K-570001-500 or equivalent.

9.6.2.1. Attach evaporation flask to concentrator tube with clamps.

9.6.3. Snyder column, three-ball macro, Kontes K-503000-0121 or equivalent.

9.6.4. Snyder column, two-ball micro, Kontes K-569001-0219 or equivalent.

9.6.5. Clamps.

9.7. Boiling stones, Teflon.

9.8. Water bath, heated, capable of temperature control within ± 5°C.

9.8.1. Place water bath in a fume hood.

9.9. Thermometer.

9.10. Grinding apparatus.

9.11. Sieve, 18-mesh (1-mm).

9.12. Balance, top loading, capable of weighing to the nearest 0.01 g.

9.13. Dispenser, set volume to 5 mL.

9.14. Dispenser, set volume to 10 mL.

9.15. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with N.I.S.T. Traceable Certification.

10. REAGENTS AND STANDARDS

10.1. Reagent water, interferant free.

10.2. Sand, washed, sea or standard Ottawa.

10.3. Drying agents:

10.3.1. Sodium sulfate, Na_2SO_4, granular, anhydrous, reagent grade or equivalent.

10.3.1.1. Purify by heating at 400°C for 4 hours in a shallow tray, or by extraction with methylene chloride. If extraction with methylene chloride is employed, then a reagent blank should be prepared to demonstrate that the drying agent is free of interferences.

10.3.2. Diatomaceous earth, pelletized, reagent grade or equivalent.

10.4. Extraction/exchange solvents:

10.4.1. Methylene chloride, CH_2Cl_2, boiling point 39.8°C, pesticide grade or equivalent.

10.4.2. Hexane, C_6H_{14}, boiling point 68.7°C, pesticide grade or equivalent.

10.4.3. Acetonitrile, CH_3CN, boiling point 81.6°C, pesticide grade or equivalent.

10.5. Pesticide-free reagents shall be used for all extractions where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

10.6. All reagents must be inspected and documented prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Refer to the specific SOPs of the determinative methods for sample collection, preservation, containers and holding times.

12. QUALITY CONTROL

12.1. Event Based Quality Control (LCS/LCSDs and MBs)

12.1.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.1.2. Solid Samples

12.1.2.1. One LCS consisting of the specified compounds spiked into washed sea sand is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. The LCSD is handled identically to the LCS.

12.1.2.2. One MB consisting of washed sea sand is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

12.1.3. Wipe Samples

12.1.3.1. One LCS consisting of the specified compounds spiked into a sterile 2-in by 2-in gauze pad is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. The LCSD is handled identically to the LCS.

12.1.3.2. One MB consisting of a sterile 2-in by 2-in gauze pad is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

12.1.4. Filter Samples

12.1.4.1. One LCS consisting of the specified compounds spiked into a clean filter paper supplied by client field personnel is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. The LCSD is handled identically to the LCS.

12.1.4.2. One MB consisting of a clean filter paper supplied by client field personnel is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

12.1.5. The MB/LCS/LCSD is processed concurrently with the associated samples. In the processing of the MB/LCS/LCSD, reagents and procedures identical

to those for actual samples are used (e.g., surrogates, internal standards, etc.).

12.2. Matrix Based Quality Control (Surrogates and MS/MSDs)

12.2.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and surrogates added to each sample.

12.2.2. One MS consisting of the actual sample matrix spiked with known concentrations of specific target analytes is required for every batch of 20 samples per matrix or portion thereof extracted concurrently. The MSD is handled identically to the MS.

12.2.3. The sample which is spiked for the MS/MSD is processed concurrently with the associated samples. In the processing of the MS/MSD, reagents and procedures identical to those for actual samples are used (e.g., surrogates, internal standards, etc.).

12.3. A variety of problems can occur during the course of the extraction process and can drastically affect the integrity of the data produced.

12.3.1. If the extract is inadvertently concentrated to dryness, the sample can be irrevocably altered. A portion of the analyte content can be lost to the atmosphere. In this case, if there is sufficient sample, the best solution is to re-extract the sample. If there is insufficient sample, first let the extractor cool and allow the vapor to condense to see how much solvent can be recovered. Then add fresh solvent to the desired final volume (see Appendix A). If the latter is the only option, a notation must be made of the error. In addition, the analyst and the client must be made aware of the error. Low surrogate recoveries are indicative of the possible loss of target analytes. To avoid this problem, extraction should never be left unattended during concentration.

12.3.2. If the Snyder column floods, special care must be taken to correct the problem without losing any of the sample. In case of flooding, gently remove the Snyder column from the concentrator. Once it has cooled sufficiently, and the vapors have condensed, gently shake the column and allow the solvent to drain back into the concentrator. If the column is shaken while it is still hot and attached to the concentrator, the pressure build-up can force vapor out of the column and into the atmosphere, irrevocably altering the sample.

13. CALIBRATION AND STANDARDIZATION

13.1. Top Loading Balance

13.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

13.1.2. Calibration shall be within ± 2% at 1 g (± 0.02 g) and at 100 g (± 2 g). If the values are not within these limits, recalibrate the balance.

13.2. Thermometer

13.2.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T042, "Thermometer Calibration."

13.3. Dispenser

13.3.1. Calibrate the dispenser using a Class A graduated cylinder.

13.3.2. Calibration shall be within 1% of the expected volume.

14. PROCEDURE

14.1. Sample Preparation

14.1.1. Homogenize sample as outlined in the current revision of SOP-M230. Use the following information as guidance for sample homogenization and sieving.

14.1.1.1. For sediment/soil samples, decant and discard any water layer on a sediment sample. Mix the sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

14.1.1.2. For dry sediment/soil and dry waste samples amenable to grinding, grind or reduce the particle size of the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Use sufficient sample to obtain at least 10 g after grinding.

14.1.1.3. Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or broken up to allow mixing and maximum exposure of the sample surfaces for extraction. Drying agent may be added to the sample to make it more amenable to grinding.

14.1.1.4. Multiphase waste samples must be prepared by separating the phases before extraction. PFE procedure is for the solid phase only.

14.1.2. The amount of sample required for analytical determination is established by the determinative method (see Appendix B) or the project's Quality Assurance Project Plan (QAPP).

14.2. Percent Dry Weight Determination

14.2.1. When sample results are to be reported on a dry weight basis, a second portion of sample should be weighed at the same time as the portion used for analytical determination.

14.2.2. Immediately after weighing the sample for extraction, weigh 5–10 g of the sample into a tared weighing dish. Dry this aliquot overnight at 105°C.

Allow the dried sample to cool in a desiccator before weighing. The formula for calculating percent dry weight is listed in Section 15.1.

14.2.3. Additional information regarding determination of solids content is provided in SOP-M700.

14.3. Weigh sufficient amount of the homogenized solid sample (Section 14.1.) for analytical determination. Record the mass of the sample to the nearest 0.1 g.

14.3.1. For solid samples, the MB/LCS/LCSD consists of washed sea sand, and the MS/MSD consists of solid sample in each analytical batch selected for spiking.

14.3.2. For wipe samples, the MB/LCS/LCSD consists of a sterile 2-in by 2-in gauze pad, and the MS/MSD consists of wipe sample in each analytical batch selected for spiking.

14.3.3. For filter samples, the MB/LCS/LCSD consists of a clean filter paper supplied by client field personnel, and the MS/MSD consists of filter sample in each analytical batch selected for spiking.

14.4. Assemble a clean extraction cell per manufacturer's instructions for each sample.

14.4.1. Select the appropriate cell size based on the total mass of sample and drying agent. Generally, a 33-mL cell can hold up to 30 g of material.

14.4.2. Write the cell identification number on the outside of the cell body with a sharpie. Do not attach any label to the cell. Attaching a label to the cell may cause misalignment in the oven during extraction process.

14.4.3. Replace the PEEK seals of the extraction cell if frequent vapor leaks are detected.

14.4.4. Insert a disposable cellulose filter using a filter insertion tool prior to filling the cell with sample.

14.4.4.1. Hand-tighten the bottom cell cap onto the cell body before installing the filter. Placing the filter in the bottom cap before installing the cap will cause improper seal and leaks.

14.5. Transfer the portion of the sample for analytical determination to the assembled extraction cell, and mix the sample with an appropriate amount of drying agent.

14.5.1. For solid sample, mix the sample with pelletized diatomaceous earth (preferable) or anhydrous sodium sulfate until a free-flowing powder is obtained. The suggested mass ratio of sample to pelletized diatomaceous earth is 4 to 1, and that of sample to anhydrous sodium sulfate is 1 to 1.

14.5.2. For wipe or filter sample, add approximately 3 g of pelletized diatomaceous earth (preferable) or anhydrous sodium sulfate to the sample.

14.6. Add the surrogate standard solution listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks.

14.6.1. If EPA Method 3640A, "Gel-Permeation Cleanup," is to be employed, add twice the volume of surrogate standard solution since half of the extract is not recovered from the GPC apparatus.

14.7. Add the spike standard solution listed in the determinative method to all matrix spikes and laboratory control samples.

14.7.1. If EPA Method 3640A, "Gel-Permeation Cleanup," is to be employed, add twice the volume of spike standard solution since half of the extract is not recovered from the GPC apparatus.

14.8. To reduce the amount of extraction solvent used, the void volume in the extraction cell may be filled with washed sea sand.

14.9. Hand-tighten the top cell cap onto the cell body. Check the end of each cap to verify that the white O-rings are in place and in good condition. Replace the O-ring with discoloration or a hole size < 0.5 mm.

14.10. Load each filled extraction cell into the cell tray. Hang the cell vertically in the cell tray slot from its top cap (the bottom cap contains a disposable cellulose filter).

14.11. Check the white O-rings at the ends of each rinse tube, and replace the O-ring with discoloration or a hole size < 0.5 mm. Load the rinse tubes in the specified cell tray slots.

14.12. Place a pre-cleaned collection vial/bottle in the vial/bottle tray for each sample. Record the sample identification number, the cell tray slot number, and the vial/bottle tray slot number in a raw data sheet, if necessary, to identify the sample extract after extraction.

14.13. Load rinse vials/bottles into the rinse slots of vial/bottle tray, and a waste vial/bottle in the solvent reservoir compartment.

14.14. Instrument Setup

14.14.1. Use the following extraction conditions as guidance.

Description	Dionex ASE 200 Extraction Condition
Oven temperature	100°C
Pressure	2000 psi
Static time	5 min (after 5 min pre-heat equilibration)
Flush volume	60% of cell volume
Nitrogen purge	60 sec at 150 psi
Static cycles	1

Description	Dionex ASE 300 Extraction Condition
Oven temperature	100°C
Pressure	1500 psi
Static time	6 min (after 5 min pre-heat equilibration)
Flush volume	60% of cell volume
Nitrogen purge	90 sec at 150 psi
Static cycles	1

14.14.2. Optimize the conditions as needed per manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500–2000 psi should suffice.

14.14.3. Once established, the same pressure should be used for all samples extracted for the same analysis type.

14.14.4. Run a rinse cycle after the instrument has been shut down for more than one day, after refilling the solvent reservoir, after changing solvents, or when there are bubbles in the solvent lines.

14.15. Ensure that a sufficient amount of extraction solvent is present in the solvent reservoir and that a sufficient unused volume exists in the rinse and waste vials/bottles at the beginning of extraction.

14.16. Begin extraction.

14.17. Collect each extract in a clean vial/bottle. Allow the extracts to cool after the extractions are complete.

14.18. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 250-mL or 500-mL evaporation flask.

14.19. Dry the extract by passing it through a glass funnel containing silicone-treated filter paper (or anhydrous sodium sulfate on untreated filter paper). Collect the dried extract in a K-D concentrator. Rinse the collection vial/bottle thoroughly with methylene chloride, and add it to the funnel to complete the quantitative transfer.

14.20. Add one or two clean boiling stones to the evaporation flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15–20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10–20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

14.21. If a solvent exchange is required (as indicated in Appendix A), momentarily remove the Snyder column, add the exchange solvent as indicated, a new boiling stone, and reattach the Snyder column. Concentrate the extract, as per Section 14.20., raising the temperature of the water bath, if necessary, to maintain proper distillation.

14.22. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1–2 mL of methylene chloride or exchange solvent. It is possible that white sulfur crystals can appear in the extract during the concentration phase. If sulfur crystals appear, proceed to EPA Method 3660B for cleanup. The

extract may be further concentrated by using the technique outlined in Section 14.23. or adjusted to final volume (see Appendix A) with the solvent last used.

14.23. If further concentration is indicated in Appendix A, either the micro Snyder column technique or nitrogen blowdown technique is used to adjust the extract to the final volume required.

14.23.1. If micro Snyder column technique is used, add another clean boiling stone to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5–10 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches about one half of the final volume, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of solvent, and adjust the final volume as indicated in Appendix A with solvent.

14.23.2. If nitrogen blowdown technique is used, place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the final volume as indicated in Appendix A by blowing a gentle stream of pre-purified, dry nitrogen (filtered through a column of activated carbon) above the extract. The internal wall of the concentrator tube must be rinsed several times with solvent during the operation. Do not allow the extract to become dry.

14.24. The extract obtained (from either Section 14.22. or 14.23.) should be transferred to a crimp-top autoinjector/autosampler vial and labeled appropriately. The extract may now be analyzed using the appropriate determinative method.

14.24.1. If necessary, perform the appropriate cleanup methods on the sample extracts prior to sample analysis. Refer to EPA Method 3600C, "Cleanup."

14.24.2. Add the internal standard solution if required in the determinative method to all sample extracts including the QC extracts at the completion of the concentration step, or the cleanup step, if applicable.

14.25. Thoroughly document all aspects of the extraction in an extraction logbook. This logbook includes:

14.25.1. Extraction date, start time, and end time.

14.25.2. Sample matrix, initial mass, and final volume.

14.25.3. Extraction/exchange solvent lot (or identification) number and volume.

14.25.4. Surrogate lot (or identification) number, concentration, and volume added.

14.25.5. Standard lot (or identification) number, concentration, and volume added.

14.25.6. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

15. CALCULATIONS

15.1. The dry weight (wet-based solids content) for a sample is calculated as follows:

$$C_s = \frac{M_2 - M_0}{M_1 - M_0} \times 100$$

where: C_s = dry weight (wet-based solids content) in %.
M_2 = mass of weighing dish and oven-dried sample in g.
M_0 = mass of weighing dish in g.
M_1 = mass of weighing dish and as-received sample in g.

15.2. Refer to the determinative method for additional calculations.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Refer to the determinative method for data assessment and acceptance criteria.

18.2. Additional information regarding internal quality control checks is provided in SOP-T020.

18.3. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly

documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Refer to the determinative method for contingencies for out-of-control or unacceptable data.

20.2. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Pressurized Fluid Extraction (PFE)*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 3545, USEPA, Revision 0, December 1996.

22.2. Pressurized Fluid Extraction (PFE), Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 3545A, USEPA, Revision 1, January 1998, http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3545a.pdf

22.3. Quality Control, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.4. Choosing the Correct Procedure, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, November 2000.

22.5. Organic Analytes, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, November 2000.

22.6. ASE 200 Accelerated Solvent Extractor Operator's Manual, Dionex Corporation, 1999.

22.7. ASE 300 Accelerated Solvent Extractor Operator's Manual, Dionex Corporation, 2000.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: EPA Method 3545 Extraction Table.

23.2. Appendix B: EPA Method 3545 Initial Sample Aliquot Mass.

23.3. Appendix C: EPA Method 3545 Pressurized Fluid Extraction Flowchart.

24. ►MODIFICATIONS

24.1. The following modifications to methods are noted.

Calscience SOP M739 Section	Reference Documents Section	Summary of Modification
N/A	N/A	None

25. ►REVISION HISTORY

Revision	Description	Author	Effective Date
1.4	SOP revision.	Y.Patel	09/25/11
1.3	SOP revision.	L. Lem	11/12/12

Appendix A

EPA METHOD 3545 EXTRACTION TABLE

Calscience Environmental Laboratories, Inc.

EPA Method 3545 Extraction Table

Analytical Method	Initial Sample Weight	Final Volume				Reporting Level (RL)
EPA Reference	gms	Extraction solvent name	Exchange Solvent name	Exchange Solvent Volume (mL)	Final Extract Volume (mL)	(ug/kg)
EPA 8081A (Lower Calibration Point)	50	MeCl2	Hexane	5	5	0.2
EPA 8081A	50	MeCl2	Hexane	5	5	1
EPA 8081A	20	MeCl2	Hexane	10	10	5
EPA 8082	50	MeCl2	Hexane	5	5	10
EPA 8082	20	MeCl2	Hexane	10	10	50
EPA 8082	1	MeCl2	Hexane	10	10	1000
EPA 8270C	20	MeCl2	N/A	N/A	2	500
EPA 8270C(M)1,4-Dioxane	20	MeCl2	N/A	N/A	1	50
EPA 8270C(M)1,4-Dioxane	10	MeCl2	N/A	N/A	2	200
EPA 8270C SIM PAHs	20	MeCl2	N/A	N/A	2	10
EPA 8270C SIM PAHs	10	MeCl2	N/A	N/A	2	20
EPA 8270C SIM SUPER	20	MeCl2	N/A	N/A	2	0.4
EPA 8270C SIM SUPER	20	MeCl2	N/A	N/A	2	10
EPA 8270C SIM PCB Congeners	20	MeCl2	Hexane	1	1	0.5
EPA 8270C SIM PCB Congeners	20	MeCl2	Hexane	2	2	1
EPA 8141B	20	MeCl2	Hexane	2	2	50
EPA 8141B	10	MeCl2	Hexane	10	10	500
EPA 8310	20	MeCl2	Acetonitrile	1	1	10

Appendix B

EPA METHOD 3545 INITIAL SAMPLE ALIQUOT MASS

Calscience Environmental Laboratories, Inc.

EPA Method 3545 Initial Sample Aliquot Mass -- Nominal*

Initial Weights				
Analytical Method	**Environmental Sample Mass (g)**	**MB Mass (g)**	**LCS/LCSD Mass (g)**	**MS/MSD Mass (g)**
EPA 8081A	50	50	50	50
EPA 8082	50	50	50	50
EPA 8141A	20	20	20	20
EPA 8270C	20	20	20	20
EPA 8270C PAH	20	20	20	20
EPA 8270C Dioxane	20	20	20	20
EPA 8310	20	20	20	20

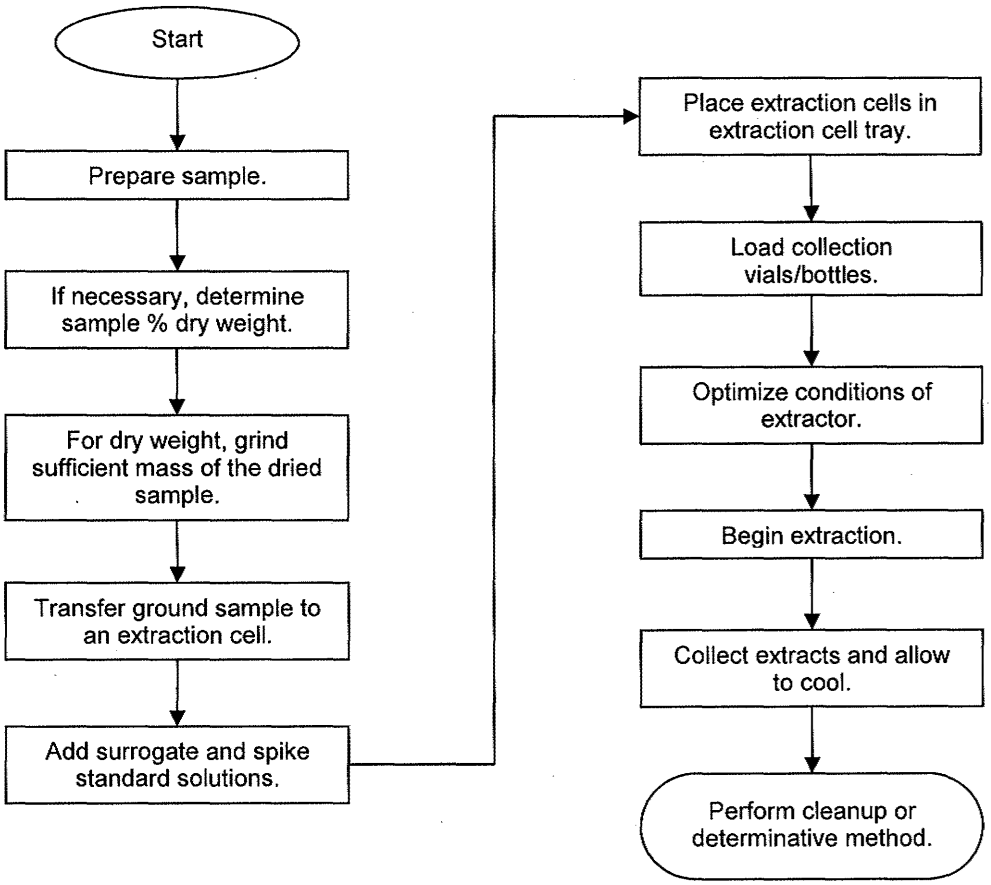
* Standard weights, reference Appendix A for other sample options.

Appendix C

EPA Method 3545 Pressurized Fluid Extraction Flowchart

Calscience Environmental Laboratories, Inc.

Pressurized Fluid Extraction Flowchart



Title : **EPA METHOD 5030C, PURGE-AND-TRAP FOR AQUEOUS SAMPLES**

Document No. : SOP-M212
Revision No. : 3.3
Supersedes : 3.2

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Revision 3.3 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 01/08/14
MANAGEMENT **DATE**

_____ 01-07-14
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 5030*C*, Purge-and-Trap for Aqueous Samples.

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous samples, water miscible liquid samples, and high concentration soil and waste sample extracts prepared in EPA Method 5035A. It is also applicable to soil and waste samples not prepared via EPA Method 5035A as a modified method.

3. ►DETECTION / QUANTITATION LIMITS

3.1. Refer to the determinative (analytical) method for detection ***and quantitation limits***.

4. SCOPE AND APPLICATION

4.1. EPA Method 5030C describes a purge-and-trap procedure for the analysis of volatile organic compounds (VOCs) in aqueous samples and water miscible liquid samples. It also describes the analysis of high concentration soil and waste sample extracts prepared in EPA Method 5035A. The gas chromatographic determinative steps are found in EPA Methods 8015C, 8021B, and 8260C.

4.1.1. This method in conjunction with EPA Method 8015C may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons (gasoline).

4.1.2. This method and EPA Method 8021B may be used for the analysis of the aromatic fraction (BTEX).

4.1.3. A total determinative analysis of gasoline fractions may be obtaining using EPA Method 8021B in series with EPA Method 8015C.

4.2. EPA Method 5030C can be used for most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, quantitation limits via GC or GC/MS analysis in some cases are approximately ten times higher with erratic precision due to poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

4.2.1. The purging efficiency can be improved for water soluble analytes (e.g. ketones and alcohols) when purging at an elevated temperature of 80°C as compared to 20°C or 40°C.

4.3. Problems are often encountered with the analysis of fuel oxygenated compounds, both with the effectiveness of the determinative methods and the evaluation of the resulting data.

4.3.1. The fuel oxygenated compounds generally include methyl t-butyl ether (MTBE), ethyl t-butyl ether (ETBE), t-amyl methyl ether (TAME), diisopropyl ether (DIPE), and t-butyl alcohol (TBA). These oxygenated compounds can be classified as volatile organics based on their boiling points and vapor pressures. However, due to the high solubility of some of these oxygenated compounds in water, using purge-and-trap procedures that have been optimized for less water-soluble volatiles can potentially lead to significantly underestimating the oxygenate concentrations in the same samples.

4.3.2. Purging at an elevated temperature of 80°C and proper analytical column can improve the low-level concentration recoveries of the oxygenate compounds.

4.4. Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system or by dilution of the sample prior to the purge-and-trap process. Samples for the analysis of the following compounds can be prepared by this method:

acetone
acetonitrile
acrolein
acrylonitrile
allyl chloride
t-amyl methyl ether (TAME)
benzene
bromochloromethane
bromodichloromethane
bromoform
bromomethane
2-butanone
t-butyl alcohol (TBA)
carbon disulfide
carbon tetrachloride
chlorobenzene
chloroethane
2-chloroethyl vinyl ether
chloroform
chloromethane
chloroprene
1,2-dibromo-3-chloropropane
1,2-dibromoethane
dibromomethane
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
t-1,4-dichloro-2-butene
dichlorodifluoromethane
1,1-dichloroethane
1,2-dichloroethane
1,1-dichloroethene
c-1,2-dichloroethene
t-1,2-dichloroethene
1,2-dichloropropane
c-1,3-dichloropropene
t-1,3-dichloropropene
diethyl ether
diisopropyl ether (DIPE)
1,4-dioxane
ethylbenzene
ethyl methacrylate
ethyl t-butyl ether (ETBE)
hexachloro-1,3-butadiene
2-hexanone
iodomethane
isobutyl alcohol
isopropylbenzene
methacrylonitrile
methyl t-butyl ether (MTBE)
methylene chloride
methyl methacrylate
4-methyl-2-pentanone (MIBK)
naphthalene
propionitrile
styrene
1,1,1,2-tetrachloroethane
1,1,2,2-tetrachloroethane
tetrachloroethene
toluene
1,2,4-trichlorobenzene
1,1,1-trichloroethane
1,1,2-trichloroethane
trichloroethene
trichlorofluoromethane
1,2,3-trichloropropane
vinyl acetate
vinyl chloride
o-xylene
p/m-xylenes

4.5. This method is restricted to use by or under the supervision of analysts/technicians experienced in the use of purge-and-trap system and apparatus required to execute the procedure.

5. METHOD SUMMARY

5.1. For aqueous sample analysis, an inert gas is bubbled through a portion of the aqueous sample at ambient temperature or an elevated temperature depending on the desired target analytes, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

5.2. For high concentration extract analysis, an aliquot of the methanol extract prepared in EPA Method 5035A is combined with organic-free reagent water and transferred to the purging chamber. The combined solution is then analyzed by purge-and-trap GC or GC/MS following the normal aqueous method.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. ►Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. ►***Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.13. ►***Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.14. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.15. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.16. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.17. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.18. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality

indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.19. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.20. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.21. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.22. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.23. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.24. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.26. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.27. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.28. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage.

7.1.1. Field and trip blanks prepared from an organic-free matrix and sample container, and carried through sampling and handling protocols serve as checks on such contamination.

7.2. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

7.2.1. The use of high purity solvents, reagents and pre-conditioning of disposables that come in contact with the sample help to minimize interference problems.

7.3. Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems.

7.3.1. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials may out-gas organic components which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

7.3.2. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks.

7.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially.

7.4.1. To reduce the potential for carryover, the sample purging devices must be thoroughly rinsed between samples with an appropriate solvent. Purge and trap devices or headspace devices should be thoroughly baked out between samples.

7.4.2. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination.

7.4.2.1. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent sample(s), the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are <u>not</u> present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

7.4.3. Suspected high-concentration samples should be diluted and analyzed at the end of the sequence to prevent carryover contamination.

7.5. The laboratory where volatile analysis is performed should be complete free of solvents except limited amount of methanol.

7.5.1. Special precautions must be taken when analyzing for methylene chloride. The analytical and sample storage area should be isolated ***from all*** atmospheric sources of methylene chloride. Otherwise random background levels can result.

7.5.2. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing.

7.5.3. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid-liquid extraction procedures can contribute to sample contamination.

7.5.4. The presence of other organic solvents in the laboratory where volatile organics are analyzed can also lead to random background levels and the same precautions must be taken.

7.6. Contamination on an autosampler position can also occur. If an autosampler position is suspected of containing a sample with unusually high concentrations of analytes, an instrument blank or solvent blank should be placed on that position and the following position. Analyze and evaluate the blank for contamination prior to analyzing the remaining samples.

7.7. Refer to the determinative method for other potential interferences.

8. SAFETY

8.1. Processes that promote vaporization of volatile chemicals into the work area should be performed in a fume hood vented to the exterior of the laboratory

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. ►Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Purge-and-Trap System: System configured with a purging chamber and the following components:

9.1.1. Purge-and-trap concentrator, equipped with a 5-mL or 25-mL fritted glass sparger, a trap, and a heater, EST Analytical Encon Purge and Trap Concentrator, OI Analytical Eclipse 4660 Purge-and-Trap Sample Concentrator, Teledyne Tekmar-Dohrmann 3100 Sample Concentrator, Teledyne Tekmar Velocity XPT Accelerated Purge and Trap System, Teledyne Tekmar Stratum PTC Purge and Trap Concentrator, or equivalent.

9.1.1.1. Condition a new trap according to manufacturer's instructions prior to initial use.

9.1.2. Purge-and-trap autosampler, EST Analytical Archon Water/Soil Autosampler, Teledyne Tekmar 2016/2032 Autosampler, Teledyne Tekmar SOLATek 72 Multi-Matrix Vial Autosampler, Varian Archon Purge and Trap Autosampler, or equivalent.

9.1.3. Trap packing material, Tenax® GC/Silica Gel/Charcoal adsorbents, Tenax® GC/Silica Gel/Carbosieve™ S-III adsorbents, Carbopack™ B/Carboxen™ 1000/ Carboxen™ 1001 adsorbents, Carbopack™ C/Carbopack™ B/Carboxen™ 1000/ Carboxen™ 1001 adsorbents, or equivalent.

9.2. Purge Gas: Helium, He, or nitrogen, N_2, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.3. Carrier Gas: Helium, He, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.4. Culture tubes, 18-mm × 150-mm (30-mL capacity), borosilicate glass, disposable.

9.4.1. The culture tubes are used as purge vessels.

9.5. VOA vials, 28-mm × 95-mm (40-mL capacity), screw top, clear or amber glass, with Teflon-lined open top or closed top screw caps and Teflon-lined septa, EPA VOA Vial or equivalent.

9.5.1. Bake VOA vials in an oven at 90°C for 24 hours prior to use.

9.5.2. The VOA vials may be used as purge vessels.

9.6. Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

9.7. Volumetric flasks, 25-mL, 50-mL, or other capacity, glass, Class A.

9.8. Dispensers, 1−10-mL, 2.5−25-mL, and 5−50-mL, analog display, adjustable volume.

9.9. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certification.

9.10. Syringes, 1-mL, 5-mL, and 25-mL, gastight, Removable Needle (RN), Teflon Luer Lock (TLL), or SampleLock (SL) termination, Hamilton 1000 Series or equivalent with NIST Traceable Certification.

9.11. pH indicator paper, narrow range (0.0 − 3.0).

9.12. Spatula, stainless steel.

9.13. Balance, top loading, capable of weighing to the nearest 0.01 g.

9.14. Drying oven, capable of maintaining 90°C.

9.15. Gloves, heat resistant.

9.16. Refer to the specific SOPs of the determinative methods for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, nano-pure.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Sodium thiosulfate, $Na_2S_2O_3$, anhydrous, white solid, reagent grade or equivalent.

10.1.4. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v).

10.1.4.1. Prepare the 10% $Na_2S_2O_3$ solution by dissolving 100 g of anhydrous $Na_2S_2O_3$ in reagent water and dilute to 1 L with additional reagent water.

10.1.5. Hydrochloric acid, HCl, 36.5–38.0% (v/v), concentrated, colorless to pale yellow liquid, reagent grade or equivalent.

10.1.6. Hydrochloric acid, HCl, 1:1 (v/v).

10.1.6.1. Prepare the 1:1 HCl solution by slowly adding concentrated HCl to equal volume of reagent water.

10.1.7. Sodium phosphate, tribasic, Na_3PO_4, dodecahydrate, white crystalline powder, reagent grade or equivalent.

10.1.8. Methanol, CH_3OH, clear colorless liquid, purge and trap grade or equivalent.

10.1.9. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Refer to the specific SOPs of the determinative methods for standards.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 40-mL pre-cleaned amber glass or clear glass VOA vials with Teflon-lined closures. Collect all samples in triplicate.

11.1.1. If the aqueous sample contains residual chlorine, collect the sample in a 125-mL amber glass container containing 4 drops of the 10% $Na_2S_2O_3$

solution. Gently swirl to mix the sample, and transfer to pre-cleaned amber glass or clear glass VOA vials.

11.1.1.1. Aqueous sample containing greater than 5 mg/L of residual chlorine may require additional amount of the dechlorinating agent.

11.1.2. Adjust the pH of the aqueous sample to < 2 by adding 1:1 HCl solution while stirring.

11.1.2.1. If a dechlorinating agent and acid are both added as preservatives, the aqueous sample must be dechlorinated first and then acidified.

11.1.2.2. Reactive compounds (e.g., acrolein, acrylonitrile, 2-chloroethyl vinyl ether, styrene, and vinyl chloride) are unstable at low pH. It is recommended that a second set of the aqueous sample without acid preservative be collected.

11.1.2.3. If fuel oxygenated compounds are the only analytes of interest, and the aqueous sample will be purged at an elevated temperature of 80°C, no acid preservation is required.

11.1.2.4. If carbonaceous materials are present, the aqueous sample should not be acid preserved due to possible effervescence and loss of volatile organic compounds.

11.1.3. Completely fill and hermetically seal the sample vial such that when the vial is inverted, no headspace is visible.

11.1.3.1. It is possible for the sample to generate some headspace in the form of micro bubbles during storage. The bubbles should not exceed ¼ in or 6 mm in diameter.

11.2. Solid samples should be collected in 4-oz or 8-oz pre-cleaned clear glass wide-mouth jars or 6-in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.3. Oil samples should be collected in 40-mL pre-cleaned clear glass VOA vials with Teflon-lined closures.

11.4. Mobility-procedure extracts should be collected in 4-mL pre-cleaned clear glass storage vials with Teflon-lined closures.

11.4.1. If the mobility-procedure extract will not be analyzed within 24 hours, collect the mobility-procedure extract in a 40-mL pre-cleaned amber glass or clear glass VOA vial, and adjust the pH to < 2 by adding 1:1 HCl solution while stirring.

11.4.1.1. If effervescence (bubbling, hissing, or foaming of liquid as gas escapes) is observed upon adding 1:1 HCl solution, do not acid preserve the mobility-procedure extract.

11.4.2. Completely fill and hermetically seal the sample vial such that when the vial is inverted, no headspace is visible.

11.4.2.1. It is possible for the sample to generate some headspace in the form of micro bubbles during storage. The bubbles should not exceed ¼ in or 6 mm in diameter.

11.5. Samples shall be maintained in a chilled state (≤ 4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.6. Upon receipt, the samples are stored in 0~6°C coolers.

11.6.1. Aqueous samples with acid preservation (pH < 2) must be analyzed within 14 days of sample collection.

11.6.2. Aqueous samples without acid preservation (pH ≥ 2) must be analyzed within 7 days of sample collection.

11.6.2.1. If reactive compounds are the analytes of interest, the aqueous samples should be analyzed as soon as possible.

11.6.3. Solid samples must be analyzed within 14 days of sample collection.

11.6.3.1. Solid samples may also be stored in a −10~−20°C freezer if solids content determination is not required.

11.6.3.1.1. Freezing solid samples within 48 hours of collection can minimize biodegradation of aromatic hydrocarbons (e.g. benzene, toluene, ethylbenzene, and xylenes).

11.6.4. High concentration (> 200 µg/kg) solid samples must be preserved with methanol and analyzed within 14 days of sample collection.

11.6.4.1. Methanol extracts shall be stored in a 0~6°C cooler with a minimum contact time of 24 hours between the solid sample and methanol prior to analysis.

11.6.5. Oil samples must be preserved with methanol and analyzed within 14 days of sample collection.

11.6.5.1. Methanol extracts shall be stored in a 0~6°C cooler with a minimum contact time of 24 hours between the oil sample and methanol prior to analysis.

11.6.6. Mobility-procedure extracts with acid preservation (pH < 2) must be analyzed within 14 days post mobility extraction for aqueous samples, or within 7 days post mobility extraction for solid samples.

11.6.6.1. Mobility-procedure extracts shall be stored in a 0~6°C cooler post mobility extraction if analysis is not to be performed within 24 hours.

11.6.7. Mobility-procedure extracts without acid preservation (pH ≥ 2) must be analyzed within 24 hours post mobility extraction.

11.7. Refer to the specific SOPs of the mobility extraction and determinative methods for additional information on sample preservation and holding times.

12. ►QUALITY CONTROL

12.1. Event Based Quality Control (MBs and LCS/LCSDs)

12.1.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), ***a laboratory control sample (LCS), and a*** laboratory control sample duplicate ***(LCSD)***.

12.1.1.1. ***One LCS shall be prepared and processed to demonstrate the performance of the measurement system.***

12.1.1.2. ***One LCSD may be prepared and processed along with the LCS if one or more conditions as outlined in the current revision of SOP-T020 are met.***

12.2. Matrix Based Quality Control (MS/MSDs)

12.2.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike ***(MS) and a matrix spike duplicate (MSD)***.

12.2.2. ***The sample which will be spiked for the MS/MSD is processed concurrently with the associated samples using identical reagents and procedures.***

12.3. ***Additional information regarding internal quality control checks is provided in the current revisions of SOP-T020.***

12.4. ***Refer to the specific SOPs of the determinative methods for additional information on quality control***

13. CALIBRATION AND STANDARDIZATION

13.1. Top Loading Balance

13.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

13.1.2. Calibration shall be within ± 2% at 1 g (± 0.02 g) and at 100 g (± 2 g). If the values are not within these limits, recalibrate the balance.

13.2. Dispenser

13.2.1. Calibrate the dispenser according to the procedure outlined in the Dispenser Calibration Check Logbook.

14. PROCEDURE

14.1. Purge-and-Trap System Setup

14.1.1. Condition (heat) the trap daily for 10 minutes while backflushing at 180°C with the analytical column at 220°C prior to purge-and-trap extraction.

14.1.2. For EPA Method 8015C, use the following purge-and-trap operating parameters as guidance to purge and trap blank, standard, or sample.

Description	Purge-and-Trap Operating Parameter	
	Aqueous	Solid
Dry purge time	1 min	1 min
Purge gas flow rate	40 mL/min	40 mL/min
Purge time	11.0 ± 0.1 min	11.0 ± 0.1 min
Purge temperature	40°C	40°C
Desorb pre-heat temperature	245°C	245°C
Desorb gas flow rate	10 mL/min	10 mL/min
Desorb time	4 min	4 min
Desorb temperature	250°C	250°C
Backflush inert gas flow rate	20−60 mL/min	20−60 mL/min
Trap stand-by temperature	40°C	40°C
Bake time	10 min	10 min
Bake temperature	260°C	260°C

14.1.3. For EPA Method 8021B, use the following purge-and-trap operating parameters as guidance to purge and trap blank, standard, or sample.

Description	Purge-and-Trap Operating Parameter	
	Aqueous	Solid
Dry purge time	1 min	1 min

Description	Purge-and-Trap Operating Parameter	
	Aqueous	Solid
Purge gas flow rate	40 mL/min	40 mL/min
Purge time	11.0 ± 0.1 min	11.0 ± 0.1 min
Purge temperature	ambient	ambient
Desorb pre-heat temperature	245°C	245°C
Desorb gas flow rate	10 mL/min	10 mL/min
Desorb time	4 min	4 min
Desorb temperature	250°C	250°C
Backflush inert gas flow rate	20−60 mL/min	20−60 mL/min
Trap stand-by temperature	40°C	40°C
Bake time	10 min	10 min
Bake temperature	260°C	260°C

14.1.3.1. Using a wide-bore capillary column, the backflush inert gas flow rate will optimize at approximately 10−15 mL/min.

14.1.4. For EPA Method 8260C, use the following purge-and-trap operating parameters as guidance to purge and trap blank, standard, or sample.

Description	Purge-and-Trap Operating Parameter	
	Aqueous	Solid
Dry purge time	0.5–2.0 min	0.5–2.0 min
Purge gas flow rate	40 mL/min	40 mL/min
Purge time	11.0 ± 0.1 min	11.0 ± 0.1 min
Purge temperature	ambient or 40°C	40°C
Desorb pre-heat temperature	245°C	245°C
Desorb gas flow rate	10 mL/min	10 mL/min
Desorb time	0.5–2.0 min	0.5–2.0 min
Desorb temperature	250°C	250°C
Backflush inert gas flow rate	20–60 mL/min	20–60 mL/min
Trap stand-by temperature	40°C	40°C
Bake time	8 min	8 min
Bake temperature	280°C	280°C

14.1.4.1. The purge temperature may be set at 80°C for analyzing fuel oxygenated compounds.

14.1.4.2. The dry purge time and desorb time are set according to the manufacturer's recommendations.

14.1.5. Proper dry purge time and trap stand-by temperature depend on the trap packing material. Consult instructions from both the manufacturer of the purge-and-trap system and the supplier of the trap packing material.

14.1.6. If cross contamination and memory effects of later eluting compounds from a high concentration sample or even a standard become a problem, adjust the bake time and temperature or replace the trap packing material.

14.2. Precaution

14.2.1. The process of opening a sample or extract vial and taking an aliquot for purge-and-trap extraction destroys the integrity of the sample or extract for future analysis. Hence, employ one of the following techniques to maintain sample or extract integrity for re-analysis.

14.2.1.1. Use a sample or extract vial that was never opened for each analysis.

14.2.1.2. Take a second aliquot of the sample or extract at the same time and prepare it for re-analysis within 24 hours.

14.2.1.3. Draw an aliquot of the sample or extract by puncturing the septum of a sample or extract vial using a syringe equipped with a needle.

14.3. Calibration and Calibration Verification Standard Preparation

14.3.1. Allow working standard solution(s) to reach ambient temperature.

14.3.2. Pull the plunger of a 5-mL syringe and draw slightly more than 5 mL of clean reagent water.

14.3.3. Slowly dispense the excess reagent water while eliminating trapped air.

14.3.4. Adjust the volume of the reagent water in the barrel to exactly 5.00 mL.

14.3.5. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.3.6. Measure the appropriate volume (refer to the determinative method) of each working standard solution using a different syringe.

14.3.7. Transfer the working standard solution(s) into the same purge vessel.

14.3.7.1. The resulting solution is the calibration or calibration verification standard solution.

14.3.8. For EPA Methods 8015C and 8021B, if autosampler is not configured to inject surrogate standard solution(s) automatically, add the appropriate volume(s) of the surrogate standard solution(s) listed in the determinative method to all calibration and calibration verification standard solutions.

14.3.9. For EPA Method 8260C, if autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate and internal standard solution(s) listed in the determinative method to all calibration and calibration verification standard solutions.

14.3.10. If the purge vessel is a VOA vial, seal it with a septum and an open top screw cap.

14.3.10.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.3.11. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.4. Calibration and Calibration Verification Standard Preparation for EPA Method 8260C Lower Limits of Quantitation

14.4.1. Allow working standard solution(s) to reach ambient temperature.

14.4.2. Pull the plunger of a 25-mL syringe and draw slightly more than 20 mL of clean reagent water.

14.4.3. Slowly dispense the excess reagent water while eliminating trapped air.

14.4.4. Adjust the volume of the reagent water in the barrel to exactly 20.0 mL.

14.4.5. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.4.6. Measure the appropriate volume (refer to the determinative method) of each working standard solution using a different syringe.

14.4.7. Transfer the working standard solution(s) into the same purge vessel.

14.4.7.1. The resulting solution is the calibration or calibration verification standard solution.

14.4.8. If autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate

and internal standard solution(s) listed in the determinative method to all calibration and calibration verification standard solutions.

14.4.9. If the purge vessel is a VOA vial, seal it with a septum and an open top screw cap.

14.4.9.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.4.10. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.5. Aqueous Sample Preparation

14.5.1. If an aqueous sample containing MTBE, ETBE, TAME, or other fuel oxygenated ethers have been acid preserved with 1:1 HCl solution, and will be purged at an elevated temperature, adjust the pH of the aqueous sample to > 10 with $Na_3PO_4 \cdot 12H_2O$.

14.5.1.1. Adjust the pH of each associated QC sample with $Na_3PO_4 \cdot 12H_2O$ to the same pH.

14.5.2. Allow an aqueous sample to reach ambient temperature, and the suspended particulates, if any, in the aqueous sample to settle.

14.5.2.1. Do not subsample the suspended particulates.

14.5.3. For a suspected high concentration aqueous sample, estimate the volume of the aqueous sample to be diluted.

14.5.3.1. To prevent excessive dilution, the highest instrument response of a target analyte in the diluted sample must be in the upper half of the calibration range.

14.5.3.2. Extremely high concentration aqueous sample may be serially diluted, if necessary.

14.5.4. If no dilution is required, prepare the aqueous sample as follows:

14.5.4.1. Pull the plunger of a 5-mL syringe and draw slightly more than 5 mL of the aqueous sample.

14.5.4.1.1. For MB/LCS/LCSD, draw slightly more than 5 mL of clean reagent water.

14.5.4.1.2. For MS/MSD, draw slightly more than 5 mL of aqueous sample in each analytical batch selected for spiking.

14.5.4.2. Slowly dispense the excess aqueous sample while eliminating trapped air.

14.5.4.3. Adjust the volume of the aqueous sample in the barrel to exactly 5.00 mL. Record the volume to the smallest graduation.

14.5.4.3.1. For MB/LCS/LCSD, adjust the volume of the reagent water to exactly 5.00 mL.

14.5.4.3.2. For MS/MSD, adjust the volume of the aqueous sample to exactly 5.00 mL.

14.5.4.4. Transfer the aqueous sample into a clean purge vessel and label the purge vessel with a sharpie.

14.5.5. If dilution is required, and the estimated volume of the aqueous sample to be diluted is greater than or equal to 50 µL, prepare the aqueous sample as follows:

14.5.5.1. Pull the plunger of a 5-mL syringe and draw the appropriate volume of clean reagent water.

14.5.5.1.1. For MB/LCS/LCSD, draw slightly more than 5 mL of clean reagent water.

14.5.5.1.2. For MS/MSD, draw the appropriate volume of clean reagent water.

14.5.5.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.5.5.3. Adjust the volume of the reagent water in the barrel such that the total volume of the reagent water and the aqueous sample to be diluted is 5.00 mL.

14.5.5.3.1. For MB/LCS/LCSD, adjust the volume of the reagent water to exactly 5.00 mL.

14.5.5.3.2. For MS/MSD, adjust the volume of the reagent water such that the total volume of the reagent water and the aqueous sample to be diluted is 5.00 mL.

14.5.5.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.5.5.5. Measure the appropriate volume of the aqueous sample using a different syringe. Record the volume to the smallest graduation.

14.5.5.5.1. For MS/MSD, measure the same volume of aqueous sample in each analytical batch selected for spiking.

14.5.5.6. Transfer the aqueous sample into the same purge vessel.

14.5.5.6.1. The resulting solution is the diluted sample.

14.5.6. If dilution is required, and the estimated volume of the aqueous sample to be diluted is less than 50 µL, prepare the aqueous sample as follows:

14.5.6.1. Pull the plunger of a 5-mL syringe and draw slightly more than 5 mL of clean reagent water.

14.5.6.1.1. For MB/LCS/LCSD/MS/MSD, draw slightly more than 5 mL of clean reagent water.

14.5.6.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.5.6.3. Adjust the volume of the reagent water in the barrel to exactly 5.00 mL.

14.5.6.3.1. For MB/LCS/LCSD/MS/MSD, adjust the volume of the reagent water to exactly 5.00 mL.

14.5.6.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.5.6.5. Measure the appropriate volume of the aqueous sample using a different syringe. Record the volume to the smallest graduation.

14.5.6.5.1. For MS/MSD, measure the same volume of aqueous sample in each analytical batch selected for spiking.

14.5.6.6. Transfer the aqueous sample into the same purge vessel.

14.5.6.6.1. The resulting solution is the diluted sample.

14.5.7. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spikes and laboratory control samples.

14.5.8. For EPA Methods 8015C and 8021B, if autosampler is not configured to inject surrogate standard solution(s) automatically, add the appropriate volume(s) of the surrogate standard solution(s) listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks.

14.5.9. For EPA Method 8260C, if autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate and internal standard solution(s) listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks.

14.5.10. If the purge vessel is a VOA vial, seal it with a septum and an open top screw cap.

14.5.10.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.5.11. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.6. Aqueous Sample Preparation for EPA Method 8260C Lower Limits of Quantitation

14.6.1. If an aqueous sample containing MTBE, ETBE, TAME, or other fuel oxygenated ethers have been acid preserved with 1:1 HCl solution, and will be purged at an elevated temperature, adjust the pH of the aqueous sample to > 10 with $Na_3PO_4 \cdot 12H_2O$.

14.6.1.1. Adjust the pH of each associated QC sample with $Na_3PO_4 \cdot 12H_2O$ to the same pH.

14.6.2. Allow an aqueous sample to reach ambient temperature, and the suspended particulates, if any, in the aqueous sample to settle.

14.6.2.1. Do not subsample the suspended particulates.

14.6.3. For a suspected high concentration aqueous sample, estimate the volume of the aqueous sample to be diluted.

14.6.3.1. To prevent excessive dilution, the highest instrument response of a target analyte in the diluted sample must be in the upper half of the calibration range.

14.6.3.2. Extremely high concentration aqueous sample may be serially diluted, if necessary.

14.6.4. If no dilution is required, prepare the aqueous sample as follows:

14.6.4.1. Pull the plunger of a 25-mL syringe and draw slightly more than 20 mL of the aqueous sample.

14.6.4.1.1. For MB/LCS/LCSD, draw slightly more than 20 mL of clean reagent water.

14.6.4.1.2. For MS/MSD, draw slightly more than 5 mL of aqueous sample in each analytical batch selected for spiking.

14.6.4.2. Slowly dispense the excess aqueous sample while eliminating trapped air.

14.6.4.3. Adjust the volume of the aqueous sample in the barrel to exactly 20.0 mL. Record the volume to the smallest graduation.

14.6.4.3.1. For MB/LCS/LCSD, adjust the volume of the reagent water to exactly 20.0 mL.

14.6.4.3.2. For MS/MSD, adjust the volume of the aqueous sample to exactly 20.0 mL.

14.6.4.4. Transfer the aqueous sample into a clean purge vessel and label the purge vessel with a sharpie.

14.6.5. If dilution is required, and the estimated volume of the aqueous sample to be diluted is greater than or equal to 250 µL, prepare the aqueous sample as follows:

14.6.5.1. Pull the plunger of a 25-mL syringe and draw the appropriate volume of clean reagent water.

14.6.5.1.1. For MB/LCS/LCSD, draw slightly more than 20 mL of clean reagent water.

14.6.5.1.2. For MS/MSD, draw the appropriate volume of clean reagent water.

14.6.5.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.6.5.3. Adjust the volume of the reagent water in the barrel such that the total volume of the reagent water and the aqueous sample to be diluted is 20.0 mL.

14.6.5.3.1. For MB/LCS/LCSD, adjust the volume of the reagent water to exactly 20.0 mL.

14.6.5.3.2. For MS/MSD, adjust the volume of the reagent water such that the total volume of the reagent water and the aqueous sample to be diluted is 20.0 mL.

14.6.5.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.6.5.5. Measure the appropriate volume of the aqueous sample using a different syringe. Record the volume to the smallest graduation.

14.6.5.5.1. For MS/MSD, measure the same volume of aqueous sample in each analytical batch selected for spiking.

14.6.5.6. Transfer the aqueous sample into the same purge vessel.

14.6.5.6.1. The resulting solution is the diluted sample.

14.6.6. If dilution is required, and the estimated volume of the aqueous sample to be diluted is less than 250 µL, prepare the aqueous sample as follows:

14.6.6.1. Pull the plunger of a 25-mL syringe and draw slightly more than 20 mL of clean reagent water.

14.6.6.1.1. For MB/LCS/LCSD/MS/MSD, draw slightly more than 20 mL of clean reagent water.

14.6.6.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.6.6.3. Adjust the volume of the reagent water in the barrel to exactly 20.0 mL.

14.6.6.3.1. For MB/LCS/LCSD/MS/MSD, adjust the volume of the reagent water to exactly 20.0 mL.

14.6.6.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.6.6.5. Measure the appropriate volume of the aqueous sample using a different syringe. Record the volume to the smallest graduation.

14.6.6.5.1. For MS/MSD, measure the same volume of aqueous sample in each analytical batch selected for spiking.

14.6.6.6. Transfer the aqueous sample into the same purge vessel.

14.6.6.6.1. The resulting solution is the diluted sample.

14.6.7. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spikes and laboratory control samples.

14.6.8. If autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate and internal standard solution(s) listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks.

14.6.9. If the purge vessel is a VOA vial, seal it with a septum and an open top screw cap.

14.6.9.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.6.10. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.7. Solid Sample Preparation

14.7.1. Label a clean VOA vial with a sharpie. Add a clean stir bar to the VOA vial and tare.

14.7.1.1. If the purge-and-trap autosampler employs a means of stirring sample other than a magnetic stirrer (e.g., sonication or other mechanical means), the stir bar may be omitted.

14.7.1.2. The VOA vial is used as the purge vessel.

14.7.2. Allow a solid sample to reach ambient temperature.

14.7.3. Composite the solid sample as outlined in the current revision of SOP-M230.

14.7.4. If sample result is to be reported on a dry weight basis, weigh a second portion of the solid sample and determine the solids content as outlined in the current revision of SOP-M700.

14.7.5. If the highest instrument response of a target analyte is suspected to exceed the calibration range, weigh and prepare a second portion of the solid sample according to Section 14.8.

14.7.6. For EPA Methods 8015C and 8021B, measure 1.00 ± 0.10 g (wet weight) of the solid sample into the tared purge vessel. Record the mass to the nearest 0.01 g.

14.7.6.1. For MB/LCS/LCSD, measure exactly 1.00 g of washed sea sand. Record the washed sea sand identification number in the sample preparation logbook.

14.7.6.2. For MS/MSD, measure exactly 1.00 g of solid sample in each analytical batch selected for spiking.

14.7.7. For EPA Method 8260C, measure 5.00 ± 0.50 g (wet weight) of the solid sample into the tared purge vessel. Record the mass to the nearest 0.01 g.

14.7.7.1. For MB/LCS/LCSD, measure exactly 5.00 g of washed sea sand. Record the washed sea sand identification number in the sample preparation logbook.

14.7.7.2. For MS/MSD, measure exactly 5.00 g of solid sample in each analytical batch selected for spiking.

14.7.8. Add 5 mL of reagent water to the purge vessel and seal it with a septum and an open top screw cap.

14.7.8.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.7.9. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spikes and laboratory control samples just prior to analysis.

14.7.9.1. Introduce the spike standard solution into the purge vessel by puncturing the septum using a syringe equipped with a small-gauge needle.

14.7.10. For EPA Methods 8015C and 8021B, if autosampler is not configured to inject surrogate standard solution(s) automatically, add the appropriate volume(s) of the surrogate standard solution(s) listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks just prior to analysis.

14.7.10.1. Introduce the surrogate standard solution into the purge vessel by puncturing the septum using a syringe equipped with a small-gauge needle.

14.7.11. For EPA Method 8260C, if autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate and internal standard solution(s) listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks just prior to analysis.

14.7.11.1. Introduce the surrogate and internal standard solution into the purge vessel by puncturing the septum using a syringe equipped with a small-gauge needle.

14.7.12. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.8. High Concentration Solid or Oil Sample Preparation

14.8.1. Label a clean VOA vial with a sharpie and tare.

14.8.2. Allow a solid or oil sample to reach ambient temperature.

14.8.3. Composite the solid sample as outlined in the current revision of SOP-M230.

14.8.4. If sample result is to be reported on a dry weight basis, weigh a second portion of the solid sample and determine the solids content as outlined in the current revision of SOP-M700.

14.8.5. For EPA Methods 8015C and 8021B, measure 1.00 ± 0.10 g (wet weight) of the solid or oil sample into the tared VOA vial. Record the mass to the nearest 0.01 g.

14.8.5.1. For MB/LCS/LCSD, measure exactly 1.00 g of washed sea sand. Record the washed sea sand identification number in the sample preparation logbook.

14.8.5.2. For MS/MSD, measure exactly 1.00 g of solid or oil sample in each analytical batch selected for spiking.

14.8.6. For EPA Method 8260C, measure 5.00 ± 0.50 g (wet weight) of the solid or oil sample into the tared VOA vial. Record the mass to the nearest 0.01 g.

14.8.6.1. For MB/LCS/LCSD, measure exactly 5.00 g of washed sea sand. Record the washed sea sand identification number in the sample preparation logbook.

14.8.6.2. For MS/MSD, measure exactly 5.00 g of solid or oil sample in each analytical batch selected for spiking.

14.8.7. Add 10 mL of methanol to the VOA vial and seal it with a septum and an open top screw cap.

14.8.7.1. Improperly sealed VOA vial may cause leakage through the septum.

14.8.8. Proceed to Section 14.10. for methanol extract preparation procedure.

14.9. Mobility-Procedure Extract Preparation

14.9.1. If a mobility-procedure extract containing MTBE, ETBE, TAME, or other fuel oxygenated ethers have been acid preserved with 1:1 HCl solution, and will be purged at an elevated temperature, adjust the pH of the mobility-procedure extract to > 10 with $Na_3PO_4 \cdot 12H_2O$.

14.9.1.1. Adjust the pH of each associated QC mobility-procedure extract with $Na_3PO_4 \cdot 12H_2O$ to the same pH.

14.9.2. Allow a mobility-procedure extract to reach ambient temperature, and the suspended particulates, if any, in the mobility-procedure extract to settle.

14.9.2.1. Do not subsample the suspended particulates.

14.9.3. Estimate the volume of the mobility-procedure extract to be diluted.

14.9.3.1. To prevent excessive dilution, the highest instrument response of a target analyte in the diluted mobility-procedure extract must be in the upper half of the calibration range.

14.9.3.2. Extremely high concentration mobility-procedure extract may be serially diluted, if necessary.

14.9.4. If the estimated volume of the mobility-procedure extract to be diluted is greater than or equal to 50 µL, prepare the mobility-procedure extract as follows:

14.9.4.1. Pull the plunger of a 5-mL syringe and draw the appropriate volume of clean reagent water.

14.9.4.1.1. For MB/LCS/LCSD/MS/MSD, draw the appropriate volume of clean reagent water.

14.9.4.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.9.4.3. Adjust the volume of the reagent water in the barrel such that the total volume of the reagent water and the mobility-procedure extract to be diluted is 5.00 mL.

14.9.4.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.9.4.5. Measure the appropriate volume of the mobility-procedure extract using a different syringe. Record the volume to the smallest graduation.

14.9.4.5.1. For MB/LCS/LCSD, measure the same volume of mobility-procedure extract designated as MB/LCS/LCSD. Refer to the mobility extraction method for information.

14.9.4.5.2. For MS/MSD, measure the same volume of mobility-procedure extract designated as MS/MSD. Refer to the mobility extraction method for information.

14.9.4.6. Transfer the mobility-procedure extract into the same purge vessel.

14.9.4.6.1. The resulting solution is the diluted mobility-procedure extract.

14.9.5. If the estimated volume of the mobility-procedure extract to be diluted is less than 50 µL, prepare the mobility-procedure extract as follows:

14.9.5.1. Pull the plunger of a 5-mL syringe and draw slightly more than 5 mL of clean reagent water.

14.9.5.1.1. For MB/LCS/LCSD/MS/MSD, draw slightly more than 5 mL of clean reagent water.

14.9.5.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.9.5.3. Adjust the volume of the reagent water in the barrel to exactly 5.00 mL.

14.9.5.3.1. For MB/LCS/LCSD/MS/MSD, adjust the volume of the reagent water to exactly 5.00 mL.

14.9.5.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.9.5.5. Measure the appropriate volume of the mobility-procedure extract using a different syringe. Record the volume to the smallest graduation.

14.9.5.5.1. For MB/LCS/LCSD, measure the same volume of mobility-procedure extract designated as MB/LCS/LCSD. Refer to the mobility extraction method for information.

14.9.5.5.2. For MS/MSD, measure the same volume of mobility-procedure extract designated as MS/MSD. Refer to the mobility extraction method for information.

14.9.5.6. Transfer the mobility-procedure extract into the same purge vessel.

14.9.5.6.1. The resulting solution is the diluted mobility-procedure extract.

14.9.6. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spike and laboratory control sample mobility-procedure extracts.

14.9.7. For EPA Methods 8015C and 8021B, if autosampler is not configured to inject surrogate standard solution(s) automatically, add the appropriate volume(s) of the surrogate standard solution(s) listed in the determinative method to all sample, matrix spike, laboratory control sample, and method blank mobility-procedure extracts.

14.9.8. For EPA Method 8260C, if autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate and internal standard solution(s) listed in the determinative method to all sample, matrix spike, laboratory control sample, and method blank mobility-procedure extracts.

14.9.9. If the purge vessel is a VOA vial, seal it with a septum and an open top screw cap.

14.9.9.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.9.10. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.10. Methanol Extract Preparation

14.10.1. Allow a methanol extract to reach ambient temperature, and the suspended particulates, if any, in the methanol extract to settle.

14.10.1.1. Do not subsample the suspended particulates.

14.10.2. Estimate the volume of the methanol extract to be diluted.

14.10.2.1. To prevent excessive dilution, the highest instrument response of a target analyte in the diluted methanol extract must be in the upper half of the calibration range.

14.10.2.2. Extremely high concentration methanol extract may be serially diluted, if necessary.

14.10.3. If the estimated volume of the methanol extract to be diluted is greater than or equal to 50 µL, prepare the methanol extract as follows:

14.10.3.1. Pull the plunger of a 5-mL syringe and draw the appropriate volume of clean reagent water.

14.10.3.1.1. For MB/LCS/LCSD/MS/MSD, draw the appropriate volume of clean reagent water.

14.10.3.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.10.3.3. Adjust the volume of the reagent water in the barrel such that the total volume of the reagent water and the methanol extract to be diluted is 5.00 mL.

14.10.3.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.10.3.5. Measure the appropriate volume of the methanol extract using a different syringe. Record the volume to the smallest graduation.

14.10.3.5.1. For MB/LCS/LCSD, measure the same volume of methanol extract designated as MB/LCS/LCSD.

14.10.3.5.2. For MS/MSD, measure the same volume of methanol extract designated as MS/MSD.

14.10.3.6. Transfer the methanol extract into the same purge vessel.

14.10.3.6.1. The resulting solution is the diluted methanol extract.

14.10.4. If the estimated volume of the methanol extract to be diluted is less than 50 µL, prepare the methanol extract as follows:

14.10.4.1. Pull the plunger of a 5-mL syringe and draw slightly more than 5 mL of clean reagent water.

14.10.4.1.1. For MB/LCS/LCSD/MS/MSD, draw slightly more than 5 mL of clean reagent water.

14.10.4.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.10.4.3. Adjust the volume of the reagent water in the barrel to exactly 5.00 mL.

14.10.4.3.1. For MB/LCS/LCSD/MS/MSD, adjust the volume of the reagent water to exactly 5.00 mL.

14.10.4.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.10.4.5. Measure the appropriate volume of the methanol extract using a different syringe. Record the volume to the smallest graduation.

14.10.4.5.1. For MB/LCS/LCSD, measure the same volume of methanol extract designated as MB/LCS/LCSD.

14.10.4.5.2. For MS/MSD, measure the same volume of methanol extract designated as MS/MSD.

14.10.4.6. Transfer the methanol extract into the same purge vessel.

14.10.4.6.1. The resulting solution is the diluted methanol extract.

14.10.5. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spike and laboratory control sample methanol extracts.

14.10.6. For EPA Methods 8015C and 8021B, if autosampler is not configured to inject surrogate standard solution(s) automatically, add the appropriate volume(s) of the surrogate standard solution(s) listed in the determinative method to all sample, matrix spike, laboratory control sample, and method blank methanol extracts.

14.10.7. For EPA Method 8260C, if autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate and internal standard solution(s) listed in the determinative method to all sample, matrix spike, laboratory control sample, and method blank methanol extracts.

14.10.8. If the purge vessel is a VOA vial, seal it with a septum and an open top screw cap.

14.10.8.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.10.9. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.11. Load the purge vessels into the purge-and-trap autosampler, set up the GC or GC/MS operating conditions as specified in the determinative method, and start purge-and-trap extraction and analysis.

14.12. Thoroughly document all aspects of the purge-and-trap sample preparation and extraction in a sample preparation logbook and an instrument run logbook, or on an instrument run sequence table.

14.13. Data Interpretation

14.13.1. If the result of a solid sample is to be reported on the dry weight basis, calculate the solids content. The formula for calculating solids content is listed in Section 15.2.

14.13.2. If the result of a methanol extracted solid or oil sample is to be reported on the wet weight basis, calculate the preparation factor without moisture correction. The formula for calculating preparation factor without moisture correction is listed in Section 15.4.

14.13.3. If the result of a methanol extracted solid sample with less than or equal to 10% of moisture content is to be reported on the dry weight basis, calculate the preparation factor without methanol/water dilution factor correction. The formula for calculating preparation factor without methanol/water dilution factor correction is listed in Section 15.5.

14.13.4. If the result of a methanol extracted solid sample with greater than 10% of moisture content is to be reported on a dry weight basis, calculate the preparation factor with methanol/water dilution factor correction. The formula for calculating preparation factor with methanol/water dilution factor correction is listed in Section 15.6.

14.14. Refer to the determinative method for additional information on instrument setup, analytical procedure, and data interpretation.

15. CALCULATIONS

15.1. The dilution factor is calculated as follows:

$$D = \frac{V_f}{V_i}$$

where: D = dilution factor.
V_f = volume of sample or extract after dilution in mL.
V_i = volume of sample or extract before dilution in mL.

15.2. The solids content for a sample is calculated as follows:

$$C_{ss} = \frac{M_2 - M_0}{M_1 - M_0} \times 100$$

where: C_{ss} = solids content in %.
M_2 = mass of weighing dish and oven-dried sample in g.
M_0 = mass of weighing dish in g.
M_1 = mass of weighing dish and as-received sample in g.

15.3. The moisture content for a sample is calculated as follows:

$$C_w = \frac{M_1 - M_2}{M_1 - M_0} \times 100 \qquad C_w = 100\% - C_{ss}$$

where: C_w = moisture content in %.
M_1 = mass of weighing dish and as-received sample in g.

M_2 = mass of weighing dish and oven-dried sample in g.
M_0 = mass of weighing dish in g.

15.4. The preparation factor without moisture correction for a methanol extracted solid (or oil) sample is calculated as follows:

$$P_1 = \frac{V_m}{W_S}$$

where: P_1 = preparation factor without moisture correction for methanol extracted solid (or oil) sample in mL/g.
V_m = volume of methanol added in mL.
Unless specified otherwise, V_m = 10.
W_S = mass of solid (or oil) sample methanol extracted in g.

15.5. The preparation factor <u>without</u> methanol/water dilution factor correction for a methanol extracted solid sample is calculated as follows:

$$P_2 = \frac{V_m}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: P_2 = preparation factor without methanol/water dilution factor correction for methanol extracted solid sample in mL/g.
V_m = volume of methanol added in mL.
Unless specified otherwise, V_m = 10.
W_S = mass of solid sample methanol extracted in g.
C_{ss} = solids content in %.

15.6. The preparation factor <u>with</u> methanol/water dilution factor correction for a methanol extracted solid sample is calculated as follows:

$$P_3 = \frac{V_m + \left(\frac{C_w}{100} \times W_S \times \rho\right)}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: P_3 = preparation factor with methanol/water dilution factor correction for methanol extracted solid sample in mL/g.
V_m = volume of methanol added in mL.
Unless specified otherwise, V_m = 10.
C_w = moisture content in %.
W_S = mass of solid sample methanol extracted in g.
ρ = density of water in mL/g. Assume ρ = 1.
C_{ss} = solids content in %.

15.7. Refer to the mobility extraction and determinative methods for additional calculations.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Refer to the determinative method for data assessment and acceptance criteria.

18.2. Additional information regarding internal quality control checks is provided in SOP-T020.

18.3. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Refer to the determinative method for contingencies for out-of-control or unacceptable data.

20.2. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. Purge-and-Trap for Aqueous Samples, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 5030C, USEPA, Revision 3, May 2003.

22.2. Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 5035A, USEPA, Revision 1, July 2002.

22.3. Determinative Chromatographic Separations, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000C, USEPA, Revision 3, March 2003.

22.4. Quality Control, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.5. Choosing the Correct Procedure, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.6. Organic Analytes, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, February 2007.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Additional Quality Control Criteria for Department of Defense Project.

23.2. Appendix B: Additional Quality Control Criteria for BP Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 5030C are noted.

24.1.1. Sample Collection, Preservation, Containers and Holding Times

24.1.1.1. The concentration and the volume of the dechlorinating agent used for aqueous sample preservation are modified.

24.1.2. Procedure

24.1.2.1. The purge temperature and desorb temperature are modified.

24.1.2.2. The sample preparation and dilution techniques are modified.

24.1.2.3. The sample volume required for purge-and-trap extraction via EPA Method 8260C lower limits of quantitation is modified.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
3.3	Section 3: Add reference to quantitation limit.	L.Lem	01/13/14
	Section 6: Update definitions.		
	Section 8: Add SDS		
	Section 12: Revise quality control and add reference to SOP-T020.		

Appendix A

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

1. METHOD IDENTIFICATION

1.1. EPA Method 5030C, Purge-and-Trap for Aqueous Samples – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

4. QUALITY CONTROL

4.1. Matrix Based Quality Control (MS/MSDs)

4.1.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

5. REFERENCES

5.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, ***Version 4.2, October 2010.***

Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR BP PROJECT

1. METHOD IDENTIFICATION

1.1. EPA Method 5030C, Purge-and-Trap for Aqueous Samples – Additional Quality Control Criteria for BP Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The use of a standard from a second lot as the second source standard is acceptable if written warranties demonstrating that the standards from two different lots are not prepared from the same reference materials are obtained from the manufacturer. "Manufacturer" refers to the producer of the standard, not the vendor.

3.2. For solid sample to be extracted with methanol, add the spike standard and surrogate standard prior to the addition of methanol.

4. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

4.1. All solid samples must be preserved within 48 hours of sample collection, and analyzed within 48 hours or 14 days of sample collection based on the preservation method chosen.

5. QUALITY CONTROL

5.1. Event Based Quality Control (LCS/LCSDs and MBs)

5.1.1. One LCS consisting of the specified compounds spiked into clean reagent water is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation/extraction event. The LCSD is handled identically to the LCS.

5.1.2. One MB consisting of clean reagent water is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation/extraction event.

5.2. Matrix Based Quality Control (MS/MSDs)

5.2.1. One MS consisting of the actual sample matrix spiked with known concentrations of specific target analytes is required for every batch of 20 samples per matrix or portion thereof extracted concurrently within an 8-hour preparation/extraction event. The MSD is handled identically to the MS.

5.2.2. The sample selected for spiking must be one of the samples collected for the specific BP project. If 10 or less BP samples are received, and no MS is designated, then a non-BP sample may be used.

5.2.3. Samples identified as trip or field blanks cannot be used for MS/MSD.

6. PROCEDURE

6.1. Organic extracts must be stored in the same type of vials (amber glass or clear glass) as the associated standards at the appropriate storage temperature.

7. REFERENCES

7.1. Technical Requirements for Environmental Laboratory Analytical Services, BP Laboratory Management Program (LaMP), Revision 09, July 30, 2007.

Title : **EPA METHOD 5035A, CLOSED SYSTEM PURGE AND TRAP**

Document No. : SOP-M213
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Revision 1.1 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 05/24/12
MANAGEMENT **DATE**

_____ 05-24-12
QA DEPARTMENT **DATE**

ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. EPA Method 5035A, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples.

2. APPLICABLE MATRICES

2.1. This method is applicable to soils, solid waste samples.

3. DETECTION LIMITS

3.1. Detection limits are defined in the determinative methods, however, low-level analyses have an estimated detection limit of 1 ug/kg, and high-level analyses may have detection limits of 100 ug/kg, or greater.

4. SCOPE AND APPLICATION

4.1. This method describes sample preparation and extraction of solid samples for the analysis of volatile organics by closed system purge-and-trap. Closed-System Purge-and-trap and subsequent gas chromatographic analysis of environmental samples are used in methods EPA 8015B, 8015M [TPH (g)], 8021B, 601, 602, and 8260B/C as well as proprietary state methods, AK101, TX1005, NWTYPH-Gx.

5. METHOD SUMMARY

5.1. An inert gas, helium, is bubbled through an aqueous solution contained in a purging chamber at 40°C and the volatile components are efficiently transferred from the prepared sample to the vapor phase. The vapor is swept through an adsorbent column where the volatile components are retained. After the purging is completed, the adsorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. Either of two types of sorbent columns listed in section 5 may be used in the purge and trap device.

5.2. Low concentration soil method - generally applicable to soils and other solid samples with VOC concentrations in the range of 0.5 to 200 µg/kg.

5.2.1. The first option is to collect an approximately 5g sample, weighed in the field at the time of collection, and place it in a pre-weighed vial with a septum-sealed screw-cap that already contains a stirring bar and a sodium bisulfate preservative solution. The vial is sealed and shipped to the laboratory for analysis. The entire vial is then placed, unopened, into the instrument carousel.

5.2.2. The second option is called empty vial technique. Using a coring tool a 5-g aliquot of undisturbed soil is transferred to a tarred empty VOA vial and capped with a PTFE-lined septa.The sealed vial with the soil aliquot is maintained either frozen (< -7° C) , or at 4 ± 2°C until laboratory receipt and analysis. Within 48 hrs of sampling add preservation to the vial or keep

frozen at (< -7° C) for storage up to 14 days from sampling before low level analysis.

5.2.3. The third option is to collect an approximately 5g sample with a sampling device such as the EnCore™ sampler, store and seal the sample in a storage pouch, and ship to the laboratory for analysis. These samples are to be transferred by extrusion to a sodium bisulfate preserved soil sample vial containing a stirring bar within 48 hours. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40°C and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

5.3. High concentration soil method - generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg.

5.3.1. The first option is to collect an approximately 5-g sample in a pre-weighed vial with a septum-sealed screw-cap that contains 10 mL of methanol. At the time of analysis, an aliquot of the solvent is removed from the vial, surrogates and internal standards (if applicable) are added to the extract, then purged using Method 5030B and analyzed by an appropriate determinative method.

5.3.2. The second option is within 48 hrs. to add methanol to empty vial either stored at 4 ± 2° C or frozen at (< -7° C) for high level analysis. If high level analysis not required immediately keep empty vial frozen at (<-7° C) up to 14 days from sampling time.

5.3.3. The third option is to collect an approximately 5g sample with a sampling device such as the EnCore™ sampler, store and seal the sample in a storage pouch, and ship to the laboratory for analysis. These samples are to be transferred by extrusion to a soil sample vial containing 10mL of methanol within 48 hours. An aliquot of the solution is added to 5 mL of reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030B, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. ►***Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility***.

6.13. ►***Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence***.

6.14.

6.15. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.16. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.17. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.18. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.19. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.20. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.21. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.22. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.23. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.24. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.25. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data

and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.26. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.27. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.28. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.29. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Performance of this method is restricted to analysts experienced in the use of the instruments and apparatus required to execute this method and interpretation of the outputs thereof. Each analyst must demonstrate the ability to generate acceptable results and receive approval by the applicable Group Leader prior to analyzing billable samples.

7.2. Samples requiring methanolic extraction are susceptible to significant loss of volatile analytes.

7.3. Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment that lead to artifacts and/or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferants under the conditions of the analysis by running laboratory method blanks.

7.3.1. The use of high purity solvents, reagents and pre-conditioning of disposables that come in contact with the sample help to minimize interference problems.

7.4. This procedure is susceptible to interferences from impurities in the purge gas, ambient atmospheric environment, and out-gassing of organic compounds from the plumbing ahead of the adsorbent column. The level of these impurities is measured by the analysis of method blanks as part of routine quality control.

7.4.1. To minimize intrusion of airborne contaminants, the atmospheric conditions of the VOC laboratory shall be maintained continuously. The environment shall be kept virtually free of all solvents. The only solvents allowable are methanol, ethanol, propanol and isopropanol. Access doors shall be kept closed.

7.5. Contamination by carryover can occur whenever high and low level samples are analyzed sequentially. Suspected high level samples should be analyzed diluted and at the end of the sequence to prevent carryover contamination. In addition, sample syringes, purging devices, and labware should be thoroughly rinsed with solvent between samples. Whenever an unusually high level sample is analyzed, it should be followed by analysis of reagent water to check for carryover. The trap and other parts of the system are susceptible to carryover contamination. To minimize carryover, baking-out and purging of the entire system is performed routinely and whenever carryover is suspected.

7.6. Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. The most common contaminants are acetone, carbon disulfide, fluorocarbons and methylene chloride. Field and trip blanks which are prepared from reagent water and accompany the sample containers to and from the sampling site and subsequent storage are analyzed to assess contamination from transport and storage.

7.7. Autosampler positional contamination can also occur and can easily go undetected. For an autosampler position which is suspected to contained sample of unusually high concentration, a blank should be analyzed on that position (and the following position) and evaluated prior to analyzing other samples.

8. SAFETY

8.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled as a potential health hazard.

8.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current Calscience Health & Safety Manual. In general, protective eyewear (i.e., safety glasses or goggles) and labwear (i.e., laboratory coats or aprons) are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals. The chosen glove material must be resistant to the chemical in use and must not introduce contaminants to the analytical process.

8.3. Processes that promote vaporization of volatile chemicals into the work area should be performed inside an exhaust hood vented to the exterior of the laboratory.

8.4. Material Safety Data Sheets (MSDS's) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Purge and trap device- AtomX-Automated VOC sample prep system, Stratum P & T concentrator and Archon Auto sampler, or equivalent. This device consists of a unit that automatically adds water, surrogates, and internal standards (if applicable) to a vial containing the sample, purges the VOCs using an inert gas stream while heating

and agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph.

9.1.1. The purging device should be capable of accepting a vial sufficiently large to contain a 5-g soil sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample (magnetic stir bar) during purging. The analytes being purged must be quantitatively transferred to an absorber trap.

9.1.2. The trap is a 0.125 inch diameter stainless steel tube produced to the specifications of the instrument manufacturer. Each trap is packed with adsorbent material appropriate for the analysis. Common column adsorbents are Carbopack B, Carboxen 1000, Carboxen 1001, Tenax, silica gel, and activated charcoal. Other packing materials may be used provided equivalent performance is demonstrated. Before using the trap it should be conditioned according to the manufacturer's instructions.

9.1.3. The desorber should be capable of rapidly heating the trap to 245°C and delivering the VOCs to the GC column in a narrow plug.

9.2. Syringes- 10, 25, 50, 100, 250, 500µl gas-tight and 5ml gas-tight with Luerlock tip and 2-way valve port.

9.3. VOA vials- 40ml, pre-cleaned.

9.4. Analytical balance- capable of weighing to the nearest 0.01g.

9.5. Spatula- stainless steel.

9.6. Helium gas- high purity.

9.7. Magnetic stirring bars, PTFE coated.

9.8. EnCore™ sampling system- T-Handle, Sampler, and Extrusion Tool.

10. REAGENTS AND STANDARDS

10.1. Reagent water- Purified water that has been shown to be free of all target analytes at the method specified reporting limits.

10.2. Methanol- Purge and trap grade.

10.3. Sodium bisulfate, $NaHSO_4$ - ACS grade.

10.4. Standards- As appropriate for the method performed.

10.5. Sea Sand- Ottawa Sand

11. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

11.1. VIAL PREPARATION (FOR FIELD PRESERVATION)

11.1.1. Sample is extruded into a vial containing reagent water and frozen on site to < -7°C. The holding time is 14 days for analysis.

11.1.2. Sample is extruded into a vial containing reagent water and cooled to 4 ± 2° C for 48 hours or less then frozen to. < -7° C upon laboratory receipt. Holding time 14 days. Analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48 hour period.

11.1.3. Sample is extruded into a vial containing reagent water and 1 g NaHSO4 and cooled to 4 ± 2° C. Holding time 14 days. Reactive compounds such as 2-Chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservative and analyze as soon as possible.

11.1.4. Sample is extruded into a vial containing methanol and cooled to 4 ± 2° C. Holding time is 14 days. Additional methanol extract storage time beyond 14 days may be acceptable if the desired VOC constituent stability can be demonstrated from appropriate performance data.

11.1.5. Sample is extruded into vial and cooled to 4 ± 2° C. Holding time 14 days.

11.2. VIAL PREPARED (EMPTY FIELD SEALED VIAL)- LOW LEVEL

11.2.1. Sample is extruded into an empty sealed vial and frozen on-site to < -7° C. Holding time 14 days.

11.2.2. Sample is extruded into an empty sealed vial and cooled to 4 ± 2° C for no more than 48 hours then frozen to < -7° C upon laboratory receipt. Holding time 14 days. Analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48 hour period.

11.2.3. Sample is extruded into an empty sealed vial and cooled to 4 ± 2° C for no more than 48 hours then preserved with methanol upon laboratory receipt. Holding time 14 days. If samples are not preserved within 48 hours with methanol analysis must be completed within 48 hours.

11.2.4. Sample is extruded into an empty sealed vial and cooled to 4 ± 2° C. Holding time 48 hours.

11.3. PREPARATION IN LAB USING A SUITABLE CORING DEVICE(e.g., EnCore ™)

11.3.1. Cool to 4 ± 2°C or freeze to < -7° C, the coring tool used as a transport device. The holding time is 48 hours and may be extended to 14 days if the sample is extruded to a sealed vial and either frozen to <-7°C or chemically preserved.

11.3.2. Freeze to < -7°C the coring tool used as a transport device. The holding time is 48 hours and can be extended to 14 days if the sample is extruded to a sealed vial and either frozen to < -7° C or chemically preserved.

11.4. ***►Coring device should not be frozen below - 20°C due to potential problems with tool seals and the loss of constituents upon sample thawing.***

11.5. ***►A longer holding time may be appropriate if it can be demonstrated that the reported VOC concentrations are not adversely affected from preservation, storage and analysis performed outside the recommended holding times.***

12. QUALITY CONTROL

12.1. For method 8021B (excepting in the case where only the LUFT target analytes are to be determined), during the initial calibration, the response for chloromethane, 1,1-dichloroethane, bromoform, and 1,1,2,2,-tetratchloroethane requires evaluation. Unacceptable responses for these compounds may indicate improper purge flow, contaminated lines, or active sites in the system.

12.1.1. Chloromethane: This compound is the most likely to be lost is the purge flow is excessive.

12.1.2. 1,1-Dichloroethane and 1,1,2,2-Tetrachloroethane: These compounds are degraded by contaminated transfer lines and/or active sites in the trap.

12.1.3. Bromoform: This compound is the most likely to purge poorly if the purge flow is too fast.

12.1.4. For GC methods the initial calibration acceptance limit for each of the above compounds is RSD ≤ 20%. If one or more of these compounds do not meet the acceptance criteria (even if the mean RSD ≤ 20%), the initial calibration is not acceptable for purge and trap analyses. Effect corrective action and re-calibrate.

12.1.5. GC/MS methods must follow the CCC and SPCC and other calibration acceptability criteria as found in SOP-M311.

12.2. The purge and trap apparatus must not introduce contaminants into the analytical system. It is recommended that the purge and trap system be baked-out at the beginning of the day to remove any contaminants that have entered the system. This procedure involves running the instrument through a complete purge cycle. The trap should be desorbed onto the GC column with the GC set to complete a normal temperature program or a shortened bakeout program.

12.3. Before processing any samples, the analyst should demonstrate that the purge and trap system is free from contamination. Positions on the autosampler that are known or suspected to be contaminated must not be used for analysis until they are demonstrated to be clean (<RL).

12.4. The trap should be monitored to determine when trapping and desorbing efficiency has degraded and corrective action necessary. A decrease in response of certain analytes, particularly bromoform, and a high degree of carryover may indicate that a trap is no longer functioning correctly. Other factors that could possibly be the source of these conditions must first be investigated and rejected as causes before concluding that a trap is no longer useable and requires replacement.

13. CALIBRATION AND STANDARDIZATION

13.1. Purge and Trap operating conditions vary with analytical requirements and trap materials used. Some common parameters are as follows, however, the optimum conditions should be determined during the method developmental processes.

Purge Gas:	High purity helium
Valve Actuator Gas:	Dry grade air

Purge Flow Rate:	20 – 40 ml/minute	
Times:	Dry purge:	0.5-2 minutes
	Bake:	8 minutes
Temperatures:	Solid purge:	40°C
	Trap stand-by:	40°C
	Desorb preheat:	245°C
	Desorb:	250°C
	Bake:	290°C

13.2. The following purge and desorb times must be adhered to when performing purge and trap analyses.

Method (min)	Purge Time (min)	Desorb Time
EPA 8260B	11	0.5-2
EPA 8021B	11	4
EPA 8015M [TPH (g)]	11	4
EPA 8015B	11	4

14. PROCEDURE

14.1. Due to the high volatility of most purge and trap analytes, care must be exercised to minimize analyte loss in the handling of the sample and transfer to the purge and trap apparatus. Sample aliquot transfer of samples shall be performed in an expeditious manner to minimize loss of volatile analytes.

14.1.1. Any re-analysis shall be performed from a separate sample vial.

14.2. LOADING SOLID SAMPLES ON A (ARCHON/TEKMAR) PURGE AND TRAP AUTOSAMPLER

14.2.1. Allow the sample to come to room temperature, place the sample vial on a top loading balance, and record the weight.

14.2.1.1. If the sample was transferred to the sample vial in the field, use the field recorded sample weight as the sample weight. The laboratory weighing provides a check on the field sampling procedure.

14.2.1.2. If the sample was transferred to the sample vial in the lab, use the lab recorded sample weight.

14.2.2. Verify that the appropriate internal/surrogate standards are properly loaded into the OI internal standard syringe. Ensure that the injection settings are correct and that sufficient volume for the analytical run exists.

14.2.3. The 40ml sample vial is loaded directly into the autosampler carousel. The apparatus will automatically add 5 mL of organic-free reagent water and the

internal standard/surrogate solution as programmed. Manual addition of internal standard/surrogates is not necessary. Prior to purging, heat the sample vial to 40°C for 1.5 minutes. The sample is now ready for analysis.

14.3. EnCore™ SAMPLE PREPARATION (FOR LAB PRESERVATION)

14.3.1. LOW LEVEL SAMPLE PREPARATION

14.3.1.1. Add approximately 1 g of sodium bisulfate to each vial. Enough sodium bisulfate should be present to ensure a sample pH of <2.

14.3.1.2. Add 5 mL of organic-free reagent water to each vial.

14.3.1.3. Seal the vial with the screw-cap and septum seal and tare the balance with the vial on it.

14.3.1.4. Attach an EnCore™ Sampler (the sample) to the EnCore™ Extrusion Tool by depressing the locking lever on the tool and inserting the sampler plunger end first into the tool. Align slots on core body with pins in the tool and turn core clockwise until it locks into place. Release the locking lever.

14.3.1.5. Keeping the sampler pointed upwards so sample does not fall out, break off tabs and rotate the plunger knob clockwise while gently pushing until the plunger slides over the wings of the coring body.

14.3.1.6. Remove cap from the sampler and push down on sampler knob extruding the sample core into the tared vial.

14.3.1.7. Weigh the prepared vial to the nearest 0.01 g, record the weight, and write it on the vial using ball point pen.

14.3.1.8. With each preparation / extraction batch of 20 samples or less of Encore (or similar sample holding device) a set of MB vials needs to prepares using sea sand and NaHSO4.

14.4. HIGH LEVEL SAMPLE PREPARATION

14.4.1.1. Add 10 mL of methanol to each vial.

14.4.1.2. Seal the vial with the screw-cap and septum seal and tare the balance with the vial on it.

14.4.1.3. Attach an EnCore™ Sampler (the sample) to the EnCore™ Extrusion Tool by depressing the locking lever on the tool and inserting the sampler plunger end first into the tool. Align slots on core body with pins in the tool and turn core clockwise until it locks into place. Release the locking lever.

14.4.1.4. Keeping the sampler pointed upwards so sample does not fall out, break off tabs and rotate the plunger knob clockwise while gently pushing until the plunger slides over the wings of the coring body.

14.4.1.5. Remove cap from the sampler and push down on sampler knob extruding the sample core into the tared vial.

14.4.1.6. Weigh the prepared vial to the nearest 0.01 g, record the weight, and write it on the vial using ball point pen.

14.4.1.7. With each preparation / extraction batch of 20 samples or less of Encore (or similar sample holding device) a single high level MB vial needs to prepare using sea sand and MeOH.

14.4.1.8. Record in 5035 extraction logbook information about sample vial weight, balance id, sand id, methanol id, NahSO4 lot number and extraction time.

14.5. FIELD PREPARED SAMPLES (TerraCore or similar)

14.5.1. After carefully checking sample ID, weigh each vial and record final weight. Initial vial weight must be pre-written on each vial. Record both initial and final weight in the logbook. Calculate net weight of each soil sample by subtracting initial weight from final weight and record in the logbook. Check and record information about preservative and any other information available from vial.

14.6. SAMPLES PREPARED USING EMPTY VIAL TECHNIQUE.

14.6.1. VOA vials needs to maintained either frozen (<- 7° C) or at 4 ± 2° C until laboratory receipt. Low level analysis must be done within 48 hours using process same as in 14.2.

14.6.2. For high level sample analysis vial maintained at 4 ± 2° C is selected for methanol extraction upon laboratory receipt. Within 48 hours of sample collection the methanol is added through the septum using a glass syringe equipped with a 23 –gage Luer Lock needle. The methanol is mixed with the soil and any pressure can be relieved by cracking the VOA vial's cap once. The methanol extract, stored at 4 ± 2°C or less, has a shelf life of up to two weeks.

14.6.3. If analysis cannot be completed within 48 hours than vial needs to freeze at < -7°C before end of 48 hours time window until ready to do analysis. Holding time 14 days from sampling time. From frozen VOC samples, initially or upon laboratory receipt, a vial may be thawed and analyzed for low level and high level analysis as described above.

14.6.4. Remember before doing high level or low level analysis using empty vial technique, net soil sample weight needs to be determined.

15. CALCULATIONS

15.1. None.

16. METHOD PERFORMANCE

16.1. Efficiency of this method is highly dependent upon field sampling and the limited manipulation of the sample, from collection to analysis.

16.2. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well-ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The upper and lower acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ±3S. All LCS/LCSD compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, the problem must be identified and corrected.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.2.3. If methylene chloride is found in the MB, no positive sample results should be reported unless the concentration of the compound in the sample exceeds 10 times the MB level. Report the data with qualification indicating the analyte was present in the corresponding MB.

18.3. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The upper and lower acceptance limits for each surrogate spike compound is based upon the historical average recovery $\pm$ 3S.

18.3.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

18.3.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.3. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.3.1. Check the internal standard and surrogate spiking solutions for degradation and contamination.

18.3.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample or extract should be re-analyzed.

18.3.3.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and/or re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-extracted and re-analyzed.

18.3.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSDs are as follows:

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for water samples and µg/kg (ppb) for oil, soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results,

analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.1. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.1. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.1. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.1. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.2.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries an MS/MSD data set is does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.2.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the unacceptable result is confirmed by the technical director.

20.2.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.2.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.2.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes which require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. REFERENCES

22.1. Method 5035A, Closed System Purge and Trap And Extraction For Volatile Organics In Soil And Waste Samples, Test Methods for Evaluating Solid Waste, Volume 1B, Laboratory Manual, Third Edition, US Environmental Protection Agency, Draft Revision 1, July 2002.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

None.

24. ►*MODIFICATIONS*

24.1. None

25. ►*REVISION HISTORY*

Revision	Description	Author	Effective Date
0.0	SOP updated based on EPA 5035A, minor changes.	Y.Patel	05/28/2012

Title : **EPA METHOD 6020, INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (ICP-MS)**

Document No. : SOP-M610
Revision No. : 4.2
Supersedes : 4.1

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Revision 4.2 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 05/24/12
MANAGEMENT **DATE**

_____ 05-24-12
QA DEPARTMENT **DATE**

ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. EPA Method 6020, Inductively Coupled Plasma – Mass Spectrometry (ICP-MS).

2. APPLICABLE MATRICES

2.1. The method is applicable to a large number of elements in water and wastes (industrial, soils, sludges, sediments, etc.).

3. DETECTION LIMITS

3.1. Instrument detection limits, sensitivities, and linear ranges for these elements will vary with the matrices, instrumentation, and operating conditions.

Element	Estimated Quantitation Limit (µg/L)
Aluminum	0.1
Antimony	0.02
Arsenic	0.4
Barium	0.02
Beryllium	0.1
Cadmium	0.07
Calcium	10.0
Chromium	0.02
Cobalt	0.01
Copper	0.03
Iron	0.2
Lead	0.02
Magnesium	0.10
Manganese	0.04
Mercury	1.00
Nickel	0.03
Potassium	1000.0
Selenium	1.0
Silver	0.04
Sodium	0.06
Thallium	0.05
Vanadium	0.03
Zinc	0.08

4. SCOPE AND APPLICATION

4.1. Inductively coupled plasma mass spectrometry (ICP/MS) is a technique which can quantitate many metallic elements in solution. When dissolved constituents are required, samples must be filtered through a 0.45µ filter and acid preserved prior to analysis. No further digestion is required prior to analysis for dissolved elements. Acid digestion prior to analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required. Elements for which Method 6020 is

applicable are listed in Section 3.1. Other elements may be added if supported by validation studies.

4.2. Use of this method is restricted to analysts who are knowledgeable in the recognition and the correction of spectral, chemical, and physical interferences in ICP/MS.

5. METHOD SUMMARY

5.1. Prior to analysis, samples which require total values must be solubilized or digested using appropriate sample preparation methods.

5.2. Method 6020 describes the multi-elemental determination of analytes by ICP/MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the neutral plasma gas and introduced, by means of a water-cooled interface into a mass spectrometer capable of providing resolution, better than or equal to 0.9amu peak width at 10% of the peak height. The water-cooled interface consisting of tandem skimmers is differentially pumped and leads into the high vacuum chamber of the mass spectrometer. The ions and ion clusters produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a dual mode electron multiplier detector. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix. The recommended elemental equations which correct for many of these interferences are listed in Section 7.2.4. Use of the internal standards is required to compensate for suppressions and enhancements caused by sample matrices.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. ►***Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.***

6.13. ►***Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.***

6.14. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.15. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.16. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.17. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.18. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.19. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.20. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.21. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.22. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.23. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.24. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.26. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.27. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

7. INTERFERENCES

7.1. Isobaric elemental interference in ICP/MS is caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z) as target analytes. The data system is used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting out the appropriate signal from the isotope of interest. Data that is corrected must be noted in the project file along with the exact calculations used. The below listed data shows the analyte concentration measured when an interferant is present at 100mg/L. Note that this information was experimentally derived and the source of the interferences presented in this data are actually from several different sources. One of these sources is the effect of resolution on adjacent peaks. Because ICP/MS instruments nominally provide unit resolution at 10% of the peak height, high ion currents at adjacent masses may also contribute to ion signals at the mass of interest. In a quadrupole mass spectrometer, due to the trapezoidal peak shape of the mass spectra, there is a larger effect at one amu less than the interferant, than at one amu greater that the interferant's mass. Another interference observed in the below listed data is that of an isobaric molecular interference (described in Section 7.2.) as a hydride ion. Hydride ion interferences only cause an interference at one amu greater than the interferant's mass. When reviewing the below listed data, it should also be remembered that interferences are not necessarily linear and attempts must not be made to extrapolate these values to a particular data set. The data has been included is for its guidance purposes only and does not contain absolute values which would be applicable in every case.

		Peak Width at 10% of the Peak Height			
		1.0amu Integration Width		0.8amu Integration Width	
Interferant					
Analyte	Element	0.9amu	0.3amu	0.9amu	0.3amu
^{121}Sb	^{120}Sn	820	5	10	1
^{121}Sb	^{122}Te	77	None	1	None
^{75}As	^{74}Se, ^{76}Se	910	4	3	None
^{9}Be	^{10}B	1,200	12	9	1
^{112}Cd	^{113}In	1,700	8	10	None
^{114}Cd	^{115}In	>5,000	150	180	18
^{116}Cd	^{115}In	30	None	5	None
^{52}Cr	^{51}V	1.4	1.5	None	None
^{53}Cr	^{54}Fe	650	7	1	None
^{59}Co	^{58}Ni, ^{60}Ni	>1,500	6	2	None
^{63}Cu	^{62}Ni, ^{64}Ni	190	1	None	None
^{63}Cu	^{64}Zn	4,000	14	9	None
^{65}Cu	^{64}Ni	1	1	None	None
^{65}Cu	^{64}Zn, ^{66}Zn	>4,400	22	15	None

^{208}Pb	^{209}Bi	140	14	57	None
^{55}Mn	^{54}Fe, ^{56}Fe	900	8	4	None
^{58}Ni	^{59}Co	>3,000	96	75	7
^{60}Ni	^{59}Co	9	4	10	5
^{62}Ni	^{63}Cu	>8,500	690	4,500	16
^{107}Ag	^{106}Pd, ^{108}Pd	>2,400	22	80	4

Peak Width at 10% of the Peak Height (Cont.)

Interferant		1.0amu Integration Width		0.8amu Integration Width	
Analyte	Element	0.9amu	0.3amu	0.9amu	0.3amu
^{107}Ag	^{106}Cd, ^{108}Cd	130	3	5	2
^{109}Ag	^{108}Pd, ^{110}Pd	1,800	12	36	3
^{109}Ag	^{108}Cd, ^{110}Cd	1,600	10	37	3
^{51}V	^{52}Cr	> 2,100	45	410	1
^{64}Zn	^{65}Cu, ^{63}Cu	> 7,800	57	410	2
^{66}Zn	^{65}Cu	2	None	3	2

7.2. Isobaric molecular and doubly charged ion interferences in ICP/MS are caused by ions consisting of more than one atom or charge. The following data lists isobaric molecular-ion interferences which could affect target analytes. Note that many of these interferences are extremely rare, but adverse effects on data quality could occur if the individual constituents occurred in the sample at sufficiently high concentrations. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections to the data must be applied or the data qualified to indicate the presence of interferences. Instrumental plasma conditions and matrix components affect the production of these ion clusters and the effects must be measured to apply appropriate correction terms. Corrections for molecular-ion interferences may either be based upon the natural isotope ratios of the molecular ion or by measuring the interference which occurs when the interferant is present. It should be noted that the below listed data does not represent all of the described interferences which need to be tested. However, it can be referred to for informational purposes if unusual samples are encountered.

	Interferences						
Analyte	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{121}Sb	PdO		AgN			AgC	
^{123}Sb	AgO		AgN	SrCl	ZrS	CdC	
^{75}As	CoO	NiOH	NiN	ArCl	CaS	CuC	
^{138}Ba	SnO	SbOH					
^{137}Ba	SbO	SnOH		MoCl			
^{136}Ba	SnO	SnOH				SnC	
^{135}Ba	SnO	SnOH		MoCl			
^{134}Ba	SnO	SnOH	SnN	MoCl		SnC	
^{132}Ba	SnO,CdO	InOH	SnN	MoCl	MoS	SnC	
^{130}Ba	CdO	CdOH	SnN,CdN	MoCl	MoS	SnC	
^{9}Be							
^{114}Cd	MoO	MoOH	MoN	SeCl	SeS		
^{112}Cd	MoO,ZrO	MoOH	MoN	SeCl,AsCl	SeS	MoC	
^{111}Cd	MoO	MoOH	MoN	GeCl			
^{110}Cd	MoO,ZrO		MoN,ZrN	GeCl,AsCl	SeS	MoC	
^{113}Cd	MoO	MoOH		SeCl,AsCl			

^{116}Cd	MoO						
^{106}Cd	ZrO		MoN,ZrN		GeS	MoC,ZrC	
^{108}Cd	MoO,ZrO	ZrOH	MoN,ZrN	GeCl	SeS,GeS	MoC,ZrC	
^{52}Cr	ArO	ClOH				ArC	
^{53}Cr	ClO	ArOH	KN	NCl,OCl		KC	
^{50}Cr	SO		ArN		SO	ArC	Mo^{2+}
^{54}Cr		ClOH	ArN,CaN			CaC	

Interferences (Cont.)

Analyte	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{59}Cr	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn^{2+}
^{63}Cu	TiO,PO_2	TiOH	TiN	SiCl,MgCl	PS	VC	ArNa
^{65}Cu	TiO	TiOH	VN	SiCl	SS,SO_2H	CrC	
^{208}Pb							
^{206}Pb							
^{207}Pb							
^{204}Pb							
^{55}Mn	KO	ArOH	KN		NaS	CaC	Cd^{2+}
^{202}Hg	WO						
^{200}Hg	WO	WOH	WN				
^{199}Hg	WO	WOH					
^{201}Hg		WOH					
^{198}Hg	WO	TaOH	WN			WC	
^{204}Hg							
^{196}Hg			WN			WC	
^{58}Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd^{2+},Sn^{2+}
^{60}Ni	CaO	CaOH	TiN	MgCl,NaCl	SiS	TiC	Sn^{2+}
^{62}Ni	TiO	ScOH	TiN	AlCl,MgCl	SiS	TiC,CrC	Sn^{2+}
^{61}Ni	ScO	CaOH	TiN	MgCl	SiS	TiC	Sn^{2+}
^{64}Ni	TiO	TiOH	TiN,CrN	SiCl,AlCl	SS	CrC	
^{80}Se	ZnO	CuOH	ZnN	ScCl,CaCl	TiS	ZnC	
^{78}Se	NiO	NiOH	ZnN	CaCl,KCl	TiS	ZnC	
^{82}Se	ZnO	CuOH	ZnN	TiCl,ScCl	TiS,CrS		
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	NiOH	CuN	CaCl,ArCl	ScS	CuC	
^{74}Se	NiO	FeOH	NiN	ClCl,KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
^{205}Tl							
^{203}Tl		WOH					
^{51}V	ClO	SOH	ClN	ClO,ClN	FeS	KC	
^{50}V	SO	ArN			ArC	Mo^{2+}	
^{64}Zn	TiO	TiOH	TiN,CrN	SiCl,AlCl	SS	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl,SiCl	SS	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{2+}
^{67}Zn	VO	TiOH,Cr	CrN	SCl	ClS	MnC	Ba^{2+}
^{70}Zn	FeO	CrOH	GeN	ClCl	ArS	NiC	

7.2.1. The first type of interference correction can be demonstrated by the use of matrix algebra to solve for the analyte of interest. In the following example, the molecular ion, molybdenum oxide, and elemental interferences of tin and palladium on cadmium are included in the matrix to be evaluated.

	Species Involved			
Observed Mass Affected	Cd	MoO	Sn	Pd
105	.0000	.0000	.0000	.2233

108	.0089	.1480	.0000	.2546
114	.2873	.2411	.0070	.0000
118	.0000	.0000	.2430	.0000

7.2.2. The values listed are the natural abundances for the element and molecular species listed at the mass observed.

7.2.3. Corrections for molecular-ion interferences must be applied with caution to avoid the introduction of errors. These errors are primarily statistical and are affected by the magnitude of the correction terms used.

7.2.4. The following are the recommended elemental equations which may be used for the analysis of the elements specified by this method. Note that these equations have been derived with various simplifying assumptions and an equation including more components may occasionally be required, such as that described by the above matrix components.

Element	Isobaric Correction	Mathematical Equation
Al	none	$(1.0000)(^{27}M)$
Sb	none	$(1.0000)(^{121}M)$
As	ArCl, Se	$(1.0000)(^{75}M) - (3.1278)(^{77}M) + (2.736)(^{82}M)$
Ba	none	$(1.0000)(^{135}M)$
Be	none	$(1.0000)(^{9}M)$
Cd	MoO, Sn	$(1.0000)(^{114}M) - (0.0149)(^{118}M) - (1.6285)(^{108}M)$
Ca	none	$(1.0000)(^{44}M)$
Cr	none	$(1.0000)(^{52}M)$
Co	none	$(1.0000)(^{59}M)$
Cu	none	$(1.0000)(^{65}M)$
Fe	none	$(1.0000)(^{57}M)$
Pb	none	$(1.0000)(^{208}M) + (1.0000)(^{207}M) + (1.0000)(^{206}M)$
Mg	none	$(1.0000)(^{25}M)$
Mn	none	$(1.0000)(^{55}M)$
Ni	none	$(1.0000)(^{60}M)$
K	none	$(1.0000)(^{39}M)$
Se	Ar_2	$(1.0000)(^{82}M) - (1.0087)(^{83}M)$
Ag	none	$(1.0000)(^{107}M)$
Na	none	$(1.0000)(^{23}M)$
Tl	none	$(1.0000)(^{205}M)$
V	ClO, Cr	$(1.0000)(^{51}M) - (3.1081)(^{53}M) + (0.3524)(^{52}M)$
Zn	none	$(1.0000)(^{66}M)$
^{6}Li	Li(natural)	$(1.0000)(^{6}M) - (0.0813)(^{7}M)$
Sc	none	$(1.0000)(^{45}M)$
Y	none	$(1.0000)(^{89}M)$
Rh	none	$(1.0000)(^{103}M)$
In	Sn	$(1.0000)(^{115}M) - (0.0149)(^{118}M)$
Tb	none	$(1.0000)(^{159}M)$
Ho	none	$(1.0000)(^{165}M)$
Bi	none	$(1.0000)(^{209}M)$

Note: M is the total ion count rate at the specific mass.

7.2.5. Including additional matrix components may very well provide superior corrections for molecular interferences, however additional noise is added for each term that is included. To evaluate the validity of the elemental equation, the relative size of the mass coefficient and the signal size at each mass must be evaluated. The data becomes more imprecise when the analyte signal is small and the interferences are high. This method evaluates this condition by the analysis of Interferants A (CL-INT-A1), but eventually the non-analyte signal may become large enough to affect the sample results. The equations were tested in a multi-laboratory study performed by the EPA. Other equations may be used but a description of the rationale for their use must exist and should be included in a case narrative or other clarifying documentation. The description must include which molecular isotopes are included, and the assumptions being made for the equation. The limitations of the equation should also be discussed. In the example, the equation for cadmium is derived to compensate for the interferences described above after simplifying by assuming that the palladium concentration is near zero and constant. This equation is limited to samples which do not contain palladium. This allows the model to be reduced to three equations and three unknowns, resulting in the listed cadmium equation.

7.2.6. In the case for which the interferant level is measured and then corrections are applied using the empirically derived value, the following example may be used. If a correction for an oxide ion is based upon the ratio of parent to oxide ion intensities, the correction may be adjusted for the effects of the sample matrix by the use of an appropriate internal standard previously demonstrated to form a similar level of oxide as the interferant. This second type of correction has been reported for oxide ion corrections using ThO/Th for the determination of rare earth elements. Most isobaric interferences that could affect ICP/MS determinations have been identified in the literature and the extent of their interferences is shown below under three sets of plasma conditions.

	Molecular Interference	Nebulizer Flow Rate High	Average	Low
Oxides				
	ScO/Sc	0.00326	0.00055	0.00116
	YO/Y	0.00568	0.00395	0.00353
	TbO/Tb	0.0156	0.00648	0.00614
	ClO/Cl	0.00725	0.00227	0.00233
Hydroxides				
	ScOH/Sc	0.00040	0.00011	0.00000
	YOH/Y	0.00078	0.00044	0.00048
	TbOH/Tb	0.00034	0.00008	0.00011
	ClOH/Cl	0.00048	0.00031	0.00029
Chlorine				
	ClO/Cl	0.00725	0.00227	0.00233
	ClOH/Cl	0.00048	0.00031	0.00029
	ArCl/Cl	0.00605	0.00091	0.00477

7.2.7. Note that the above information was experimentally derived, and attempts must not be made to extrapolate the values to a particular data set. It has been included for its guidance purposes only and does not contain absolute values which should be expected.

7.3. Physical interferences are effects associated with sample nebulization and transport processes as well as ion-transmission efficiencies. Nebulization and transport processes are those in which a matrix component causes a change in surface tension or viscosity in a manner different from the standards used in performing calibration. Internal standards have successfully been used to correct for these interferences. Physical interferences resulting in changes to ion transmission efficiencies are primarily suppressions. Lighter elements are suppressed more than the heavier elements due to space-charge effects. Changes in matrix composition therefore can cause significant suppressions (and enhancements) in analyte signal intensity. Dissolved solids can also deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and therefore changing the ion transmission efficiencies). Therefore total dissolved solid levels below 0.2% (2,000ppm) are recommended to minimize solid deposition. Internal standards must be affected to the same degree as the analyte to demonstrate that they compensate for these interferences. The following internal standards are recommended: ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when sample contain significant amounts of the recommended internal standards. When the intensity level of an internal standard is less than 30 or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed for the affected analytes after performing a fivefold (1+4) dilution. Analyst Note: In the performance of this method, it has been observed that the use of new or newly cleaned skimmer cones result in large initial changes in the ion transmission efficiencies. These changes may produce a large instrumental drift which can cause drift-sensitive quality assurance parameters to exceed control limits. It has been found that by conditioning the skimmer cones, by exposure to solutions (such as the ICS solutions) which are similar to the samples analyzed, the changes in ion transmission efficiencies will be mitigated. This conditioning appears to form an oxide layer on the skimmer cones which insulates and therefore stabilizes the ion transmission efficiencies.

7.4. Memory interferences are effects which are dependent upon the relative concentration differences between samples, standards, and blanks which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer used, affect the extent of the memory interferences which are present.

7.4.1. The rinse period between samples must be long enough to eliminate significant memory interference.

8. SAFETY

8.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.2. All sample preparation activities must be performed in an operational fume hood appropriate for use with acids.

8.3. All operational fume hoods are to remain energized continuously in order to prevent the atmosphere in the trace metal laboratories from becoming acidic.

8.4. Many metal containing solutions are extremely toxic if inhaled or swallowed. The analyst should wash hands thoroughly after handling.

8.5. Material Safety Data Sheets (MSDS's) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Inductively Coupled Plasma-Mass Spectrometer

9.1.1. The Perkin Elmer Elan DRCE ICP/MS is capable of providing resolution, less than or equal to 0.70amu at 10% peak height. The quadrupole mass range is 2 to 260amu with a full mass scan time of 100msec. The data system allows corrections for isobaric interferences and the application of the internal standard technique. Mass-flow controllers for the nebulizer argon and peristaltic pumps for the sample and internal standards are used. Detection is achieved by the use of dual mode electron multiplier with a linear dynamic range of eight orders of magnitude.

9.1.2. Argon gas supply: High-purity grade (99.99%).

9.2. ►***Instrument Software***

9.2.1. ***Requires a PC based data system or equivalent.***

9.2.2. ***PerkinElmer ELAN Version 3.4 Hotfix 1 (Build 3.4.57.1110), or equivalent.***

9.3. ►***Instrument Maintenance and Troubleshooting***

9.3.1. ***Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.***

9.3.2. ***Additional information can be found in the user manual or operating guide for the specific instrument.***

9.4. Operating Conditions

9.4.1. The analyst must follow the instructions provided by the instrument manufacturer. Operating conditions will vary depending upon the instrument manufacturer. Sensitivity, instrument detection limits (IDLs), precision, linear dynamic range and interference effects must be established for each analyte. The analyst must maintain quality control data confirming instrument performance and analytical results.

9.4.2. Precautions must be taken to protect the electron multiplier from high ion currents. Electron multipliers suffer from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, calibration response factors are constantly changing. This invalidates the calibration curve, causes instability, and invalidates sample analyses.

10. REAGENTS AND STANDARDS

10.1. Because HCl is added for stabilization, corrections for the chloride molecular-ion interference must be applied to all data generated.

10.2. ASTM Type I water (ASTM D1193) is required: Water must be monitored for analytes by the analysis of reagent blanks.

10.3. Standard stock solutions are purchased from reputable manufacturers specializing in ultra trace level ICP/MS standards. Standards and solutions are purchased to be largely compliant with CLP requirements. The following are the standards which are purchased. These solutions are considered stock standard solutions from which working standards are made.

10.3.1. Tuning Solution 1, "CL-TUNE-1"
Matrix: 2%HNO_3/5%HCl

Analyte	Conc (µg/mL)	Analyte	Conc (µg/mL)
Ba	10.00	Mg	10.00
Be	10.00	Pb	10.00
Ce	10.00	Rh	10.00
Co	10.00	Tl	10.00
In	10.00	U	10.00
^{7}Li	10.00	Y	10.00

10.3.2. Instrument Calibration Standard 2, "CL-CAL-2"
Matrix: 5% HNO_3/tr Tartaric Acid/tr HF

Analyte	Conc (µg/mL)	Analyte	Conc (µg/mL)
Ag	100.00	Mn	100.00
Al	100.00	Mo	100.00
As	100.00	Na	100.00
Ba	100.00	Ni	100.00
Be	100.00	Pb	100.00
Ca	100.00	Sb	100.00
Cd	100.00	Se	100.00
Co	100.00	Sn	100.00

Cr	100.00	Sr	100.00
Cu	100.00	Ti	100.00
Fe	100.00	Tl	100.00
K	100.00	V	100.00
Mg	100.00	Zn	100.00

10.3.3. Interferants A, "CL-INT-A1"
Matrix: 5% HNO_3/tr HF

Analyte	Conc (µg/mL)	Analyte	Conc (µg/mL)
Cl	21,215.00	Mg	1,000.00
Ca	3,000.00	P	1,000.00
Na	2,500.00	K	1,000.00
Fe	2,500.00	S	1,000.00
C	2,000.00	Mo	20.00
Al	1,000.00	Ti	20.00

10.3.4. Multi-Element Internal Standard, "CLISS-1"
Matrix: 2% HNO_3/tr Tartaric Acid

Analyte	Conc (µg/mL)	Analyte	Conc (µg/mL)
Bi	10.00	Sc	10.00
Analyte	**Conc (µg/mL)**	**Analyte**	**Conc (µg/mL)**
Ho	10.00	Tb	10.00
In	10.00	Y	10.00
^{6}Li	10.00		

10.3.5. Spike Solution 1
Matrix: 5% HNO_3

Analyte	Conc (µg/mL)	Analyte	Conc (µg/mL)
Ag	100.00	Mo	100.00
Be	100.00	Ni	100.00
Cd	100.00	P	100.00
Co	100.00	Se	100.00
Cr	100.00	Sr	100.00
Cu	100.00	Tl	100.00
Fe	100.00	Sn	100.00
Pb	100.00	Ti	100.00
Mg	100.00	V	100.00
Mn	100.00	Zn	100.00

10.3.6. Spike Solution 2
Matrix: 5% HNO_3

Analyte	Conc (µg/mL)	Analyte	Conc (µg/mL)
Na	1000.00	Ba	100.00
K	1000.00	Ag	50.00
Al	100.00	Si	100.00
B	100.00		

10.3.7. Three certified blanks are maintained as follows: 1) A 2% nitric acid blank designated "CLBLK-HNO3", 2) a 2% hydrochloric acid blank designated "CLBLK-HCL", and 3) a water blank designated "CLBLK-H2O".

10.4. Mixed calibration standard solutions: Dilute the stock-standard solution using 1% (v/v) HNO_3 in ASTM Type I water to levels within the linear range of the instrument. In addition, each calibration standard must contain the appropriate internal standard element which is introduced just prior to nebulization using a secondary peristaltic pump channel. Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control sample (see Section 10.8.) and monitored weekly for stability.

10.4.1. Internal standards must be used to monitor and correct for changes that occur from differences between standards and samples. The changes for which internal standards correct are primarily physical interferences. A minimum of three internal standards must be added, at identical levels, to all standards and samples prior to nebulization. The three internal standards used must be selected to bracket the mass range, and must include one internal standard from each of the following mass ranges (1 - 70), (71 - 125), and (126 - 250). The use of internal standards is accomplished by using a second channel of the peristaltic pump for on-line addition of internal standard to the uptake tube. If on-line addition is not used, then internal standard spiking may be performed by adding a constant volume of internal standard solution to identical volumes of the standards and prepared samples. One typical example is to measure out 10.0mL of all standards and samples into individual containers, then add 0.100mL of a 10mg/L solution of the internal standard mixture to each container. This adds identical amounts of the internal standard to each solution for analysis. The concentrations of the analyte levels in the standards do not have to be corrected for the dilution which occurs because the dilution of the samples and standards are identical.

10.4.2. In the determination of trace elements, containers can introduce either positive or negative errors in the measurement of trace elements by contributing contaminants through leaching or surface desorption and/or by depleting concentrations through absorption. Thus, the collection and treatment of the samples prior to analysis requires particular attention. The following cleaning treatment sequence is adequate to minimize contamination in the sample bottles, whether borosilicate glass, linear polyethylene, or Teflon: Detergent, Type II water, 1+1 hydrochloric acid, ASTM Type I water, 1+1 nitric acid, and Type I water. Chromic acid must not be used for cleaning as chromium is a common target analyte and its use may lead to contamination.

10.4.3. Containers used for storage of standards must be linear (as opposed to cross-linked) polyethylene or polypropylene. Cross linked polymers use zinc as a catalyst which will leach into the standards over extended time periods.

10.5. Three types of blanks are typically required for the analysis. The calibration blank is used in establishing the calibration curve. The reagent blank is used to monitor for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

10.5.1. The calibration blank generally consists of 2% HNO_3 (v/v) in ASTM Type I water along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes.

10.5.2. The reagent blank must contain all the reagents in the same volumes used for sample preparation. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solutions used for analysis.

10.5.3. The rinse blank generally consists of 1-2 percent HNO_3 (v/v) in ASTM Type I water. Prepare a sufficient quantity to flush the system between standards and samples.

10.6. The instrument check standard is the Continuing Calibration Verification (CCV) solution which the analyst prepares by combining compatible elements at concentrations near the midpoint of the respective calibration range.

10.7. The interference check solution(s) (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. For example, the chloride concentration present provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^+$ on ^{51}V and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Since the natural abundance of ^{35}Cl of 75.8 percent is 3.13 times the ^{37}Cl abundance of 24.2 percent, the ion corrections can be calculated with adjustments for isobaric contributions. Similarly, the iron in the ICS solutions is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement scheme to correct for various molecular-ion isobaric interferences. The ICS solutions follow and are used to verify that the interference levels are corrected by the data system within quality.

Analyte	Conc (µg/mL)	Analyte	Conc (µg/mL)
Cl	21,215.00	Mg	1,000.00
Ca	3,000.00	P	1,000.00
Na	2,500.00	K	1,000.00
Fe	2,500.00	S	1,000.00
C	2,000.00	Mo	20.00
Al	1,000.00	Ti	20.00

10.7.1. Interference checks are required at the beginning of each sequence. Although there is no specific action required for interferences, where

interference is determined to be present, the analyst should document same and determine if sample data has been affected.

10.8. The quality control sample is the Initial Calibration Verification (ICV) solution which must be prepared in the same acid matrix as the calibration standards in accordance with the instructions provided by the supplier. The ICV must be from a source different from those used in the standards for instrument calibration.

10.9. ►***All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. The following are the sample collection, preservation, containers, and associated holding times for metals analysis by ICP/MS.

Matrix	Parameter	Container	Preservative	Holding Time
Aqueous	Total Metals	P/G, 250mL	pH<2, HNO_3	6 months
Aqueous	Dissolved Metals	P/G, 250mL	pH<2, HNO_3 Note 1	6 months
Solid/Waste	Total Metals	G, 4 oz.	T ≤ 4°C	6 months

Note 1: For dissolved metals, the sample should be field filtered using a 0.45µ filter and immediately preserved after filtration.

11.2. ►***Samples should be maintained in a chilled state (≤ 4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).***

11.3. ►***Upon receipt, the samples are stored in a 0–6°C cooler.***

11.4. Aqueous Sample Preparation

11.4.1. This procedure is used to determine the total (acid leachable) amount of the element in the sample. This digestion procedure is used in the preparation of aqueous samples and wastes that contain suspended solids for analysis by ICP/MS for the elements specified in Section 3.1.

11.4.2. Reference Calscience SOP-M221 (EPA 3020A).

11.5. Soil/Sediment/Sludge Sample Preparation

11.5.1. This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by ICP/MS for the following elements:

Aluminum	Lead
Antimony	Magnesium
Arsenic	Manganese
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium
Calcium	Silver

Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc

11.5.2. Reference Calscience SOP-M222 (EPA 3050B).

11.5.3. Soil sample extracts must be diluted 1:10 with reagent water prior to analysis.

12. QUALITY CONTROL

12.1. Instrument Detection Limits (IDL's) (in µg/L) shall be determined quarterly. IDLs are determined by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution each target analyte in reagent water at a concentration of 3 - 25 times the expected IDL) with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally employed between the analysis of separate samples.) IDL's must be determined and reported for each equation used in the analysis of the samples. An IDL must exist, which at a minimum meets the reporting limit for each analyte. Other elemental equations may be used for quantitation, provided that an explanation regarding the use of the equation is stipulated by the laboratory. For example, if quantitation for arsenic is normally performed using one equation, but the equation cannot provide correction for an interferant which occurs in a given sample, an alternate equation may be used which does correct for the interferant, provided that the CCB and CCV criteria have been met.

12.2. The sample concentration is not to be corrected for the reagent blank value. The results of the reagent blank are to be less than the reporting limit. If it is not, all samples associated with the blank with an analyte concentration less than 10 times the blank concentration and above the IDL, must be re-digested and re-analyzed for that element.

12.3. The intensities of all internal standards must be monitored for every analysis. When the intensity of an internal standard fails to fall between 30 and 120 percent of the intensity of that internal standard in the initial calibration standard the following procedure is followed. The sample must be diluted fivefold (1+4) and re-analyzed with the addition of appropriate amounts of internal standard. This procedure must be repeated until the internal standard intensity falls within the prescribed window. The intensity levels of the internal standards for the CCB and CCV must agree within ±20% of the intensity level of the internal standard of the original calibration solution. If they do not agree within this limit, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and re-analyze the affected samples.

12.3.1. Alternately, if the reason for the internal standard intensity falling outside the acceptance window is instrumental drift, then the analysis must be terminated, the problem corrected, the instrument re-calibrated, and the affected samples rerun.

12.3.2. Records of the monitoring the internal standards intensities (ISIs) must be documented and maintained in the ICP/MS ISI log book. It is used to monitor the overall internal standard intensities of each sample by comparing the sample internal standard intensity to the internal standard intensity when calibration was performed. This is determined by calculating the percent relative internal standard intensity (%RI) as follows:

$$\%RI = (In/Io) \times 100$$

where,

I_n = internal standard intensity of the sample
I_o = internal standard intensity of the calibration blank

12.4. To obtain analyte data of known quality, it is necessary to measure for more than the analytes of interest in order to know the required interference corrections. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are below the levels that show an effect on the analyte level, uncorrected equations may be used provided that all QC criteria are met. To verify that interference sources do not affect the reported analyte levels, the interference sources must be monitored and documented. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interference. The monitored masses must include those elements whose oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions which could impact the analytes of interest. As a minimum the masses identified in Section 8.8 which are boldfaced and underlined, must be monitored and documented. When an interference source is present, the sample target analytes impacted must be qualified to indicate the presence of an interference for the analyte of interest.

12.5. If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of 100 or 20 above the reagent blank concentration or reporting limit, respectively), an analysis of a fivefold dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected. One serial dilution must be analyzed for each twenty samples or less of each matrix in a batch. Samples identified as Field Blanks cannot be used for serial dilution analysis.

12.6. A post digestion spike addition added following digestion of a sample of each matrix must be recovered to within 75% to 125% (or, if less, within the laboratory statistically derived limits) of the established value.

12.7. To verify linearity near the reporting limit for ICP/MS analysis, a standard at two times the reporting limit must be analyzed. A RL standard is not required for Al, Ba, Ca, Fe, Mg, Na, and K.

12.8. Laboratory Control Sample Analysis

12.8.1. A Laboratory Control Sample (LCS) analysis must be prepared for each analyte using the same sample preparations, analytical methods and QC procedures employed for the actual samples. The aqueous LCS solution is

the ICV solution. One aqueous LCS must be prepared for each batch of 20 samples or less.

12.8.2. A LCS analysis must be prepared for each analyte using the same sample preparations, analytical methods and QC procedures employed for the actual samples. The solid LCS solution is the ICV solution. One solid LCS must be prepared for each 20 samples or less in a batch.

12.9. Each analytical run must specify the concentration beyond which results cannot be reported without dilution of the analytical sample. The reported concentration may either be the most concentrated standard used during calibration or a linear range verification check standard which was analyzed during the course of the analytical run. If a linear range verification check standard is used, the analytical determined concentration of the standard must be within ± 10% of the true value.

12.10. Check the instrument calibration by analyzing appropriate quality control solutions as follows:

12.10.1. Check instrument calibration using a calibration blank (described in Section 10.5.1.) and the Initial Calibration Verification (ICV) solution (described in Section 10.8.).

12.10.2. Verify calibration at a frequency of 10% which means once every 10 analytical samples using the CCV solution (described in Section 10.6.) and the Continuing Calibration Blank (CCB) solution (described in Section 10.5.1.). These solutions must also be analyzed for each analyte at the beginning of the run and after the last analytical sample.

12.10.2.1. The results of the ICV and CCV solutions must agree within ± 10% of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be reanalyzed or reported with qualification.

12.10.2.2. The results of the calibration blank must be less than the RL or 3 times the IDL for each element. If they are not, terminate the analysis, correct the problem, recalibrate, and reanalyze all samples. Any samples analyzed under an out-of-control calibration must be reanalyzed or reported with qualification. If the concentration of the calibration blank is consistently greater that 3 times the IDL, the IDL may be indicative of an estimated IDL and should be re-evaluated.

12.10.3. Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of each run or once every twelve hours, whichever is more frequent. Do this by analyzing the Interferants A (CL-INT-A1) solution. The results of the interference check solution analysis must not exceed ± the RL.

12.11. Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 20 samples.

12.11.1. The relative percent difference between duplicate determinations is calculated as follows:

$$RPD = [(|D1-D2|) / \{(D1+D2) / 2\}] \times 100$$

where:

RPD = relative percent difference.

D_1 = first sample value.

D_2 = second sample value (duplicate)

A control limit of 20% RPD should not be exceeded for sample values greater than or equal to 5 or 100 times the RL or IDL, respectively. If this limit is exceeded, the reason for the out-of-control situation must be determined, corrected, and any samples analyzed during the out-of-control condition must be re-analyzed.

12.12. When considering all of the aforementioned quality assurance requirements, the following run sequence becomes apparent from an operational point of view. The runs listed are to take place after instrument initialization and warm up.

Run 1:	Perform mass calibration
Run 2:	Perform resolution check
Run 3:	Validate tuning criteria
Run 4:	Calibration blank
Run 5:	Calibration standard 1
Run 6:	
Run 7:	
Run 8:	Calibration standard n
Run 9:	ICV 1
Run 10:	ICV 2
Run 11:	ICV 3
Run 12:	ICV 4
Run 13:	Initial calibration blank
Run 14:	
Run 15:	
Run 16:	CCV1
Run 17:	CCB1
Run 18:	ICS A or at end before last ccv
Run 19:	ICS AB or at end before last ccv
Run 20:	CRDL
Run 21:	Aqueous or soil preparation blank
Run 22:	Aqueous or soil LCS
Run 23:	sample n
Run 24:	sample n duplicate
Run 25:	sample n serial dilution
Run 26:	sample n spike
Run 27:	sample n + 1
Run 28:	CCV2
Run 29:	CCB2
Run 30:	sample n + 2
Run 31:	sample n + 3
Run 32:	sample n + 4
Run 33:	sample n + 5
Run 34:	sample n + 6
Run 35:	sample n + 7

Run 36:	sample n + 8
Run 37:	sample n + 9
Run 38:	sample n + 10
Run 39:	sample n + 11
Run 40:	CCV3
Run 41:	CCB3
Run 42:	return to running samples (see sample n + 2)
Run 43:	CRDL (completion of run sequence)
Run 44:	CCV n
Run 45:	CCB n

13. CALIBRATION AND STANDARDIZATION

13.1. Calibrate the instrument for the analytes of interest using the calibration blank and at least a single standard (described in Section 10.4.) according to the manufacturer's recommended procedure for each detector configuration which will be used in analysis. Flush the system with the rinse blank (described in Section 10.5.3.) between each standard solution. Report each integration during the calibration and sample analysis and use the average of the multiple integrations for both standardization and sample analysis. A minimum of three replicate integrations are required for both calibration and sample analysis.

13.2. Some elements (such as Hg, W, and Mo) require extended flushing times which need to be determined. Run the Memory Test (described in Section 7.4.) on the solution in to verify that memory problems will not affect the data quality.

13.3. As a minimum, masses which would affect data quality must be monitored to determine potential effects from matrix components on the analyte peaks. This information will be used to assess data quality and as a minimum must include the following masses which are bold-faced and underlined. Monitoring and reporting of this data is required. Aside from the masses which are required to be monitored (boldfaced and underlined), it is strongly recommended that the other masses be monitored to indicate other potential molecular interferences which could affect the data quality. When an interference source is present, the sample data impacted must be qualified to indicate the presence of an interference of the analyte of interest. The masses associated with the italicized elements are not required to be monitored if the element is not used as an internal standard.

14. PROCEDURE

14.1. Solubilization and digestion procedures are presented in Sections 11.2. and 11.3.

14.2. Initiate appropriate operating configuration of the instrument and data system.

14.3. Set up the instrument with the proper operating parameters established in Section 9.2. Allow at least 45 minutes for the instrument to equilibrate before analyzing any samples. Acceptable instrument conditions must be verified by analyzing the tuning solution and obtaining at least four integrations with relative standard deviations not exceeding 5% (≤ 5%) for the analytes contained in the tuning solution.

14.4. Conduct mass calibration and resolution checks using the tuning solution which contains 10µg/mL each of Ba, Be, Ce, Co, ^{7}Li, Mg, Pb, Rh, Tl, U, Y and In. The ion abundance criteria found below are recommendations which might be helpful when setting up the instrument, but are not required criteria. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed under this contract. If the mass calibration exceeds a difference of more than 0.1amu from the true value, then the mass calibration must be adjusted to the correct values. The resolution must also be verified to be less than 0.9amu full width at 10 percent peak height. The tuning solution must be analyzed at the beginning of each run prior to calibration and after the mass calibration and resolution checks are performed.

14.4.1. The tuning acceptance criteria are given below:

Note: It has been shown that 0.65 amu at 10% peak height is equivalent to 0.75 amu peak height at 5% peak height.

Run X-Y adjustment, to get the maximum intensity. (Use 10 ppb tuning solution.)

Run Nebulizer gas flow optimization to get the maximum intensity.(Use 10ppb tuning solution.)

Run Lens Voltage Optimization. (Use 10 ppb tuning solution.)

Run Auto Lens Optimization. (Use 10 ppb tuning solution.)

Run Cross Calibrate Dual Detectors. (Use 200 ppb standard.)

Run daily performance check using 10 ppb tuning standard.

A) Check background at Mass 220. Intensity<=2 cps.

B) Check sensitivity:

Mg ≥ 3000cps / 1ppb

Rh ≥ 15000cps / 1ppb

In ≥ 15000cps / 1ppb

U ≥ 15000cps / 1ppb

C) Check Doubly Charge and Oxide:

Ba^{2+}/Ba < 3%, CeO/Ce < 3%

D) Check RSD: RSD ≤ 5%

If the performance check is satisfactory, the instrument is ready to start analyses.

If the performance check is not satisfactory, redo Nebulizer gas flow optimization for Doubly Charge and Oxide, and redo calibrate Autolens. Then rerun daily performance check, if still unsatisfactory, refer ICP-MS Software Guide pp 4-23, Complete Optimization Flowchart.

Mass	Element of Interest

27	Aluminum
121, 123	Antimony
75	Arsenic
130, 132, 134, 135, 136, 137, 138	Barium
9	Beryllium
106, 108, 110, 111, 112, 113, 114, 116	Cadmium
42, 43, 44, 46, 48	Calcium
50, 52, 53, 54	Chromium
59	Cobalt
63, 65	Copper
54, 56, 57, 58	Iron
204, 206, 207, 208	Lead
24, 25, 26	Magnesium
55	Manganese
199, 200, 199, 202	Mercury
58, 60, 61, 62, 64	Nickel
39	Potassium
74, 76, 77, 78, 80, 82	Selenium
107, 109	Silver
23	Sodium
203, 205	Thallium
50, 51	Vanadium
64, 66, 67, 68, 70	Zinc
83	Krypton
72	Germanium
139	Lanthanum
140	Derium
129	Xenon
118	Tin
105	Palladium
47, 49	Titanium
Mass	**Element of Interest (Cont.)**
125	Tellurium
69	Gallium
35, 37	Chlorine
92, 94, 96, 97, 98	Molybdenum
6, 7	*Lithium*
45	*Scandium*
89	*Yttrium*
103	*Thorium*
115	*Indium*
159	*Terbium*
165	*Holmium*
210	*Bismuth*

14.5. Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the Initial Calibration Verification (ICV) solution. When measurements exceed ± 10% of the accepted value the analysis must be terminated, the problem corrected, the instrument re-calibrated, and the initial calibration re-verified. Any samples analyzed under an out-of-control calibration must be re-analyzed.

14.5.1. During the course of an analytical run, the instrument may be "resloped" or re-calibrated to correct for instrument drift. The re-calibration may only be performed after the successful analysis of a CCV or CCB. The re-calibration then must be followed immediately by a new analysis of a CCV and CCB before any further samples may be analyzed. Any samples analyzed under an out-of-control CCV and CCB must be re-analyzed.

14.6. ►Flush the system with the rinse blank solution (described in Section 10.5.3.) for at least 30* seconds (or until the signal levels return to the method's levels of quantitation) before the analysis of each sample. Aspirate each sample for at least 30 seconds before collecting data. Analyze the CCV (described in Section 10.6.) and the CCB (described in Section 10.5.1.) at a frequency of 10%. A frequency of 10% means once every 10 analytical samples.

14.6.1. ►***For instruments equipped with a Fast Autosampler System, the rinse time is at least 12 seconds, not 30.***

14.6.2. Calibration blanks (ICB/CCB) and calibration verification (ICV/CCV) solutions are not counted as analytical samples when determining the 10% frequency.

14.7. ►***Dilute all solid samples digested using EPA method 3050B by a factor of 20x before analyzing on the ICP-MS.***

14.7.1. ***Measure 9.5mL nano-pure water into a test tube, add 0.5mL sample digestate and mix.***

14.8. Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate less-abundant isotope for which quality control data has already been established and exhibits linear response at the concentration involved. No analyte may be reported from an analysis of a diluted sample, in which the analyte concentration is less than 5% of the linear dynamic range or less than 5 times the IDL, whichever is lower. For practical purposes the analysis of solutions which contain concentrations of analytes at levels higher than the linear range standard may be analyzed by either dilution, or adjustment of the mass spectrometer or detector to reduce sensitivity for the analytes. If the sensitivity of the mass spectrometer or detector is reduced, than all QC criteria must be met under the reduced sensitivity instrument operating conditions.

15. CALCULATIONS

15.1. Appropriate concentration units must be specified on the required forms. The quantitative values shall normally be reported in units of micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values. Analytical results must be reported to two significant figures if the resulting value is less than 10 and to three significant figures if the value is greater than or equal to 10.

15.2. If appropriate, or required, calculate results for solids on a dry-weight basis as follows:

15.2.1. A separate determination of percent solids must be performed.

15.2.2. The concentrations determined in the digest are to be reported on the basis of the dry weigh of the sample.

Conc (dry weight)(mg/kg) = (C × V) / ((W × S)

where,

C = Digest Concentration (mg/L)

V = Final Volume in liters post sample preparation

W = Weight in kg of wet sample

S = %Solids / 100

15.2.3. Calculations should include appropriate interference corrections, internal standard normalizations, and the summation of signals at 206, 207, 208 m/z for lead (to compensate for any difference in the abundances of these isotopes between samples and standards.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The upper and lower acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S. All LCS/LCSD compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, the problem must be identified and corrected.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.2.3. If methylene chloride is found in the MB, no positive sample results should be reported unless the concentration of the compound in the sample exceeds 10 times the MB level. Report the data with qualification indicating the analyte was present in the corresponding MB.

18.3. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The upper and lower acceptance limits for each surrogate spike compound is based upon the historical average recovery ± 3S.

18.3.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

18.3.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.3. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.3.1. Check the internal standard and surrogate spiking solutions for degradation and contamination.

18.3.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample or extract should be re-analyzed.

18.3.3.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and/or re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-extracted and re-analyzed.

18.3.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSDs are as follows:

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically causes unacceptable % REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L(ppb) for water samples and µg/kg(ppb) for oil, soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly

documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set is then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries are subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries an MS/MSD data set is does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical

batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. REFERENCES

22.1. Method 6020: Inductively Coupled Plasma - Mass Spectrometry, Test Method for Evaluating Solid Waste. Volume 1A, November 1986, SW-846, Third Edition, Revision 0, September 1994.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Metals Quality Control Tables.

23.2. ►***Appendix B: Additional Quality Control Criteria for Department of Defense Projects.***

24. ►*MODIFICATIONS*

24.1. ***None.***

25. ►*REVISION HISTORY*

Revision	Description	Author	Effective Date
4.2	Section 6: Update definitions. Section 9: Update equipment. Section 10: Update standards. Section 11: Update sample storage. Section 14: Update procedure. Section 23: Add Appendix B. Section 24: Add Modification section. Section 25: Add Revision History section.	K. Burney	

Appendix A

METALS QUALITY CONTROL TABLES

Calscience Environmental Laboratories, Inc.

EPA METHOD 7000A: METALS BY FLAME, GRAPHITE FURNACE AAS AND FIMS

The following parameters shall apply for all routine methods referencing the QC section of EPA Method 7000A.
These requirements shall be superseded by the project QAPP or may be subordinate to other established project-specific requirements should they exist.

QC SAMPLES	FREQUENCY	CRITERIA
INITIAL CALIBRATION VERIFICATION (ICV)	Analyze after ICAL.	ICV (prepared from an independent source) must recovery within 90-110%R. If not, correct problem, recalibrate and re-verify.
INITIAL CALIBRATION BLANK (ICB)	Analyze after ICV.	No contaminants should be detected in the blanks. Source method does not specify criteria. For handling of unsuitable blanks, refer to SOP-T020, Internal Quality Control Checks.
CONTINUING CALIBRATION VERIFICATION (CCV)	Analyze after every 10 sample injections, and at the end of the analytical run.	CCV must recovery within 80-120%R. If unacceptable, reanalyze all samples following the most previous acceptable CCV.
METHOD BLANK (MB)	1 per batch prepared of similar matrix not to exceed 20 samples.	No contaminants should be detected in the blanks. Source method does not specify criteria. For handling of unsuitable blanks, refer to SOP-T020, Internal Quality Control Checks.
MATRIX SPIKE /DUPLICATE (MS/MSD)	1 set per batch of similar matrix not to exceed 20 samples. Open batch shall not exceed ***24 hours***.	Spike recovery (%R) must be within established acceptance limits. If not, LCS %R must be evaluated. If sample concentration exceeds spike concentration by a factor of 4 or more, recovery limits do not apply and data should be qualified as such. The relative percent difference (RPD) must be within established acceptance limits. If not, LCS/LCSD RPD must be evaluated.
LAB CONTROL SAMPLE /DUPLICATE (LCS/LCSD)	1 set per batch prepared of similar matrix not to exceed 20 samples.	Evaluate and report when MS/MSD parameters are unacceptable. %R's and RPD must be within established acceptance limits.
POST DIGESTION SPIKE (PDS)	1 per matrix per analytical run.	PDS should be prepared at 2 to 5 times the original concentration. If all samples are below the detection limit, spike the selected sample at approximately 20 times the detection limit. If PDS recovery is less than 85% or greater than 115%, a diluted analysis may be used if it agrees within ± 10% with the original determination. If unacceptable, a matrix effect should be suspected and MSA performed on all samples within the batch.

EPA METHOD 6010B: METALS BY ICP-AES

These requirements shall be superseded by the project QAPP or may be subordinate to other established project-specific requirements should they exist.

QC SAMPLES	FREQUENCY	CRITERIA
INITIAL CALIBRATION VERIFICATION (ICV)	Analyze after ICAL.	ICV (prepared from an independent source) must recovery within 90-110%R. If not, correct problem, recalibrate and re-verify.
INITIAL CALIBRATION BLANK (ICB)	Analyze after ICV.	Result of ICB is to agree within 3 standard deviations (*s*) of the mean blank value. If not, repeat analysis two more times and average results. If average is not within 3*s*, correct problem and recalibrate.
HIGH CALIBRATION STANDARD REANALYSIS	Analyze before beginning the sample run.	Reanalysis of the highest mixed calibration standard as a sample should recover within 95-105%. If not, follow the recommendations of the instrument manufacturer to correct for this condition.
INTERFERENCE CHECK SAMPLE (ICS)	Analyze at the beginning and end of analytical run or twice every 8-hour work shift, whichever is more frequent.	ICS should recover within 80-120%R. If not, correct problem and recalibrate or refer to the actions specified in the USEPA Functional Guidelines for Evaluating Inorganic Analyses for appropriate data qualification.
CONTINUING CALIBRATION VERIFICATION (CCV)	Analyze after every 10 sample injections, and at the end of the analytical run.	CCV must recovery within 90-110%R. If not, correct problem and reanalyze all samples following the most previous acceptable CCV.
CONTINUING CALIBRATION BLANK (CCB)	Analyze after every 10 sample injections, and at the end of the analytical run.	Results of CCB's are to agree within 3 standard deviations (*s*) of the mean blank value. If not, repeat analysis two more times and average results. If average is not within 3*s*, terminate analysis, correct problem, recalibrate and reanalyze samples following the most previous acceptable calibration blank.
METHOD BLANK (MB)	1 per batch prepared of similar matrix not to exceed 20 samples.	No contaminants should be detected in the blanks. Source method does not specify criteria. For handling of unsuitable blanks, refer to SOP-T020, Internal Quality Control Checks.
MATRIX SPIKE /DUPLICATE (MS/MSD)	1 set per batch of similar matrix not to exceed 20 samples. Open batch shall not exceed ***24 hours***.	Spike recovery (%R) must be within 80-120%. If not, LCS %R must be evaluated. If sample concentration exceeds spike concentration by a factor of 4 or more, recovery limits do not apply and data should be qualified as such. The relative percent difference (RPD) must be within 0-20 for aqueous samples and 0-35 for soil/solids. If not, LCS/LCSD RPD must be evaluated.
LAB CONTROL SAMPLE /DUPLICATE (LCS/LCSD)	1 set per batch prepared of similar matrix not to exceed 20 samples.	Evaluate and report when MS/MSD parameters are unacceptable. %R's and RPD must be within the same limits established for the MS/MSD.
POST DIGESTION SPIKE (PDS)	When a new or unusual sample matrix is encountered.	If PDS at 10 to 100 times the IDL is not within 75-125%R, a diluted analysis may be used if it agrees within ±10% with the original determination. If unacceptable, a matrix effect should be suspected and MSA performed on all samples within the batch.

EPA METHOD 6020: METALS BY ICP-MS

These requirements shall be superseded by the project QAPP or may be subordinate to other established project-specific requirements should they exist.

QC SAMPLES	FREQUENCY	CRITERIA
TUNING SOLUTION	Analyze prior to calibration.	At least 4 integrations with a RSD ≤ 5% for the analytes contained in the tuning solution.
INITIAL CALIBRATION VERIFICATION (ICV)	Analyze after ICAL.	ICV (prepared from an independent source) must recovery within 90-110%R. If not, correct problem, recalibrate and re-verify.
DETECTION LIMIT SAMPLE	Analyze prior to samples.	Must recover within 50-150% of true value. If not, correct problem, recalibrate and re-verify.
INTERFERENCE CHECK SAMPLE (ICS)	Analyze at the beginning.	ICS should recover within established limits. If not, correct problem and recalibrate or refer to the actions specified in the USEPA Functional Guidelines for Evaluating Inorganic Analyses for appropriate data qualification.
INTERNAL STANDARDS (IS)	Every sample analysis.	Intensities of all IS's must fall within 30 to 120% of that IS in the initial calibration. If not, the sample must be diluted fivefold (1+4) and reanalyzed with addition of appropriate amounts of IS. Repeat until IS intensities fall within prescribed window.
	Every CCB and CCV analysis.	Intensities of all IS's must fall within 80 to 120% of that IS in the initial calibration. If not, terminate analysis, correct problem, recalibrate, verify new calibration, and reanalyze affected samples since most previous acceptable run.
CONTINUING CALIBRATION BLANK (CCB)	Analyze after every 10 samples, and at the end of the analytical run.	Result of CCB must be less than 3 times the IDL for each element. If not, correct problem and reanalyze all samples following the most previous acceptable CCB. Also see IS criteria.
CONTINUING CALIBRATION VERIFICATION (CCV)	Analyze after every 10 samples, and at the end of the analytical run.	CCV must recovery within 90-110%R. If not, correct problem and reanalyze all samples following the most previous acceptable CCV. Also see IS criteria.
REAGENT BLANK (RB)	1 per batch prepared of similar matrix not to exceed 20 samples.	Results of RB are to be less than the reporting limit. If it is not, all samples associated with the blank with an analyte concentration less than 10 times the blank concentration and above the IDL, must be re-digested and re-analyzed for that analyte.
SAMPLE DUPLICATE	1 per batch prepared of similar matrix not to exceed 20 samples.	The relative percent difference (RPD) must be within 0-20 for aqueous samples and 0-35 for soil/solids. If this limit is exceeded, the reason for the out-of-control situation must be determined, corrected, and any affected samples re-analyzed.
LAB CONTROL SAMPLE (LCS)	1 per batch prepared of similar matrix not to exceed 20 samples.	Spike recovery (%R) must be within 80-120%.
POST DIGESTION SPIKE (PDS)	1 per matrix per analytical run.	If PDS is not within 75-125%R, a diluted analysis may be used if it agrees within ± 10% with the original determination. If unacceptable, a matrix effect should be suspected and MSA performed on all samples within the batch.

EPA METHOD 200.8: METALS BY ICP-MS

These requirements shall be superseded by the project QAPP or may be subordinate to other established project-specific requirements should they exist.

QC SAMPLES	FREQUENCY	CRITERIA
TUNING SOLUTION	Analyze prior to calibration.	At least 5 integrations with a RSD ≤ 5% for the analytes contained in the tuning solution.
INITIAL CALIBRATION VERIFICATION (ICV)	Analyze after ICAL.	ICV (prepared from an independent source) must recovery within 90-110%R. If not, correct problem, recalibrate and re-verify.
DETECTION LIMIT SAMPLE	Analyze prior to samples.	None required.
INTERFERENCE CHECK SAMPLE (ICS)	Analyze at the beginning.	ICS should recover within established limits. If not, correct problem and recalibrate or refer to the actions specified in the USEPA Functional Guidelines for Evaluating Inorganic Analyses for appropriate data qualification.
INTERNAL STANDARDS (IS)	Every sample analysis.	Intensities of all IS's must fall within 60 to 125% of that IS in the initial calibration. If not, the sample must be diluted twofold (1+1) and reanalyzed with addition of appropriate amounts of IS. Repeat until IS intensities fall within prescribed window.
	Every CCB and CCV analysis.	Intensities of all IS's must fall within 60 to 125% of that IS in the initial calibration. If not, terminate analysis, correct problem, recalibrate, verify new calibration, and reanalyze affected samples since most previous acceptable run.
CONTINUING CALIBRATION BLANK (CCB)	Analyze after every 10 samples, and at the end of the analytical run.	Result of CCB must be less than the RL for each element. If not, correct problem and reanalyze all samples following the most previous acceptable CCB. Also see IS criteria.
CONTINUING CALIBRATION VERIFICATION (CCV)	Analyze after every 10 samples, and at the end of the analytical run.	CCV must recovery within 90-110%R. If not, correct problem and reanalyze all samples which are outside of 85-115% following the most previous acceptable CCV. Also see IS criteria.
REAGENT BLANK (RB)	1 per batch prepared of similar matrix not to exceed 20 samples.	Results of RB are to be less than the reporting limit. If it is not, all samples associated with the blank with an analyte concentration less than 10 times the blank concentration and above the IDL, must be re-digested and re-analyzed for that analyte.
SAMPLE DUPLICATE	1 per batch prepared of similar matrix not to exceed 20 samples.	The relative percent difference (RPD) must be within 0-20 for aqueous samples and 0-35 for soil/solids. If this limit is exceeded, the reason for the out-of-control situation must be determined, corrected, and any affected samples re-analyzed.
LAB CONTROL SAMPLE (LCS)	1 per batch prepared of similar matrix not to exceed 20 samples.	Spike recovery (%R) must be within 85-115%.
POST DIGESTION SPIKE (PDS)	1 per matrix per analytical run.	If PDS is not within 75-125%R, a diluted analysis may be used if it agrees within ±10% with the original determination. If unacceptable, a matrix effect should be suspected and MSA performed on all samples within the batch.

▶*Appendix B*

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECTS

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 6020, Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) – Additional Quality Control Criteria for Department of Defense (DoD) Projects.

2. DETECTION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Method Detection Limit (MDL)

5.1.1. MDL study shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, or when a change in instrumentation that affects the sensitivity of the analysis.

5.1.2. MDL verification must be performed immediately following an MDL study and quarterly thereafter.

5.1.2.1. MDL verification sample shall be prepared by spiking an appropriate matrix at approximately 2–3 times the detection limit for single-analyte test, or 1–4 times the detection limit for multiple-analyte test.

5.1.2.2. MDL verification is deemed valid if the apparent signal to noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the MDL study and verification at a higher concentration. Set the MDL at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive MDL verifications at a higher concentration. Set the MDL at the higher concentration.

5.1.3. No samples shall be analyzed without a valid MDL.

5.2. Initial Calibration Blank (ICB)

5.2.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > MDL.

5.2.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and reanalyze the ICB.

5.3. Continuing Calibration Verification (CCV)

5.3.1. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.4. Continuing Calibration Blank (CCB)

5.4.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > MDL.

5.4.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and reanalyze the CCB. Reanalyze all samples since the last acceptable calibration blank.

5.4.2.1. The results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the CCB.

5.5. Event Based Quality Control (LCS/LCSDs and MBs)

5.5.1. Laboratory Control Samples (LCS/LCSDs)

5.5.1.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.5.1.1.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.5.1.1.2. The current in-house lower and upper acceptance limits for %REC of each LCS/LCSD element in aqueous matrix are 70% and 130%, respectively.

5.5.1.2. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.5.2. Method Blanks (MBs)

5.5.2.1. The MB is considered to be contaminated if one of the following conditions is met.

5.5.2.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.2.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.2.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.5.2.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the MDL.

5.5.2.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.6. Matrix Based Quality Control (MS/MSDs)

5.6.1. Matrix Spikes (MS/MSDs)

5.6.1.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.1.1.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.6.1.1.2. The current in-house lower and upper acceptance limits for %REC of each MS/MSD element in aqueous matrix are 50% and 150%, respectively. The RPD is ≤ 30%.

5.6.1.2. No marginal exceedance is allowed for any project-specific analyte of concern.

6. PROCEDURE

6.1. After instrument initialization and warm up, standard and sample vessels are loaded in the following or other logical order:.

Run 1:	Perform mass calibration
Run 2:	Perform resolution check
Run 3:	Validate tuning criteria
Run 4:	Calibration blank
Run 5:	Calibration standard 1

Run 6:	
Run 7:	
Run 8:	Calibration standard n
Run 9:	ICV 1
Run 10:	ICV 2
Run 11:	ICV 3
Run 12:	ICV 4
Run 13:	Initial calibration blank
Run 14:	
Run 15:	
Run 16:	CCV1
Run 17:	CCB1
Run 18:	ICS A or at end before last ccv
Run 19:	ICS AB or at end before last ccv
Run 20:	CRDL
Run 21:	Aqueous or soil preparation blank
Run 22:	Aqueous or soil LCS
Run 23:	sample n
Run 24:	sample n duplicate
Run 25:	sample n serial dilution
Run 26:	sample n spike
Run 27:	sample n + 1
Run 28:	CCV2
Run 29:	CCB2
Run 30:	sample n + 2
Run 31:	sample n + 3
Run 32:	sample n + 4
Run 33:	sample n + 5
Run 34:	sample n + 6
Run 35:	sample n + 7
Run 36:	sample n + 8
Run 37:	sample n + 9
Run 38:	sample n + 10
Run 39:	sample n + 11
Run 40:	CCV3
Run 41:	CCB3
Run 42:	return to running samples (see sample n + 2)
Run 43:	CRDL (completion of run sequence)
Run 44:	CCV n
Run 45:	CCB n

6.1.1. Run 26: The MS is the actual sample matrix spiked with known concentration of specific target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.1.1.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.1.2. Run 27: The MSD (if done) is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD (or sample plus a sample duplicate) can be used to assess the precision of the analytical

measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Title : **EPA METHOD 7470A, MERCURY IN LIQUID WASTE (COLD-VAPOR TECHNIQUE)**

Document No. : SOP-M619
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Revision 3.0 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 08/08/13
MANAGEMENT **DATE**

_____ 08-08-13
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 7470A, Mercury in Liquid Waste (Cold-Vapor Technique).

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous wastes, ground waters, and mobility-procedure extracts.

3. DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for this method are as follows:

	Aqueous
Mercury	0.50 µg/L
Lower-QL Mercury	0.05 µg/L

3.2. The EQLs will be proportionally higher for samples which require dilution.

3.3. The EQLs will be proportionally lower or higher for samples which require mobility extraction.

3.4. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices.

4. SCOPE AND APPLICATION

4.1. EPA Method 7470A is a cold-vapor atomic absorption procedure for determining the concentration of mercury (Hg). All samples must be subjected to an appropriate dissolution step prior to analysis.

4.1.1. The method can also be used for analyzing certain solid and sludge-type wastes; however, EPA Method 7471B is usually the method of choice for these waste types.

4.2. This method is restricted to use by or under the supervision of analysts experienced in the use of atomic absorption spectrometer, skilled in the interpretation of atomic absorption spectra, and knowledgeable in the correction of interferences described in this method.

5. METHOD SUMMARY

5.1. Cold-vapor atomic absorption (CVAA) technique is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrometer. Absorbance (peak height) is measured as a function of mercury concentration.

5.2. Prior to analysis, the appropriate sample preparation procedure (Appendix A) must be performed on each sample.

5.2.1. Aqueous samples are digested with acids.

5.2.2. Aqueous and solid samples for waste characteristic analysis are prepared via the appropriate mobility extraction method, and the resulting mobility-procedure extracts (leachates) are digested with acids.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client specific QAPP guidance overrides this directive to a lesser time period or the method specific SOP provides a different time period, but in no case to exceed 24 hours***. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.

6.12. Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a

product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.27. Terms Specific to Mercury Analysis

6.27.1. Contract Required Quantitation Limit (CRQL): Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

6.27.2. Dissolved Mercury: The concentration of mercury determined in a filtered sample following digestion with acids.

6.27.3. Lower Limit of Quantitation (LLOQ): The lowest point of quantitation, or in most cases, the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels based on the stated project requirements. Analysis of a standard prepared at the LLOQ concentration level or use of the LLOQ as the lowest point calibration standard provides confirmation of the established quantitation sensitivity of the method.

6.27.4. Method of Standard Addition (MSA): An alternative calibration procedure employed when the signal response of the analyte of interest is different in a particular matrix than when it is in reagent water. The standard addition technique involves the addition of known amounts of the target analyte to

each of a series of replicate sample aliquots. The final concentrations of the sample replicates should span the calibration range of the method. The analytical response versus the standard addition concentration for each of the replicates is plotted. After performing a linear regression, the curve is extrapolated to the x-axis. The analyte concentration in the original unspiked sample is equal to the inverse of the x-intercept.

6.27.5. Post Digestion (Matrix) Spike: A sample which has been extracted in the same manner as the other samples, but to which a known amount of target analytes has been added to the sample extractant. Post digestion spikes are used to evaluate the accuracy of the method without the losses incurred through the extraction process.

6.27.6. Sensitivity: The ability of an analytical technique or instrument to discriminate between small differences in analyte concentration. For atomic absorption, the concentration of metal, in mg/L, that produces a transmission of 1% is commonly employed to determine sensitivity.

6.27.7. Total Mercury: The concentration of mercury determined in an unfiltered sample following digestion with acids.

7. INTERFERENCES

7.1. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

7.2. Copper may interfere; however, copper concentrations as high as 10 mg/L has no effect on the recovery of mercury from spiked samples.

7.3. Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) due to the fact that during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm.

7.3.1. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent (25 mL).

7.4. Certain volatile organic materials that absorb at the wavelength of 253.7 nm may also cause interference.

7.4.1. A preliminary run without reagents may be used to determine whether this type of interference is present.

8. SAFETY

8.1. Acids are corrosive. Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of acids and mercury standards.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Atomic Absorption Spectrometer: PerkinElmer Flow Injection Mercury System (FIMS) 400 or equivalent configured with the following components:

9.1.1. *Computer-controlled atomic absorption spectrometer, single-beam optical system, with 254-nm maximum sensitivity.*

9.1.2. *Solar-blind detector.*

9.1.3. Mercury lamp, high intensity, *low pressure.*

9.1.4. Absorption cell, *240-mm × 7-mm OD × 4-mm ID*, quartz.

9.1.5. *Two* peristaltic pumps, *20–120-rpm variable speed, computer controlled.*

9.1.6. *Sample loop, 200-µL.*

9.1.7. Autosampler, PerkinElmer AS-90 Autosampler or equivalent.

9.1.8. Autosampler vessels, *16*-mm *OD* (15-mL capacity), *translucent* polypropylene, *disposable.*

9.1.9. *Autosampler vessels, 30-mm OD (50-mL capacity), with screw caps, translucent polypropylene, disposable.*

9.2. Instrument Software

9.2.1. Requires a PC based data system or equivalent.

9.1.10.9.2.2. PerkinElmer WinLab 32 for AA or equivalent, capable of automatic baseline offset correction.

9.3. Instrument Maintenance and Troubleshooting

9.1.11.9.3.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.1.12.9.3.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.2.9.4. Carrier Gas: Argon, Ar, 99.998%, cryogenic liquid, Praxair Argon Cryogenic Liquid or equivalent.

9.3.9.5. Graduated cylinders, 100-mL or other capacity, glass, Class A.

9.4.9.6. Volumetric flask, 100-mL or other capacity, glass, Class A.

9.5.9.7. Pipetters, 100–1000-µL, 0.5–5.0-mL, and 1–10-mL, calibrated, adjustable, with disposable tip.

9.6.9.8. Refer to Appendix A for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, nano-pure.

10.1.2. Hydrochloric acid, HCl, 32–35% or 34–37% (v/v), concentrated, clear colorless liquid, Fisher Scientific TraceMetal or Optima grade, EMD OmniTrace grade, or equivalent.

10.1.3. Hydrochloric acid, HCl, 3% (v/v).

10.1.3.1. Prepare the 3% HCl solution by slowly adding 60 mL of concentrated HCl to 500 mL of reagent water and dilute to 2 L with additional reagent water.

10.1.3.2. The 3% HCl solution is used as the carrier solution.

10.1.3.3. It is also used as a rinse blank to flush the system between standards and samples to minimize interferences.

10.1.4. Nitric acid, HNO_3, 67–70% (v/v), concentrated, clear colorless to light yellow liquid, Fisher Scientific TraceMetal or Optima grade, EMD OmniTrace grade, or equivalent.

10.1.5. Nitric acid, HNO_3, 1:1 (v/v).

10.1.5.1. Prepare the 1:1 HNO_3 solution by slowly adding 500 mL of concentrated HNO_3 to 400 mL of reagent water and dilute to 1 L with additional reagent water.

10.1.6. Stannous chloride, $SnCl_2$, dihydrate, white crystalline powder, reagent grade or equivalent.

10.1.7. Stannous chloride solution, $SnCl_2 \cdot 2H_2O/HCl$.

10.1.7.1. Prepare the stannous chloride solution by adding 11 g of $SnCl_2 \cdot 2H_2O$ to 1 L of 3% HCl solution.

10.1.7.2. The stannous chloride solution is used as the reducing agent.

10.1.8. Refer to Appendix A for additional reagents.

10.1.9. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Stock Standard Solutions

10.2.1.1. Pre-certified stock standard solutions, 99.990–99.999% source purity, each in sealed polyethylene bottles, containing 1000/100 ppm of mercury are used to prepare calibration and check standards.

10.2.1.2. Prepare each mercury working standard solution by diluting the appropriate volume of the mercury stock standard and 5 mL of concentrated HNO_3 to 100 mL with reagent water.

10.2.1.3. The working standards are prepared as follows:

	Initial		Final	
Analyte	Conc (ppm)	Volume (mL)	Conc (ppm)	Volume (mL)
Hg	1000	0.2	2.0	100

Note: The working standard solution contains 5% (v/v) of HNO_3.

	Initial		Final	
Analyte	Conc (ppm)	Volume (mL)	Conc (ppm)	Volume (mL)
Hg	100	1.0	1.0	100

Note: The working standard solution contains 5% (v/v) of HNO_3.

10.2.1.4. The working standard solutions must be replaced after one month or sooner if comparison with check standards indicates a problem.

10.2.2. Initial Calibration Standard Solutions

10.2.2.1. Measure 0.5 mL of the 2.0-ppm mercury working standard solution and 50 mL of reagent water into a clean digestion tube. Mix thoroughly.

10.2.2.2. Slowly add 2.5 mL of concentrated H_2SO_4 to the digestion tube and mix.

10.2.2.3. Slowly add 1.25 mL of concentrated HNO_3 to the digestion tube and mix.

10.2.2.4. Add 7.5 mL of the 5% $KMnO_4$ solution to the digestion tube, and allow the mixture to stand for at least 15 minutes.

10.2.2.5. Add 4.0 mL of the 5% $K_2S_2O_8$ solution to the digestion tube.

10.2.2.6. Place the digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 hours in the water bath maintained at 95°C.

10.2.2.7. Remove the digestion tube from the block digester and allow the digested standard solution to cool.

10.2.2.8. Add 3 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested standard solution to reduce excess permanganate.

10.2.2.9. Adjust the volume of the digested standard solution to 100 mL with calibration blank to obtain the 10.0-ppb initial calibration standard.

10.2.2.10. Dilute the appropriate volumes of the 10.0-ppb initial calibration standard to 20 mL with calibration blank to obtain other initial calibration standards.

10.2.2.11. Use the following calibration levels as guidance to prepare the initial calibration standards.

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.25	10.0	0.5	20.0
1.0	10.0	2.0	20.0
2.0	10.0	4.0	20.0
5.0	10.0	10.0	20.0
10.0	10.0	20.0	20.0

10.2.2.12. Use the following calibration levels as guidance to prepare the initial calibration standards for lower limit of quantitation.

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.025	10.0	0.05	20.0
0.25	10.0	0.5	20.0
1.0	10.0	2.0	20.0
2.0	10.0	4.0	20.0
5.0	10.0	10.0	20.0
10.0	10.0	20.0	20.0

10.2.2.13. The 2.0-ppb initial calibration standard is also used as the continuing calibration verification solution.

10.2.2.14. The initial calibration standard solutions must be prepared fresh daily.

10.2.3. Calibration Blank (CB)

10.2.3.1. Designate a minimum of five clean digestion tubes for calibration blank preparation.

10.2.3.2. Measure 50 mL of reagent water into each clean digestion tube.

10.2.3.3. Slowly add 2.5 mL of concentrated H_2SO_4 to each digestion tube and mix.

10.2.3.4. Slowly add 1.25 mL of concentrated HNO_3 to each digestion tube and mix.

10.2.3.5. Add 7.5 mL of the 5% $KMnO_4$ solution to each digestion tube, and allow the mixture to stand for at least 15 minutes.

10.2.3.6. Add 4.0 mL of the 5% $K_2S_2O_8$ solution to each digestion tube.

10.2.3.7. Place each digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 hours in the water bath maintained at 95°C.

10.2.3.8. Remove the digestion tubes from the block digester and allow the digested reagent water to cool.

10.2.3.9. Add 3 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested reagent water to reduce excess permanganate.

10.2.3.10. The CB is used to establish the zero point of the calibration curve or to dilute standards and samples.

10.2.3.11. The CB is also used either as initial calibration blank (ICB) or as continuing calibration blank (CCB) to monitor contamination.

10.2.4. Method Blank (MB)

10.2.4.1. Process the MBs using the appropriate sample preparation procedure.

10.2.4.2. The MB is used to identify possible contamination resulting from either the reagents or the equipment used during sample processing.

10.2.5. Initial Calibration Verification (ICV) Solution

10.2.5.1. Measure 0.5 mL of the 1.0-ppm mercury working standard solution and 50 mL of reagent water into a clean digestion tube. Mix thoroughly.

10.2.5.2. Slowly add 2.5 mL of concentrated H_2SO_4 to the digestion tube and mix.

10.2.5.3. Slowly add 1.25 mL of concentrated HNO_3 to the digestion tube and mix.

10.2.5.4. Add 7.5 mL of the 5% $KMnO_4$ solution to the digestion tube, and allow the mixture to stand for at least 15 minutes.

10.2.5.5. Add 4.0 mL of the 5% $K_2S_2O_8$ solution to the digestion tube.

10.2.5.6. Place the digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 hours in the water bath maintained at 95°C.

10.2.5.7. Remove the digestion tube from the block digester and allow the digested standard solution to cool.

10.2.5.8. Add 3 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested standard solution to reduce excess permanganate.

10.2.5.9. Adjust the volume of the digested standard solution to 100 mL with calibration blank to obtain the 5.0-ppb ICV solution.

10.2.5.10. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.5.11. The ICV solution must be prepared fresh daily.

10.2.6. Continuing Calibration Verification (CCV) Solution

10.2.6.1. Dilute 4.0 mL of the 10.0-ppb initial calibration standard to 20 mL with calibration blank to obtain the 2.0-ppb CCV solution.

10.2.6.2. The CCV solution is of a source same as that used for the initial multi-point calibration.

10.2.6.3. The CCV solution must be prepared fresh daily.

10.2.7. Refer to Appendix A for additional standards.

10.2.8. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 250-mL pre-cleaned high density polyethylene (HDPE) containers with Teflon-lined closures.

11.1.1. Aqueous samples for dissolved mercury determination shall be field filtered through a 0.45-µm filter within 15 minutes of sample collection and preserved with 1:1 HNO_3 solution to pH < 2.

11.1.1.1. If the samples are field filtered but not preserved, upon receipt at the laboratory, the samples must be preserved with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion and analysis.

11.1.2. Aqueous samples for total mercury determination shall be preserved with 1:1 HNO_3 solution to pH < 2.

11.1.2.1. If the samples are not preserved, upon receipt at the laboratory, the samples must be preserved with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion and analysis.

11.2. Mobility-procedure extracts should be collected in 3-oz pre-cleaned polypropylene digestion tubes with polypropylene lids, or 250-mL pre-cleaned HDPE containers with Teflon-lined closures.

11.2.1. Mobility-procedure extracts shall be preserved with 1:1 HNO_3 solution to pH < 2.

11.2.2. If precipitate is observed upon the addition of 1:1 HNO_3 solution to a small aliquot of the mobility-procedure extract, do not acid preserve the mobility-procedure extract. Digest the mobility-procedure extract within 24 hours.

11.3. Aqueous samples shall be maintained in a chilled state (≤ 6°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.4. Upon receipt, the samples are stored in a 0~6°C cooler.

11.4.1. Unfiltered aqueous samples for dissolved mercury determination must be filtered as soon as possible and preserved with 1:1 HNO_3 solution to pH < 2 immediately after filtration.

11.4.1.1. The samples may then be digested and analyzed within 28 days of sample collection.

11.4.2. Filtered aqueous samples with acid preservation (pH < 2) for dissolved mercury determination must be digested and analyzed within 28 days of sample collection.

11.4.3. Filtered aqueous samples without acid preservation (pH ≥ 2) for dissolved mercury determination must be preserved with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion, and digested and analyzed within 28 days of sample collection.

11.4.4. Aqueous samples with acid preservation (pH < 2) for total mercury determination must be digested and analyzed within 28 days of sample collection.

11.4.5. Aqueous samples without acid preservation (pH ≥ 2) for total mercury determination must be preserved with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion, and digested and analyzed within 28 days of sample collection.

11.4.6. Mobility-procedure extracts with acid preservation (pH < 2) must be digested and analyzed within 28 days post mobility extraction.

11.4.6.1. Mobility-procedure extracts shall be stored at ambient temperature prior to digestion and analysis.

11.4.7. Mobility-procedure extracts without acid preservation (pH ≥ 2) must be preserved with 1:1 HNO_3 solution to pH < 2 immediately after mobility extraction.

11.4.7.1. The mobility-procedure extracts may then be digested and analyzed within 28 days post mobility extraction.

11.4.7.2. Mobility-procedure extracts shall be stored at ambient temperature prior to digestion and analysis.

12. QUALITY CONTROL

12.1. Initial Calibration (IC)

12.1.1. The initial multi-point calibration must be established daily prior to the processing of samples.

12.1.1.1. The calibration curve is established with one calibration blank and five or six calibration standards.

12.1.2. The IC is deemed valid if the correlation coefficient, r, for linear least squares regression of each analyte is ≥ 0.995.

12.1.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2. Initial Calibration Verification (ICV)

12.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 10%.

12.2.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective action, which may include re-preparation of standard solutions, and recalibrate.

12.3. Initial Calibration Blank (ICB)

12.3.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration ≥ RL (or the limit specified in the project specific DQO).

12.3.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and reanalyze the ICB.

12.4. Continuing Calibration Verification (CCV)

12.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily after every batch of 10 samples or portion thereof, and at the end of sequence.

12.4.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

12.4.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.5. Continuing Calibration Blank (CCB)

12.5.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration ≥ RL (or the limit specified in the project specific DQO).

12.5.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and reanalyze the CCB.

12.6. Contract Required Quantitation Limit (CRQL) Check

12.6.1. A CRQL check standard is analyzed immediately following the ICV/ICB analyses.

12.6.1.1. The concentration of each analyte in the CRQL check solution shall be at the lowest calibration level.

12.6.2. The linearity of the calibration curve is deemed verified if the recovery of each analyte is within 70−130%.

12.6.3. CRQL check is performed per client request or project specific DQOs to verify the linearity of the calibration curve.

12.7. Lower Limit of Quantitation (LLOQ) Check

12.7.1. An LLOQ check sample is analyzed immediately following the ICV/ICB analyses.

12.7.1.1. The concentration of each analyte in the LLOQ check sample is at the established laboratory reporting limit.

12.7.1.2. The LLOQ check sample shall be carried through the entire preparation and analytical procedure.

12.7.2. The lower limit of quantitation is deemed verified if each analyte is detected at within ± 30% of its expected value.

12.7.3. LLOQ check is performed per client request or project specific DQOs to demonstrate the desired detection capability.

12.8. Event Based Quality Control (LCS/LCSDs and MBs)

12.8.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.8.2. The acceptance criteria for LCS/LCSD elements are as follows:

12.8.2.1. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.8.2.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each LCS/LCSD element are 80% and 120%, respectively. The RPD is ≤ 20%.

12.8.2.1.2. The acceptance limits derived from historical data should not be wider than ± 20% for accuracy and 20% for precision.

12.8.2.2. All LCS/LCSD elements must be within acceptance limits. If the LCS/LCSD elements are not acceptable, determine the cause of the problem and effect corrective action.

12.8.3. Ideally, the concentration of target analyte in an MB should be less than the respective limit specified in the project specific data quality objective (DQO). In the absence of project specific DQO, the concentration of target analyte in an MB should be less than or equal to one half of the respective RL. If regulatory limit is available, the concentration of target analyte in an MB should be less than 10% of the respective regulatory limit. If the concentration of target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.8.3.1. If the target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.8.3.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.9. Matrix Based Quality Control (MS/MSDs and PDSs)

12.9.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and a post digestion spike (PDS).

12.9.2. The acceptance criteria for MS/MSD elements are as follows:

12.9.2.1. The lower and upper acceptance limits for %REC and RPD of each MS/MSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.9.2.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each MS/MSD element are 80% and 120%, respectively. The RPD is ≤ 20%.

12.9.2.1.2. The acceptance limits derived from historical data should not be wider than ± 20% for accuracy and 20% for precision.

12.9.2.2. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.9.2.3. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

12.9.3. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.10. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.11. Dilution Test

12.11.1. If the analyte concentration is sufficiently high (minimally, a factor of 10 above the reporting limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination.

12.11.2. If this criterion is not met, then a chemical or physical interference effect should be suspected. Perform post digestion spike addition.

12.11.3. Dilution test is performed per client request or project specific DQOs.

12.12. Post Digestion Spike Addition

12.12.1. A PDS sample is prepared by adding the spike standard to a portion of a digested sample, or its dilution. The spike addition should produce a concentration of 10−100 times the RL.

12.12.2. The acceptance criteria for PDS elements are as follows:

12.12.2.1. The lower and upper acceptance limits for %REC of each PDS element are 85% and 115%, respectively.

12.12.2.2. If the %REC of a PDS element is not within the established acceptance limits, then matrix effects should be suspected. Perform MSA on all samples in the same preparation batch.

12.12.3. Matrix effects are confirmed if the %REC values of both the MS/MSD and the PDS are unacceptable.

12.12.4. Post digestion spike addition is performed per client request or project specific DQOs.

12.13. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Pipetter

13.1.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

13.2. Spectrometer Initial Calibration

13.2.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.2.2. After obtaining an acceptable multi-point calibration curve and prior to processing field or QC sample digestates, an ICV standard and ICB must be analyzed to verify the initial calibration. The acceptance criteria for the ICV and ICB are listed in Section 12.2. and Section 12.3.

13.2.2.1. Per client request or project specific DQOs, a CRQL check standard must be analyzed immediately following the ICV/ICB analyses to verify the linearity of the calibration curve. The acceptance criteria for the CRQL are listed in Section 12.6.

13.2.2.2. Per client request or project specific DQOs, an LLOQ check sample must be analyzed immediately following the ICV/ICB analyses to verify the lower limit of quantitation. The acceptance criteria for the LLOQ are listed in Section 12.7.

13.2.3. The initial multi-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

14. PROCEDURE

14.1. Instrument Setup

14.1.1. Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable (usually requiring at least 15 minutes of operation) prior to calibration. Follow the instructions provided by the instrument manufacturer for operating conditions.

14.1.1.1. Use the following CVAA operating conditions as guidance.

Description	Operating Condition
Carrier gas flow	40~70 mL/min
Pump #1 speed	100 rpm
Pump #2 speed	120 rpm
Carrier solution / sample diluent (3.0% HCl)	9~11 mL/min
Reductant (1.1% $SnCl_2$ in 3.0% HCl)	5~7 mL/min
Reaction coil	110-mm × 1.0-mm ID
Wavelength	253.7 nm
Number of replicates	2

14.1.1.2. Autosampler is set to inject 200 µL of field or QC sample digestate.

14.1.2. Place the inlet of the blue/yellow carrier solution pump tube in the hydrochloric acid reservoir. Place the inlet of the red/red reductant pump tube in the stannous chloride reservoir. Position the sampling probe in the reagent water reservoir.

14.1.3. Check the carrier solution and reductant flow rates. The reductant flow rate should be approximately one half of the carrier solution flow rate.

14.1.3.1. Check the flow rate by placing the inlet of the tube in a graduated cylinder filled with reagent water, and then measure the volume decrease after one minute.

14.1.3.2. If the flow rate is not within the appropriate range, adjust the pump pressure for the tube until the flow rate is within range.

14.1.4. Program the system to average two integrations on each blank, standard, and sample. Report the average.

14.1.4.1. If the %RSD for an analyte in a standard is > 10%, document the unacceptable result and reanalyze the standard. If the %RSD criterion remains unacceptable, investigate, effect corrective action, which may include re-preparation of the standard solution, and recalibrate, if necessary.

14.1.4.2. If the %RSD for an analyte in a sample is > 20%, and the analyte concentration exceeds its RL, document the unacceptable result and reanalyze the sample. If the %RSD criterion remains unacceptable, investigate and effect corrective action.

14.2. Establish a calibration curve to cover the appropriate concentration range (see Section 13.2.).

14.3. Following the establishment of a valid initial calibration, a CCV standard and CCB must be analyzed daily after every batch of 10 samples or portion thereof, and at the end of sequence. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.4. and Section 12.5.

14.3.1. If a failed CCV/CCB is the first of the day, effect corrective action and reanalyze all samples since the last acceptable ICV/ICB.

14.3.2. If a failed CCV/CCB is <u>not</u> the first of the day, effect corrective action and reanalyze all samples since the last acceptable CCV/CCB.

14.4. Following preparatory procedures specified in Appendix A, the digestates for the QC and actual environmental samples are received in digestion tubes. After transferring aliquots of the digestates to autosampler vessels, the autosampler vessels are then loaded onto the system sample tray.

14.5. Standard and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standards
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) CRQL or LLOQ Check (per client request or project specific DQOs)
6) Method Blank (MB)
7) Laboratory Control Samples (LCS)
8) Laboratory Control Sample Duplicates (LCSD)
9) Samples (up to 10 per batch, including QC check samples and MBs)

10) Continuing Calibration Verification (CCV)
11) Continuing Calibration Blank (CCB)
12) Matrix Spike (MS)
13) Matrix Spike Duplicate (MSD)
14) Dilution Test Sample (per client request or project specific DQOs)
15) Post Digestion Spike (PDS) (per client request or project specific DQOs)
16) Samples (up to 10 per batch, including QC check samples and MBs)
17) Ending CCV
18) Ending CCB

14.5.1. Item 1: The CB is an aliquot of reagent water digestate used to establish the zero point of the initial calibration curve.

14.5.2. Item 2: The initial calibration standards are used to establish the initial calibration curve.

14.5.3. Item 3: The ICV is a second source standard used to verify the acceptance of the initial multi-point calibration. An acceptable ICV is required daily after initial calibration.

14.5.4. Item 4: The ICB is an aliquot of reagent water digestate used to monitor contamination. An acceptable ICB is required immediately following ICV.

14.5.5. Item 5: The CRQL check standard is used to verify the linearity of the calibration curve. The LLOQ check sample is used to verify the lower limit of quantitation. Per client request or project specific DQOs, an acceptable CRQL or LLOQ check is required immediately following ICV and ICB.

14.5.6. Item 6: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.5.6.1. For aqueous samples, the MB consists of clean reagent water. For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB.

14.5.6.2. One MB is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.5.6.3. When samples that are processed together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of reagent water digestate must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.5.7. Item 7: The LCS is a known matrix which has been spiked with known concentration of specific target analyte. The purpose of the LCS is to

demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.5.7.1. For aqueous samples, the LCS consists of the specified element spiked into clean reagent water. For mobility-procedure extracts, the LCS consists of the specified element spiked into the mobility-procedure extract designated as LCS.

14.5.7.2. One LCS is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.5.8. Item 8: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.5.9. Items 9 and 16: Up to 10 sample (including QC check sample and method blank) digestates per batch. Digestates with concentrations exceeding the calibration range should be sufficiently diluted. Dilution of digestates will result in increased reporting limits.

14.5.9.1. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.5.10. Items 10 and 17: A CCV is a standard used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily after every batch of 10 samples or portion thereof, and at the end of sequence.

14.5.11. Items 11 and 18: A CCB is an aliquot of reagent water digestate used to monitor contamination. An acceptable CCB is required immediately following CCV.

14.5.12. Item 12: The MS is the actual sample matrix spiked with known concentration of specific target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.5.12.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analyte (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.5.12.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.5.13. Item 13: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.5.14. Item 14: The dilution test sample is prepared from the five-fold dilution of a high concentration sample post digestion. The high concentration sample is diluted to one-fifth of the original concentration post digestion to confirm that no interference is observed in the original sample.

14.5.14.1. The purpose of the dilution test sample is to assess matrix effects.

14.5.14.2. To comply with client request or project specific DQOs, one dilution test sample is required daily for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.5.15. Item 15: The PDS is the same sample matrix from which the MS/MSD samples were prepared, and is spiked with known concentration of specific target analyte post digestion. The sample which will be spiked for the PDS is processed concurrently with the associated samples. In the processing of the PDS, reagents and procedures identical to those for actual samples are used.

14.5.15.1. The purpose of the PDS is to confirm matrix effects. The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.5.15.2. The number of PDS required is based upon client request or project specific DQOs.

14.5.16. Rinse blanks consisting of 3% HCl solution may be added elsewhere in the sequence to rinse the analytical system.

14.6. Ensure that sufficient amounts of 3% HCl solution and stannous chloride solution are present in the 3% HCl and stannous chloride reservoirs, respectively, and that a sufficient unused volume exists in the waste container at the beginning of the sequence.

14.7. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or on the sequence table printout.

14.7.1. Record the reagent and standard identification numbers on the sequence table printout.

14.8. Initiate the sequence.

14.9. Data Interpretation

14.9.1. Quantitation of a target analyte is based on a reproducible response of the spectrometer within the calibration range and a direct proportionality of the magnitude of response between absorbances in the sample digestate and the calibration standards.

14.9.1.1. Proper quantitation requires the appropriate selection of a wavelength from which the absorbance of an element can be determined.

14.9.1.2. Determine the concentration based on the initial calibration curve.

14.9.1.2.1. The data system is programmed to perform the calculation of concentration via the Beer-Lambert Law.

14.9.1.3. If the instrument response exceeds the calibration range, dilute the digestate and reanalyze.

14.10. Method of Standard Additions (MSA)

14.10.1. The standard addition technique involves adding known amounts of a standard solution to one or more aliquots of a processed sample. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. However, it will not correct for additive interferences which cause a baseline shift.

14.10.1.1. The MSA may be appropriate for analyses of digestates, on analyses submitted as part of a delisting petition, whenever a new sample matrix is being analyzed, and on every batch that fails the post digestion spike addition.

14.10.2. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_s of a standard analyte solution of concentration C_s. To the second aliquot (labeled B) is added the same volume V_s of the digested reagent water. The analytical signals of A and B, S_A and S_B, are measured and corrected for non-analyte signals. The unknown sample concentration C_x is calculated using the formula listed in Section 15.8. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

14.10.3. Improved results can be obtained by employing a series of standard additions. A series of standard solutions containing different known quantities of the analyte are added to equal volumes of the sample, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50% of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations

are approximately 100% and 150% of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot is shown in Appendix B. A linear regression program may be used to obtain the intercept concentration.

14.10.4. For the results of the MSA technique to be valid, the following limitations must be taken into consideration:

14.10.4.1. The apparent concentrations from the calibration curve must be linear (correlation coefficient of 0.995 or greater) over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve.

14.10.4.2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

14.10.4.3. The determination must be free of spectral interference and corrected for nonspecific background interference.

15. CALCULATIONS

15.1. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{A_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the absorbances for the target analyte.
A_{ave} = mean of the absorbances for the target analyte.

15.2. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent difference.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.

Note: Concentrations must be in equivalent units.

15.3. The recovery of each LCS element is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.4. The recovery of each MS element is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD/PDS).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.6. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_x \times V_x \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_x = concentration of target analyte in digestate in µg/L.
V_x = volume of digestate in mL.
V_A = volume of aqueous sample digested in mL.
D = dilution factor, if the sample or digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.7. The target analyte concentration for a mobility-procedure extract is calculated as follows:

$$C_{MP} = \frac{C_x \times V_x \times D}{V_{MP}}$$

where: C_{MP} = concentration of target analyte in mobility-procedure extract in µg/L.
C_x = concentration of target analyte in digestate in µg/L.
V_x = volume of digestate in mL.
V_{MP} = volume of mobility-procedure extract digested in mL. Unless specified otherwise, V_{MP} = 10.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.8. The target analyte concentration from single-addition method is calculated as follows:

$$C_x = \frac{S_B \times V_s \times C_s}{(S_A - S_B) \times V_x}$$

where: C_x = concentration of target analyte in sample.
S_A = analytical signal (corrected for the blank) of sample aliquot A.
S_B = analytical signal (corrected for the blank) of sample aliquot B.
V_s = volume of target analyte in standard solution.
C_s = concentration of target analyte in standard solution.
V_x = volume of target analyte in sample.

Note: Concentrations and volumes must be in equivalent units.

15.9. Refer to the mobility extraction method(s) for additional calculations.

15.10. All concentrations shall be reported in mg/L (ppm) for aqueous samples.

15.11. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD elements vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD element are based upon the historical average recovery ± 3S that is updated at least annually. All LCS/LCSD elements must be within acceptance limits.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentration of target analyte in an MB should be less than the respective limit specified in the project specific DQO. In the absence of project specific DQO, the concentration of target analyte in an MB should be less than or equal to one half of the respective RL. If regulatory limit is available, the concentration of target analyte in an MB should be less than 10% of the respective regulatory limit. If the concentration of the target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If the target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.3. The acceptance criteria for MS/MSD elements vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each MS/MSD element are based upon the historical average recovery ± 3S that is updated at least annually.

18.3.1. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.2. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. The acceptance criteria for PDS elements are predetermined. The lower and upper acceptance limits for %REC of each PDS element are 85% and 115%, respectively.

18.4.1. If the %REC of the PDS element and the %REC of the MS/MSD elements are not within the established acceptance limits, matrix effects are confirmed. Perform MSA (see Section 14.10.) on all samples in the same preparation batch.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in mg/L (ppm) for aqueous samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD/PDS: Acceptability of the MS/MSD/PDS recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD/PDS data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported element, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject element is to be reported in samples within that analytical batch, the samples reported with that failed element must be reanalyzed with a valid LCS recovery for the element.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject element is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. Mercury in Liquid Waste (Manual Cold-Vapor Technique), Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 7470A, USEPA, Revision 1, September 1994.

http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/7470a.pdf

22.2. Flame Atomic Absorption Spectrophotometry, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 7000B, USEPA, Revision 2, February 2007.

22.3. Quality Control, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.4. Choosing the Correct Procedure, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.5. Inorganic Analytes, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Three, USEPA, Revision 4, February 2007.

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Sample Preparation and Digestion Procedures.

23.2. Appendix B: Standard Addition Plot (Example).

23.3. Appendix C: Additional Quality Control Criteria for Department of Defense Project.

23.4. Appendix D: Additional Quality Control Criteria for BP Project.

23.5. ***Appendix E: Multiple Calibration Standard Digestion.***

24. MODIFICATIONS

24.1. The following modifications from EPA Method 7470A are noted.

24.1.1. Reagents and Standards

24.1.1.1. Standard preparations are modified.

24.2. The following modifications from EPA Method 7000B are noted.

24.2.1. Quality Control

24.2.1.1. The criteria of method blank and post digestion spike addition are modified.

25. ►REVISION HISTORY

Description	Author	Effective Date
SOP revision.	X. Xu	11/15/10
SOP revision.	L. Lem	11/12/12
Added Appendix E	X. Xu, L. Lem	08/12/13

Appendix A

SAMPLE PREPARATION AND DIGESTION PROCEDURES

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 7470A, Mercury in Liquid Waste (Cold-Vapor Technique) – Sample Preparation and Digestion Procedures.

2. SCOPE AND APPLICATION

2.1. The procedure described herein is in addition to the standard procedure.

2.2. This method is restricted to use by or under the supervision of analysts/technicians experienced in the use of the equipments and apparatus required to execute the procedure.

3. METHOD SUMMARY

3.1. EPA Method 7470A provides digestion and cold-vapor atomic absorption conditions for the analysis of mercury in liquid waste.

4. INTERFERENCES

4.1. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

4.2. Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) due to the fact that during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm.

5. SAFETY

5.1. Acids are corrosive. Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of acids and mercury standards.

5.2. All sample preparation activities must be performed in a fume hood vented to the exterior of the laboratory.

5.2.1. All operational fume hoods are to remain energized continuously in order to minimize acidic atmospheric or toxic gas buildup.

5.3. For the safety of the analyst, cracked or broken glassware should be immediately discarded into a broken glassware receptacle. Broken glassware shall not be used in any step of the digestion.

5.4. To ensure the safety of the analyst during any possible emergency situation, it is recommended that chemists do not perform digestions alone. Another chemist should be present during any digestion process.

5.5. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current

version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

5.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

6. EQUIPMENT AND SUPPLIES

6.1. Digestion tubes (vials), 4-oz (120-mL), 90-mm × 43-mm ID, graduated, snap closure, with hinged lids, polypropylene, disposable, Capitol Vial P/N 04HPLS or equivalent.

6.2. pH indicator paper, narrow range. pH range should include the desired pH.

6.3. Watch glass, ribbed or equivalent, glass, appropriate diameter to cover vial.

6.4. Pipetters, 100–1000-µL, 0.5–5.0-mL, and 1–10-mL, calibrated, adjustable, with disposable tip.

6.5. Dispensers, 1–10-mL, 2.5–25-mL, and 5–50-mL, calibrated, adjustable.

6.6. Thermometer, calibrated, capable of accurately measuring at 95°C.

6.7. Block digester, equipped with water bath, capable of maintaining 95°C.

6.8. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

6.9. Syringe filtration apparatus:

6.9.1. Syringe, 10-mL, polypropylene, eccentric tip, disposable, BD Lab Syringe P/N 305462 or equivalent.

6.9.2. Filter, 0.45-µm effective pore size, 30-mm diameter, hydrophilic polyvinylidene difluoride (PVDF) membrane, polypropylene housing, disposable, National Scientific Company F2500-5 Target Syringe Filter or equivalent.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Reagent water, interferant free, nano-pure.

7.1.2. Nitric acid, HNO_3, 67–70% (v/v), concentrated, clear colorless to light yellow liquid, Fisher Scientific TraceMetal or Optima grade, EMD OmniTrace grade, or equivalent.

7.1.3. Nitric acid, HNO_3, 1:1 (v/v).

7.1.3.1. Prepare the 1:1 HNO_3 solution by slowly adding 500 mL of concentrated HNO_3 to 400 mL of reagent water and dilute to 1 L with additional reagent water.

7.1.4. Sulfuric acid, H_2SO_4, 93–98% (v/v), concentrated, clear colorless to yellow liquid, Fisher Scientific TraceMetal or Optima grade, EMD OmniTrace grade, or equivalent.

7.1.5. Sodium chloride, NaCl, fine white crystals, reagent grade or equivalent.

7.1.6. Hydroxylamine hydrochloride, $H_3NO{\cdot}HCl$, fine white crystalline powder, reagent grade or equivalent.

7.1.7. Sodium chloride-hydroxylamine hydrochloride solution, NaCl-$H_3NO{\cdot}HCl$.

7.1.7.1. Prepare the sodium chloride-hydroxylamine hydrochloride solution by dissolving 2400 g of NaCl and 2400 g of $H_3NO{\cdot}HCl$ in reagent water and dilute to 20 L with additional reagent water.

7.1.8. Potassium permanganate, $KMnO_4$, dark purple to green crystals, low mercury (≤ 0.05-ppm Hg), reagent grade or equivalent.

7.1.9. Potassium permanganate, $KMnO_4$, 5% (w/v).

7.1.9.1. Prepare the 5% $KMnO_4$ solution by dissolving 1000 g of $KMnO_4$ in 20 L of reagent water.

7.1.10. Potassium persulfate, $K_2S_2O_8$, fine white crystals, low mercury (≤ 0.05-ppm Hg), reagent grade or equivalent.

7.1.11. Potassium persulfate, $K_2S_2O_8$, 5% (w/v).

7.1.11.1. Prepare the 5% $K_2S_2O_8$ solution by dissolving 500 g of $K_2S_2O_8$ in 10 L of reagent water.

7.1.12. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

7.2. Standards

7.2.1. Stock Standard Solution

7.2.1.1. Pre-certified stock standard solution, 99.990–99.999% source purity, in sealed polyethylene bottle, containing 1000 ppm of mercury is used to prepare check standards.

7.2.1.2. Prepare the 2.0-ppm mercury working standard solution by diluting 0.2 mL of the mercury stock standard and 5 mL of concentrated HNO_3 to 100 mL with reagent water.

7.2.2. Spike Standard Solution

7.2.2.1. Use the 2.0-ppm mercury working standard solution as the spike standard solution.

7.2.2.2. The spike standard is used to prepare QC check samples such as matrix spikes (MS/MSDs), post digestion spikes (PDSs), and laboratory control samples (LCS/LCSDs).

7.2.2.3. Add 250 µL of the spike standard to each 50-mL aliquot of aqueous MS/MSD and LCS/LCSD sample prior to digestion.

7.2.2.4. Add 250 µL of the spike standard to each 10-mL aliquot of mobility-procedure extract designated as MS/MSD and LCS/LCSD prior to dilution and acidification.

7.2.2.5. Add 25 µL of the spike standard to each 10-mL aliquot of PDS sample after digestion.

7.2.3. Unless specified otherwise, all working standards must be replaced after one month or sooner if comparison with check standards indicates a problem.

7.2.4. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

8. CALIBRATION AND STANDARDIZATION

8.1. Top Loading Balance

8.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

8.1.2. Calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If the values are not within these limits, recalibrate the balance.

8.2. Thermometer

8.2.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

8.3. Pipetter

8.3.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

8.4. Dispenser

8.4.1. Calibrate the dispenser according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

9. PROCEDURE

9.1. Unfiltered Aqueous Sample Preparation for Dissolved Mercury Determination

9.1.1. If an aqueous sample was not filtered within 15 minutes of sample collection, filter the sample as soon as possible upon receipt at the laboratory.

9.1.2. Pull the plunger of the syringe and draw a sufficient volume of the aqueous sample into the barrel.

9.1.2.1. For MB/LCS/LCSD, draw a sufficient volume of clean reagent water.

9.1.2.2. For MS/MSD, draw a sufficient volume of aqueous sample in each analytical batch selected for spiking.

9.1.3. Attach a clean 0.45-µm membrane filter and press the plunger to filter the sample. Record the membrane filter lot (or identification) number in the Acid Preservation and Filtration Logbook.

9.1.4. Collect at least 50 mL of the aqueous sample filtrate in a clean digestion tube and label appropriately. Record the digestion tube lot (or identification) number in the Acid Preservation and Filtration Logbook.

9.1.5. Preserve the aqueous sample filtrate with 1:1 HNO_3 solution to pH < 2 immediately after filtration. Record the date and time when the 1:1 HNO_3 solution was added and the 1:1 HNO_3 solution identification number in the Acid Preservation and Filtration Logbook.

9.1.5.1. If the sample will be filtered and then immediately digested, record the filtration information and check the "Filter and Digest" column in the logbook.

9.1.5.2. If the sample will be held after filtration and preservation, and then digested prior to analysis, check the "Filter and Preserve" column in the logbook.

9.1.6. Mix an aqueous sample filtrate thoroughly.

9.1.7. Measure exactly 50 mL of the well-mixed aqueous sample filtrate or exactly 50 mL of the diluted filtrate into a clean digestion tube. Record the volume of filtrate used to the nearest 1 mL.

9.1.7.1. For MB/LCS/LCSD, measure exactly 50 mL of reagent water filtrate designated as MB/LCS/LCSD.

9.1.7.2. For MS/MSD, measure exactly 50 mL of aqueous sample filtrate designated as MS/MSD.

9.1.8. Add 250 µL of the spike standard solution to all matrix spikes and laboratory control samples.

9.1.9. Proceed to Section 9.7. for digestion procedure.

9.2. Filtered Aqueous Sample Preparation for Dissolved Mercury Determination

9.2.1. Mix an aqueous sample filtrate thoroughly.

9.2.2. Check the pH by transferring a few drops of the aqueous sample filtrate onto a narrow-range pH paper.

9.2.2.1. If the pH is ≥ 2, preserve the aqueous sample filtrate with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion. Record the date and time when the 1:1 HNO_3 solution was added and the 1:1 HNO_3 solution identification number in the Acid Preservation and Filtration Logbook.

9.2.2.1.1. Check the "Preserve Only" column in the logbook.

9.2.3. Measure exactly 50 mL of the well-mixed aqueous sample filtrate or exactly 50 mL of the diluted filtrate into a clean digestion tube. Record the volume of filtrate used to the nearest 1 mL.

9.2.3.1. For MB/LCS/LCSD, measure exactly 50 mL of clean reagent water.

9.2.3.2. For MS/MSD, measure exactly 50 mL of aqueous sample filtrate in each analytical batch selected for spiking.

9.2.4. Add 250 µL of the spike standard solution to all matrix spikes and laboratory control samples.

9.2.5. Proceed to Section 9.7. for digestion procedure.

9.3. Aqueous Sample Preparation for Total Mercury Determination

9.3.1. Mix an aqueous sample thoroughly.

9.3.2. Check the pH by transferring a few drops of the aqueous sample onto a narrow-range pH paper.

9.3.2.1. If the pH is ≥ 2, preserve the aqueous sample with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion. Record the date and time when the 1:1 HNO_3 solution was added and the 1:1 HNO_3 solution identification number in the Acid Preservation and Filtration Logbook.

9.3.2.1.1. Check the "Preserve Only" column in the logbook.

9.3.3. Measure exactly 50 mL of the well-mixed aqueous sample or exactly 50 mL of the diluted sample into a clean digestion tube. Record the volume of sample used to the nearest 1 mL.

9.3.3.1. For MB/LCS/LCSD, measure exactly 50 mL of clean reagent water.

9.3.3.2. For MS/MSD, measure exactly 50 mL of aqueous sample in each analytical batch selected for spiking.

9.3.4. Add 250 µL of the spike standard solution to all matrix spikes and laboratory control samples.

9.3.5. Proceed to Section 9.7. for digestion procedure.

9.4. Mobility-Procedure Extract Preparation

9.4.1. Mix a mobility-procedure extract thoroughly.

9.4.2. Measure exactly 10.0 mL of the well-mixed mobility-procedure extract into a clean digestion tube. Record the volume of extract used to the nearest 0.1 mL.

9.4.2.1. For MB/LCS/LCSD, measure exactly 10.0 mL of mobility-procedure extract designated as MB/LCS/LCSD. Refer to the mobility extraction method for information.

9.4.2.2. For MS/MSD, measure exactly 10.0 mL of mobility-procedure extract designated as MS/MSD. Refer to the mobility extraction method for information.

9.4.3. Adjust the volume of the mobility-procedure extract to 50 mL with reagent water.

9.4.4. Proceed to Section 9.7. for digestion procedure.

9.5. CRQL Check Standard Preparation

9.5.1. Measure 12.5 µL of the 2.0-ppm mercury working standard solution and 50 mL of reagent water into a clean digestion tube. Mix thoroughly.

9.5.1.1. For lower limit of quantitation, measure 2.5 µL of the 1.0-ppm mercury working standard solution and 50 mL of reagent water.

9.5.2. Proceed to Section 9.7. for digestion procedure.

9.6. LLOQ Check Sample Preparation

9.6.1. Measure 12.5 µL of the 2.0-ppm mercury working standard solution and 50 mL of reagent water into a clean digestion tube. Mix thoroughly.

9.6.2. Proceed to Section 9.7. for digestion procedure.

9.7. Digestion

9.7.1. Slowly add 2.5 mL of concentrated H_2SO_4 to the digestion tube and mix.

9.7.2. Slowly add 1.25 mL of concentrated HNO_3 to the digestion tube and mix.

9.7.3. Add 7.5 mL of the 5% $KMnO_4$ solution to the digestion tube, and allow the mixture to stand for at least 15 minutes.

9.7.4. Shake and add additional portions of the 5% $KMnO_4$ solution to the digestion tube, if necessary, until the purple color persists for at least 15 minutes.

9.7.4.1. Sewage samples may require additional permanganate.

9.7.4.2. Ensure that equal amounts of permanganate are added to standards and blanks.

9.7.5. Add 4.0 mL of the 5% $K_2S_2O_8$ solution to the digestion tube.

9.7.6. Place the digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 hours in the water bath maintained at 95°C.

9.7.7. Remove the digestion tube from the block digester and allow the digestate to cool.

9.7.8. Add 3 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digestate to reduce excess permanganate.

9.7.9. Adjust the final volume of the digestate to 100 mL with calibration blank.

9.7.10. Transfer a sufficient volume of the digestate to an autosampler vessel and label appropriately. The digestate may now be analyzed.

9.7.10.1. For post digestion spike addition, add 25 µL of the spike standard to 10.0 mL of digestate designated as PDS.

9.8. Thoroughly document all aspects of the digestion in the Mercury Sample Preparation Logbook. This logbook includes, but is not limited to:

9.8.1. Digestion date, start time, and finish time.

9.8.1.1. The start and stop time of each sample digestion must be accurately recorded in the logbook. If all samples were started and finished at the same time, then an 'arrow down' approach may be used in the logbook. If a batch is open, and a sample is added on after the digestion process of the other batch samples has begun, then the actual start and stop time for each additional sample must be recorded in the logbook.

9.8.1.2. All samples must undergo the entire digestion process regardless when the digestion process was started.

9.8.2. Sample matrix, pH, initial volume, and final volume.

9.8.3. Digestion temperature.

9.8.4. Reagent and supply lot (or identification) numbers.

9.8.5. Standard lot (or identification) number, concentration, and volume added.

9.8.6. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

10. MODIFICATIONS

10.1. The following modifications from EPA Method 7470A are noted.

10.1.1. Reagents and Standards

10.1.1.1. Reagents and standard preparations are modified.

10.1.2. Procedure

10.1.2.1. The volumes of aqueous sample and reagents used for digestion are reduced.

10.1.2.2. The final volume of the digestate is modified.

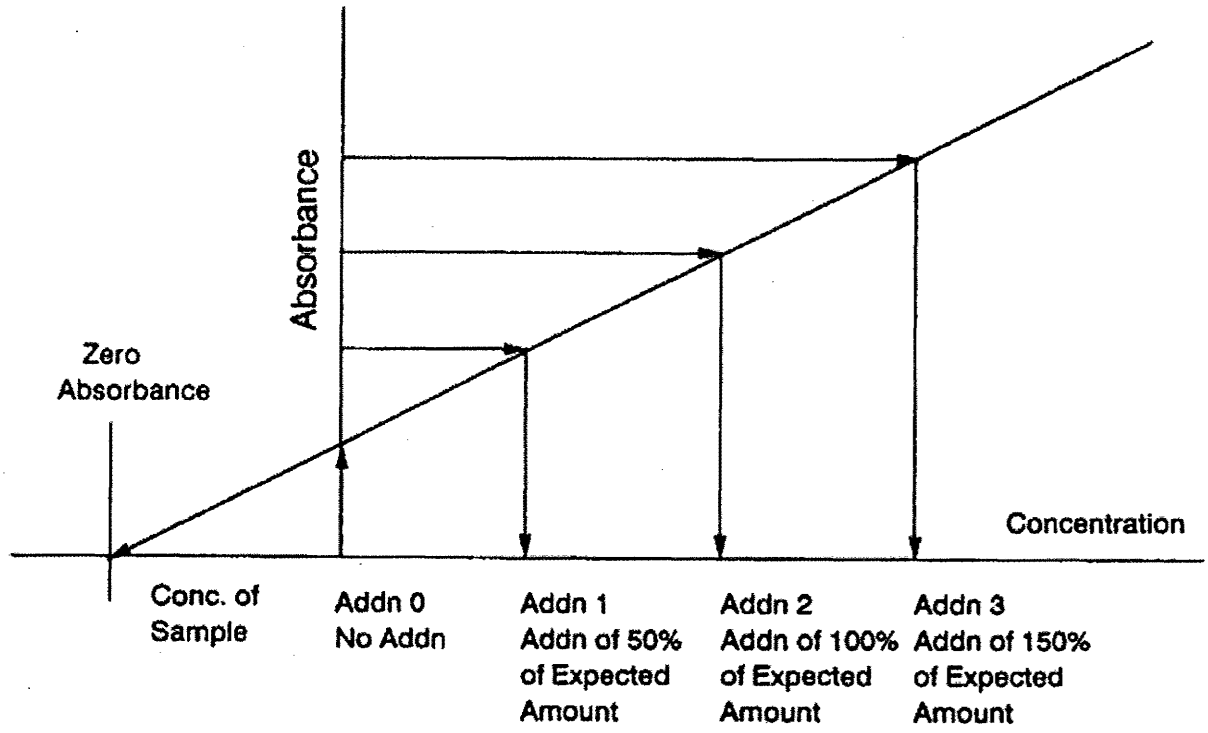
Appendix B

STANDARD ADDITION PLOT (EXAMPLE)

Calscience Environmental Laboratories, Inc.

Appendix B

Standard Addition Plot (Example)



Appendix C

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 7470A, Mercury in Liquid Waste (Cold-Vapor Technique) – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Method Detection Limit (MDL)

5.1.1. MDL study shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, or when a change in instrumentation that affects the sensitivity of the analysis.

5.1.2. MDL verification must be performed immediately following an MDL study and quarterly thereafter.

5.1.2.1. MDL verification sample shall be prepared by spiking an appropriate matrix at approximately 2–3 times the detection limit for single-analyte test, or 1–4 times the detection limit for multiple-analyte test.

5.1.2.2. MDL verification is deemed valid if the apparent signal to noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the MDL study and verification at a higher concentration. Set the MDL at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive MDL verifications at a higher concentration. Set the MDL at the higher concentration.

5.1.3. No samples shall be analyzed without a valid MDL.

5.2. Initial Calibration Blank (ICB)

5.2.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > MDL.

5.2.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and reanalyze the ICB.

5.3. Continuing Calibration Verification (CCV)

5.3.1. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.4. Continuing Calibration Blank (CCB)

5.4.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > MDL.

5.4.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and reanalyze the CCB. Reanalyze all samples since the last acceptable calibration blank.

5.4.2.1. The results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the CCB.

5.5. Event Based Quality Control (LCS/LCSDs and MBs)

5.5.1. Laboratory Control Samples (LCS/LCSDs)

5.5.1.1. The lower and upper acceptance limits for %REC of each LCS/LCSD element in aqueous matrix are 80% and 120%, respectively.

5.5.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.5.1.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.5.1.3. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.5.2. Method Blanks (MBs)

5.5.2.1. The MB is considered to be contaminated if one of the following conditions is met.

5.5.2.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.2.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.2.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.5.2.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the MDL.

5.5.2.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.6. Matrix Based Quality Control (MS/MSDs)

5.6.1. Matrix Spikes (MS/MSDs)

5.6.1.1. The lower and upper acceptance limits for %REC of each MS/MSD element in aqueous matrix are 80% and 120%, respectively. The RPD is ≤ 20%.

5.6.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.1.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

6. PROCEDURE

6.1. Standard and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standards
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) Method Blank (MB)
6) Laboratory Control Samples (LCS)
7) Laboratory Control Sample Duplicates (LCSD)
8) Samples (up to 10 per batch, including QC check samples and MBs)

9) Continuing Calibration Verification (CCV)
10) Continuing Calibration Blank (CCB)
11) Matrix Spike (MS)
12) Matrix Spike Duplicate (MSD)
13) Samples (up to 10 per batch, including QC check samples and MBs)
14) Ending CCV
15) Ending CCB

6.1.1. Item 11: The MS is the actual sample matrix spiked with known concentration of specific target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.1.1.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.1.2. Item 12: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Appendix D

ADDITIONAL QUALITY CONTROL CRITERIA FOR BP PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 7470A, Mercury in Liquid Waste (Cold-Vapor Technique) – Additional Quality Control Criteria for BP Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The spike standard solutions shall contain all anticipated target analytes.

3.2. The use of a standard from a second lot as the second source standard is acceptable if written warranties demonstrating that the standards from two different lots are not prepared from the same reference materials are obtained from the manufacturer. "Manufacturer" refers to the producer of the standard, not the vendor.

4. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

4.1. Holding time begins at the date and time the sample is collected as documented on the chain of custody record.

5. QUALITY CONTROL

5.1. Method Detection Limit (MDL)

5.1.1. MDL study should be performed annually for each analyte and matrix.

5.1.2. MDL verification must be performed immediately following an MDL study.

5.1.2.1. MDL verification sample must be spiked at the calculated MDL value.

5.1.2.2. MDL verification is deemed valid if all analytes in the verification sample are recovered.

5.1.3. At a minimum, the MDL study shall be performed on a single instrument, and the calculated MDL value must be confirmed by analyzing an MDL verification sample on all instruments used to analyze BP samples.

5.2. Initial Calibration Blank (ICB)

5.2.1. The absolute value of the concentration of a target analyte in an ICB shall be $\leq 2 \times$ MDL.

5.3. Continuing Calibration Verification (CCV)

5.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily after every 10 analyses or portion thereof, and at the end of sequence.

5.3.2. Documentation for multiple (more than one) injection trials of CCV standards must include the reason for the multiple trials, the corrective action and which trial was used and why.

5.4. Continuing Calibration Blank (CCB)

5.4.1. The absolute value of the concentration of a target analyte in a CCB shall be ≤ 2 × MDL.

5.5. Low-Level Reporting Limit (LLRL) Check

5.5.1. An LLRL check standard must be analyzed daily prior to sample analysis, every 8 hours thereafter during analysis, and at the end of sequence.

5.5.1.1. The concentration of each analyte in the LLRL check solution shall be within 2 × RL.

5.5.2. The low-level reporting limit is validated if the recovery of each analyte is within 50–150%.

5.6. Event Based Quality Control (LCS/LCSDs and MBs)

5.6.1. Method Blanks (MBs)

5.6.1.1. Contamination observed in the MB at a concentration greater than 1/2 of the RL is acceptable if either one of the following conditions is met.

5.6.1.1.1. No contaminant is detected in the associated samples.

5.6.1.1.2. The concentration of the contaminant in the associated samples is greater than 10 times the concentration in the MB.

5.7. Multiple Integrations

5.7.1. Evaluation of %RSD between multiple integrations (replicates) for each sample analysis is required.

5.7.2. Sample with analyte concentration greater than the RL must be reanalyzed if the %RSD is > 20%.

6. PROCEDURE

6.1. Following the establishment of a valid initial calibration, a CCV standard and CCB must be analyzed daily after every 10 analyses or portion thereof, and at the end of sequence. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume.

6.1.1. If a failed CCB is the first of the day, and the concentration of a target analyte in a sample bracketed by the unacceptable ICB or CCB is less than

or equal to 10 times the absolute value of the concentration of the target analyte in the ICB or CCB, reanalyze the sample.

6.1.2. If a failed CCB is not the first of the day, and the concentration of a target analyte in a sample bracketed by the unacceptable CCB is less than or equal to 10 times the absolute value of the concentration of the target analyte in the CCB, reanalyze the sample.

6.2. Standard and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standards
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) LLRL Check
6) Method Blank (MB)
7) Laboratory Control Samples (LCS)
8) Laboratory Control Sample Duplicates (LCSD)
9) Samples (up to 10 analyses, excluding ICV or CCV analyses)
10) Continuing Calibration Verification (CCV)
11) Continuing Calibration Blank (CCB)
12) Matrix Spike (MS)
13) Matrix Spike Duplicate (MSD)
14) Samples (up to 10 analyses, excluding CCV analyses)
15) Ending CCV
16) Ending CCB

6.2.1. Item 5: The LLRL check standard is used to validate the low-level reporting limit. An acceptable LLRL check is required daily prior to sample analysis, every 8 hours thereafter during analysis, and at the end of sequence.

6.2.2. Item 6: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

6.2.2.1. One MB is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation event.

6.2.3. Item 7: The LCS is a known matrix which has been spiked with known concentration of specific target analyte. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

6.2.3.1. One LCS is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every

batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation event.

6.2.4. Item 8: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD).

6.2.5. Item 12: The MS is the actual sample matrix spiked with known concentration of specific target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.2.5.1. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently within an 8-hour preparation event.

6.2.5.2. The sample selected for spiking must be one of the samples collected for the specific BP project. If 10 or fewer BP samples are received, and no sample is designated for MS/MSD analyses, then a non-BP sample may be used.

6.2.5.3. Samples identified as trip or field blanks cannot be used for MS/MSD.

6.2.6. Item 13: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Technical Requirements for Environmental Laboratory Analytical Services, BP Laboratory Management Program (LaMP), Revision 09, July 30, 2007.

Appendix E

MULTIPLE CALIBRATION STANDARD DIGESTION

Calscience Environmental Laboratories, Inc.

►MULTIPLE CALIBRATION STANDARD DIGESTION

1. ***Initial Calibration Standard Solutions***

1.1. ***Measure 0.01, 0.1, 0.2, 0.5, 1.0 mL of the 1.0-ppm mercury working standard solution and 50 mL of reagent water into five certified clean digestion tubes. Mix thoroughly.***

1.2. ***Slowly add 2.5 mL of concentrated H_2SO_4 to each digestion tube and mix.***

1.3. ***Slowly add 1.25 mL of concentrated HNO_3 to each digestion tube and mix.***

1.4. ***Add 7.5 mL of the 5% $KMnO_4$ solution to each digestion tube, and allow the mixture to stand for at least 15 minutes.***

1.5. ***Add 4.0 mL of the 5% $K_2S_2O_8$ solution to each digestion tube.***

1.6. ***Place the digestion tubes in the pre-heated block digester, cover the digestion tubes with a clean watch glass, and heat for 2 hours in the water bath maintained at 95°C.***

1.7. ***Remove the digestion tubes from the block digester and allow the digested standard solutions to cool.***

1.8. ***Add 3 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested standard solutions to reduce excess permanganate.***

1.9. ***Adjust the volume of the digested standard solutions to 100 mL with calibration blank to obtain 0.025, 0.1, 1.0, 2.0, 5.0 and 10.0 ppb initial calibration standards.***

1.10. ***Use the following calibration levels as guidance to prepare the initial calibration standards.***

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.10	1000	0.01	100
1.0	1000	0.1	100
2.0	1000	0.2	100
5.0	1000	0.5	100
10.0	1000	1.0	100

1.11. ***Use the following calibration levels as guidance to prepare the initial calibration standards for lower limit of quantitation.***

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.025	100*	0.025	100
0.10	1000	0.01	100
1.0	1000	0.1	100
2.0	1000	0.2	100
5.0	1000	0.5	100
10.0	1000	1.0	100

1.12. **** 100 ppb standard is diluted from 1.0 ppm working standard daily.***

1.13. ***The 2.0-ppb initial calibration standard is also used as the continuing calibration verification solution.***

1.14. ***The initial calibration standard solutions must be prepared fresh daily.***

Title : **EPA METHOD 7471A, MERCURY IN SOLID OR SEMI-SOLID WASTE (COLD-VAPOR TECHNIQUE)**

Document No. : SOP-M620
Revision No. : 3.5
Supersedes : 3.4

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Revision 3.5 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ **MANAGEMENT** 08/08/13 **DATE**

_____ **QA DEPARTMENT** 08-08-13 **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 7471A, Mercury in Solid or Semisolid Waste (Cold-Vapor Technique).

2. APPLICABLE MATRICES

2.1. This method is applicable to soils, sediments, bottom deposits, and sludge-type materials. It is also applicable to marine and freshwater tissues as a modified method.

3. DETECTION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

	Solid	Sediment/Tissue
Mercury	0.0835 mg/kg	0.0200 mg/kg

3.2. The RLs will be proportionally higher for samples which require reduced sample size.

3.3. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices.

3.4. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. EPA Method 7471A is a cold-vapor atomic absorption procedure for measuring total (organic and inorganic) mercury. All samples must be subjected to an appropriate dissolution step prior to analysis.

4.1.1. If the dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

4.2. This method is restricted to use by or under the supervision of analysts experienced in the use of atomic absorption spectrometer, skilled in the interpretation of atomic absorption spectra, and knowledgeable in the correction of interferences described in this method.

5. METHOD SUMMARY

5.1. Cold-vapor atomic absorption (CVAA) technique is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrometer. Absorbance (peak height) is measured as a function of mercury concentration.

5.2. Prior to analysis, the appropriate sample preparation procedure (Appendix A) must be performed on each sample.

5.2.1. Solid, sediment, and tissue samples are digested with acids.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client specific QAPP guidance overrides this directive to a lesser time period or the method specific SOP provides a different time period, but in no case to exceed 24 hours***. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-

laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.

6.12. Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.27. Terms Specific to Mercury Analysis

6.27.1. Contract Required Quantitation Limit (CRQL): Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

6.27.2. Lower Limit of Quantitation (LLOQ): The lowest point of quantitation, or in most cases, the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels based on the stated project requirements. Analysis of a standard prepared at the LLOQ concentration level or use of the LLOQ as the lowest point calibration standard provides confirmation of the established quantitation sensitivity of the method.

6.27.3. Method of Standard Addition (MSA): An alternative calibration procedure employed when the signal response of the analyte of interest is different in a particular matrix than when it is in reagent water. The standard addition technique involves the addition of known amounts of the target analyte to each of a series of replicate sample aliquots. The final concentrations of the sample replicates should span the calibration range of the method. The analytical response versus the standard addition concentration for each of the replicates is plotted. After performing a linear regression, the curve is extrapolated to the x-axis. The analyte concentration in the original unspiked sample is equal to the inverse of the x-intercept.

6.27.4. Post Digestion (Matrix) Spike: A sample which has been extracted in the same manner as the other samples, but to which a known amount of target analytes has been added to the sample extractant. Post digestion spikes

are used to evaluate the accuracy of the method without the losses incurred through the extraction process.

6.27.5. Sensitivity: The ability of an analytical technique or instrument to discriminate between small differences in analyte concentration. For atomic absorption, the concentration of metal, in mg/L, that produces a transmission of 1% is commonly employed to determine sensitivity.

6.27.6. Total Mercury: The concentration of mercury determined in a sample following digestion with acids.

7. INTERFERENCES

7.1. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

7.2. Copper may interfere; however, copper concentrations as high as 10 mg/kg has no effect on the recovery of mercury from spiked samples.

7.3. Samples high in chlorides require additional permanganate (as much as 25 mL) due to the fact that during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm.

7.3.1. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent (25 mL).

7.3.2. Free chlorine may be removed by allowing a sample to stand for at least an hour under a hood.

7.4. Certain volatile organic materials that absorb at the wavelength of 253.7 nm may also cause interference.

7.4.1. A preliminary run without reagents may be used to determine whether this type of interference is present.

8. SAFETY

8.1. Acids are corrosive. Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of acids and mercury standards.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Atomic Absorption Spectrometer: PerkinElmer Flow Injection Mercury System (FIMS) 400 or equivalent configured with the following components:

9.1.1. Computer-controlled atomic absorption spectrometer, single-beam optical system, with 254-nm maximum sensitivity.

9.1.2. Solar-blind detector.

9.1.3. Mercury lamp, high intensity, low pressure.

9.1.4. Absorption cell, 240-mm × 7-mm OD × 4-mm ID, quartz.

9.1.5. Two peristaltic pumps, 20–120-rpm variable speed, computer controlled.

9.1.6. Sample loop, 200-µL.

9.1.7. Autosampler, PerkinElmer AS-90 Autosampler or equivalent.

9.1.8. Autosampler vessels, 16-mm OD (15-mL capacity), translucent polypropylene, disposable.

9.1.9. Autosampler vessels, 30-mm OD (50-mL capacity), with screw caps, translucent polypropylene, disposable.

9.2. Instrument Software

9.2.1. PerkinElmer WinLab 32 for AA Version 6.4.0.0191 or equivalent, capable of automatic baseline offset correction.

9.3. Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.

9.4. Carrier Gas: Argon, Ar, 99.998%, cryogenic liquid, Praxair Argon Cryogenic Liquid or equivalent.

9.5. Graduated cylinders, 100-mL or other capacity, glass, Class A.

9.6. Volumetric flask, 100-mL or other capacity, glass, Class A.

9.7. Pipetters, 100–1000-µL, 0.5–5.0-mL, and 1–10-mL, calibrated, adjustable, with disposable tip.

9.8. Refer to Appendix A for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, nano-pure.

10.1.2. Chips, Teflon.

10.1.3. Beads, glass.

10.1.4. Hydrochloric acid, HCl, 32–35% or 34–37% (v/v), concentrated, clear colorless liquid, Fisher Scientific TraceMetal or Optima grade, EMD OmniTrace grade, or equivalent.

10.1.5. Hydrochloric acid, HCl, 3% (v/v).

10.1.5.1. Prepare the 3% HCl solution by slowly adding 60 mL of concentrated HCl to 500 mL of reagent water and dilute to 2 L with additional reagent water.

10.1.5.2. The 3% HCl solution is used as the carrier solution.

10.1.5.3. It is also used as a rinse blank to flush the system between standards and samples to minimize interferences.

10.1.6. Nitric acid, HNO_3, 67–70% (v/v), concentrated, clear colorless to light yellow liquid, Fisher Scientific TraceMetal or Optima grade, EMD OmniTrace grade, trace metals grade or equivalent.

10.1.7. Stannous chloride, $SnCl_2$, dihydrate, white crystalline powder, reagent grade or equivalent.

10.1.8. Stannous chloride solution, $SnCl_2 \cdot 2H_2O/HCl$.

10.1.8.1. Prepare the stannous chloride solution by adding 11 g of $SnCl_2 \cdot 2H_2O$ to 1 L of 3% HCl solution.

10.1.8.2. The stannous chloride solution is used as the reducing agent.

10.1.9. Refer to Appendix A for additional reagents.

10.1.10. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Stock Standard Solutions

10.2.1.1. Pre-certified stock standard solutions, 99.990–99.999% source purity, each in sealed polyethylene bottles, containing 1000/100 ppm of mercury are used to prepare calibration and check standards.

10.2.1.2. Prepare each mercury working standard solution by diluting the appropriate volume of the mercury stock standard and 5 mL of concentrated HNO_3 to 100 mL with reagent water.

10.2.1.3. The working standards are prepared as follows:

Analyte	Initial		Final	
	Conc (ppm)	Volume (mL)	Conc (ppm)	Volume (mL)
Hg	1000	0.2	2.0	100

Note: The working standard solution contains 5% (v/v) of HNO_3.

Analyte	Initial		Final	
	Conc (ppm)	Volume (mL)	Conc (ppm)	Volume (mL)
Hg	100	1.0	1.0	100

Note: The working standard solution contains 5% (v/v) of HNO_3.

10.2.1.4. The working standard solutions must be replaced after one month or sooner if comparison with check standards indicates a problem.

10.2.2. Initial Calibration Standard Solutions

10.2.2.1. Measure 0.5 mL of the 2.0-ppm mercury working standard solution into a clean digestion tube.

10.2.2.2. Add 10 mL of the diluted aqua regia solution to the digestion tube.

10.2.2.3. Place the digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 minutes in the water bath maintained at 95°C.

10.2.2.4. Remove the digestion tube from the block digester and allow the digested standard solution to cool.

10.2.2.5. Add 50 mL of reagent water and 15 mL of the 5% $KMnO_4$ solution to the digestion tube.

10.2.2.6. Mix the contents of the digestion tube thoroughly.

10.2.2.7. Place the digestion tube in the pre-heated block digester, cover the digestion tube with the same watch glass, and continue to heat for 30 minutes in the water bath maintained at 95°C.

10.2.2.8. Remove the digestion tube from the block digester and allow the digested standard solution to cool.

10.2.2.9. Add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested standard solution to reduce excess permanganate.

10.2.2.10. Adjust the volume of the digested standard solution to 100 mL with calibration blank to obtain the 10.0-ppb initial calibration standard.

10.2.2.11. Dilute the appropriate volumes of the 10.0-ppb initial calibration standard to 20 mL with calibration blank to obtain other initial calibration standards.

10.2.2.12. Use the following calibration levels as guidance to prepare the initial calibration standards.

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.25	10.0	0.5	20.0
1.0	10.0	2.0	20.0
2.0	10.0	4.0	20.0
5.0	10.0	10.0	20.0
10.0	10.0	20.0	20.0

10.2.2.13. Use the following calibration levels as guidance to prepare the initial calibration standards for lower limit of quantitation.

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.025	10.0	0.05	20.0
0.25	10.0	0.5	20.0
1.0	10.0	2.0	20.0
2.0	10.0	4.0	20.0
5.0	10.0	10.0	20.0
10.0	10.0	20.0	20.0

10.2.2.14. The 2.0-ppb initial calibration standard is also used as the continuing calibration verification solution.

10.2.2.15. The initial calibration standard solutions must be prepared fresh daily.

10.2.3. Calibration Blank (CB)

10.2.3.1. Designate a minimum of five clean digestion tubes for calibration blank preparation.

10.2.3.2. Measure 0.5 mL of reagent water into each clean digestion tube.

10.2.3.3. Add 10 mL of the diluted aqua regia solution to each digestion tube.

10.2.3.4. Place each digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 minutes in the water bath maintained at 95°C.

10.2.3.5. Remove the digestion tubes from the block digester and allow the digested reagent water to cool.

10.2.3.6. Add 50 mL of reagent water and 15 mL of the 5% $KMnO_4$ solution to each digestion tube.

10.2.3.7. Mix the contents of each digestion tube thoroughly.

10.2.3.8. Place each digestion tube in the pre-heated block digester, cover the digestion tube with the same watch glass, and

continue to heat for 30 minutes in the water bath maintained at 95°C.

10.2.3.9. Remove the digestion tube from the block digester and allow the digested reagent water to cool.

10.2.3.10. Add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested reagent water to reduce excess permanganate.

10.2.3.11. The CB is used to establish the zero point of the calibration curve or to dilute standards and samples.

10.2.3.12. The CB is also used either as initial calibration blank (ICB) or as continuing calibration blank (CCB) to monitor contamination.

10.2.4. Method Blank (MB)

10.2.4.1. Process the MBs using the appropriate sample preparation procedure.

10.2.4.2. The MB is used to identify possible contamination resulting from either the reagents or the equipment used during sample processing.

10.2.5. Initial Calibration Verification (ICV) Solution

10.2.5.1. Measure 0.5 mL of the 1.0-ppm mercury working standard solution into a clean digestion tube.

10.2.5.2. Add 10 mL of the diluted aqua regia solution to the digestion tube.

10.2.5.3. Place the digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 minutes in the water bath maintained at 95°C.

10.2.5.4. Remove the digestion tube from the block digester and allow the digested standard solution to cool.

10.2.5.5. Add 50 mL of reagent water and 15 mL of the 5% $KMnO_4$ solution to the digestion tube.

10.2.5.6. Mix the contents of the digestion tube thoroughly.

10.2.5.7. Place the digestion tube in the pre-heated block digester, cover the digestion tube with the same watch glass, and continue to heat for 30 minutes in the water bath maintained at 95°C.

10.2.5.8. Remove the digestion tube from the block digester and allow the digested standard solution to cool.

10.2.5.9. Add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested standard solution to reduce excess permanganate.

10.2.5.10. Adjust the volume of the digested standard solution to 100 mL with calibration blank to obtain the 5.0-ppb ICV solution.

10.2.5.11. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.5.12. The ICV solution must be prepared fresh daily.

10.2.6. Continuing Calibration Verification (CCV) Solution

10.2.6.1. Dilute 4.0 mL of the 10.0-ppb initial calibration standard to 20 mL with calibration blank to obtain the 2.0-ppb CCV solution.

10.2.6.2. The CCV solution is of a source same as that used for the initial multi-point calibration.

10.2.6.3. The CCV solution must be prepared fresh daily.

10.2.7. Refer to Appendix A for additional standards.

10.2.8. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Solid samples should be collected in 4-oz or 8-oz pre-cleaned clear glass wide-mouth jars with Teflon-lined closures, or 6-in decontaminated brass or stainless steel sleeves with Teflon-lined closures.

11.2. Tissue samples should be collected in 4-oz (or other appropriate capacity) pre-cleaned clear glass or quartz wide-month jars with Teflon or aluminum foil-lined closures. Refer to SOP-M229 for additional information on sample collection, preservation, and containers.

11.3. Solid samples shall be maintained in a chilled state (≤ 4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.4. Tissue samples shall be maintained in a frozen state (≤ −20°C) post sample collection until received at the laboratory. Refer to SOP-M229 for additional information on sample collection and preservation.

11.5. Upon receipt, the solid samples are stored in a 0~6°C cooler, and the tissue samples are stored in a −10~−20°C freezer.

11.5.1. Solid and tissue samples must be digested and analyzed within 28 days of sample collection.

12. ►QUALITY CONTROL

12.1. Initial Calibration (IC)

12.1.1. The initial multi-point calibration must be established daily prior to the processing of samples.

12.1.1.1. The calibration curve is established with one calibration blank and five or six calibration standards.

12.1.2. The IC is deemed valid if the correlation coefficient, r, for linear least squares regression of each analyte is ≥ 0.995.

12.1.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2. Initial Calibration Verification (ICV)

12.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 10%.

12.2.2. ►If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective action, which may include re-preparation of standard solutions ***or instrument maintenance***, and recalibrate.

12.3. Initial Calibration Blank (ICB)

12.3.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration ≥ RL (or the limit specified in the project specific DQO).

12.3.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and reanalyze the ICB.

12.4. Continuing Calibration Verification (CCV)

12.4.1. ►Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily after every batch of 10 samples or portion thereof ***within a 24-hour shift***, and at the end of sequence.

12.4.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

12.4.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.5. Continuing Calibration Blank (CCB)

12.5.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration ≥ RL (or the limit specified in the project specific DQO).

12.5.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and reanalyze the CCB.

12.6. Contract Required Quantitation Limit (CRQL) Check

12.6.1. A CRQL check standard is analyzed immediately following the ICV/ICB analyses.

12.6.1.1. The concentration of each analyte in the CRQL check solution shall be at the lowest calibration level.

12.6.2. The linearity of the calibration curve is deemed verified if the recovery of each analyte is within 70−130%.

12.6.3. CRQL check is performed per client request or project specific DQOs to verify the linearity of the calibration curve.

12.7. Lower Limit of Quantitation (LLOQ) Check

12.7.1. An LLOQ check sample is analyzed immediately following the ICV/ICB analyses.

12.7.1.1. The concentration of each analyte in the LLOQ check sample is at the established laboratory reporting limit.

12.7.1.2. The LLOQ check sample shall be carried through the entire preparation and analytical procedure.

12.7.2. The lower limit of quantitation is deemed verified if each analyte is detected at within ± 30% of its expected value.

12.7.3. LLOQ check is performed per client request or project specific DQOs to demonstrate the desired detection capability.

12.8. ►Event Based Quality Control (MBs and LCS/LCSDs)

12.8.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB) and a laboratory control sample and laboratory control sample duplicate (LCS/LCSD).

12.8.2. ***The acceptance criteria for MBs are as follows:***

12.8.2.1. Ideally, the concentration of target analyte in an MB should be less than the respective limit specified in the project specific data quality objective (DQO). In the absence of project specific DQO, the concentration of target analyte in an MB should be less than or equal to one half of the respective RL. If regulatory limit is available, the concentration of target analyte in an MB should be less than 10% of the respective regulatory limit. If the concentration of target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated.

12.8.2.2. If the target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.8.2.3. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect

on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.8.3. The acceptance criteria for LCS/LCSD elements are as follows:

12.8.3.1. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.8.3.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each LCS/LCSD element are 80% and 120%, respectively. The RPD is ≤ 20%.

12.8.3.1.2. The acceptance limits derived from historical data should not be wider than ± 20% for accuracy and 20% for precision.

12.8.3.2. All LCS/LCSD elements must be within acceptance limits. If the LCS/LCSD elements are not acceptable, determine the cause of the problem and effect corrective action.

12.9. Matrix Based Quality Control (MS/MSDs and PDSs)

12.9.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and a post digestion spike (PDS).

12.9.2. The acceptance criteria for MS/MSD elements are as follows:

12.9.2.1. The lower and upper acceptance limits for %REC and RPD of each MS/MSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.9.2.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each MS/MSD element are 80% and 120%, respectively. The RPD is ≤ 20%.

12.9.2.1.2. The acceptance limits derived from historical data should not be wider than ± 20% for accuracy and 20% for precision.

12.9.2.2. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.9.2.3. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

12.9.3. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.10. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.11. Dilution Test

12.11.1. If the analyte concentration is sufficiently high (minimally, a factor of 10 above the reporting limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination.

12.11.2. If this criterion is not met, a chemical or physical interference effect should be suspected. Perform post digestion spike addition.

12.11.3. Dilution test is performed per client request or project specific DQOs.

12.12. Post Digestion Spike Addition

12.12.1. A PDS sample is prepared by adding the spike standard to a portion of a digested sample, or its dilution. The spike addition should produce a concentration of 10–100 times the RL.

12.12.2. The acceptance criteria for PDS elements are as follows:

12.12.2.1. The lower and upper acceptance limits for %REC of each PDS element are 85% and 115%, respectively.

12.12.2.2. If the %REC of a PDS element is not within the established acceptance limits, then matrix effects should be suspected. Perform MSA on all samples in the same preparation batch.

12.12.3. Matrix effects are confirmed if the %REC values of both the MS/MSD and the PDS are unacceptable.

12.12.4. Post digestion spike addition is performed per client request or project specific DQOs.

12.13. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Pipetter

13.1.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

13.2. Spectrometer Initial Calibration

13.2.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.2.2. After obtaining an acceptable multi-point calibration curve and prior to processing field or QC sample digestates, an ICV standard and ICB must be analyzed to verify the initial calibration. The acceptance criteria for the ICV and ICB are listed in Section 12.2. and Section 12.3.

13.2.2.1. Per client request or project specific DQOs, a CRQL check standard must be analyzed immediately following the ICV/ICB analyses to verify the linearity of the calibration curve. The acceptance criteria for the CRQL are listed in Section 12.6.

13.2.2.2. Per client request or project specific DQOs, an LLOQ check sample must be analyzed immediately following the ICV/ICB analyses to verify the lower limit of quantitation. The acceptance criteria for the LLOQ are listed in Section 12.7.

13.2.3. The initial multi-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

14. PROCEDURE

14.1. Instrument Setup

14.1.1. Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable (usually requiring at least 15 minutes of operation) prior to calibration. Follow the instructions provided by the instrument manufacturer for operating conditions.

14.1.1.1. Use the following CVAA operating conditions as guidance.

Description	Operating Condition
Carrier gas flow	40~70 mL/min
Pump #1 speed	100 rpm
Pump #2 speed	120 rpm
Carrier solution / sample diluent (3.0% HCl)	9~11 mL/min
Reductant (1.1% $SnCl_2$ in 3.0% HCl)	5~7 mL/min
Reaction coil	110-mm × 1.0-mm ID
Wavelength	253.7 nm
Number of replicates	2

14.1.1.2. Autosampler is set to inject 200 µL of field or QC sample digestate.

14.1.2. Place the inlet of the blue/yellow carrier solution pump tube in the hydrochloric acid reservoir. Place the inlet of the red/red reductant pump tube in the stannous chloride reservoir. Position the sampling probe in the reagent water reservoir.

14.1.3. Check the carrier solution and reductant flow rates. The reductant flow rate should be approximately one half of the carrier solution flow rate.

14.1.3.1. Check the flow rate by placing the inlet of the tube in a graduated cylinder filled with reagent water, and then measure the volume decrease after one minute.

14.1.3.2. If the flow rate is not within the appropriate range, adjust the pump pressure for the tube until the flow rate is within range.

14.1.4. Program the system to average two integrations on each blank, standard, and sample. Report the average.

14.1.4.1. If the %RSD for an analyte in a standard is > 10%, document the unacceptable result and reanalyze the standard. If the %RSD criterion remains unacceptable, investigate, effect corrective action, which may include re-preparation of the standard solution, and recalibrate, if necessary.

14.1.4.2. If the %RSD for an analyte in a sample is > 20%, and the analyte concentration exceeds its RL, document the unacceptable result and reanalyze the sample. If the %RSD criterion remains unacceptable, investigate and effect corrective action.

14.2. Establish a calibration curve to cover the appropriate concentration range (see Section 13.2.).

14.3. Following the establishment of a valid initial calibration, a CCV standard and CCB must be analyzed daily after every batch of 10 samples or portion thereof, and at the end of sequence. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.4. and Section 12.5.

14.3.1. If a failed CCV/CCB is the first of the day, effect corrective action and reanalyze all samples since the last acceptable ICV/ICB.

14.3.2. If a failed CCV/CCB is <u>not</u> the first of the day, effect corrective action and reanalyze all samples since the last acceptable CCV/CCB.

14.4. Following preparatory procedures specified in Appendix A, the digestates for the QC and actual environmental samples are received in digestion tubes. After transferring aliquots of the digestates to autosampler vessels, the autosampler vessels are then loaded onto the system sample tray.

14.5. Standard and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standards
3) Initial Calibration Verification (ICV)

4) Initial Calibration Blank (ICB)
5) CRQL or LLOQ Check (per client request or project specific DQOs)
6) Method Blank (MB)
7) Laboratory Control Samples (LCS)
8) Laboratory Control Sample Duplicates (LCSD)
9) Samples (up to 10 per batch, including QC check samples and MBs)
10) Continuing Calibration Verification (CCV)
11) Continuing Calibration Blank (CCB)
12) Matrix Spike (MS)
13) Matrix Spike Duplicate (MSD)
14) Dilution Test Sample (per client request or project specific DQOs)
15) Post Digestion Spike (PDS) (per client request or project specific DQOs)
16) Samples (up to 10 per batch, including QC check samples and MBs)
17) Ending CCV
18) Ending CCB

14.5.1. Item 1: The CB is an aliquot of reagent water digestate used to establish the zero point of the initial calibration curve.

14.5.2. Item 2: The initial calibration standards are used to establish the initial calibration curve.

14.5.3. Item 3: The ICV is a second source standard used to verify the acceptance of the initial multi-point calibration. An acceptable ICV is required daily after initial calibration.

14.5.4. Item 4: The ICB is an aliquot of reagent water digestate used to monitor contamination. An acceptable ICB is required immediately following ICV.

14.5.5. Item 5: The CRQL check standard is used to verify the linearity of the calibration curve. The LLOQ check sample is used to verify the lower limit of quantitation. Per client request or project specific DQOs, an acceptable CRQL or LLOQ check is required immediately following ICV and ICB.

14.5.6. Item 6: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.5.6.1. For solid and tissue samples, the MB consists of clean Teflon chips or glass beads.

14.5.6.2. One MB is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof,. whichever is more frequent.

14.5.6.3. When samples that are processed together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of reagent water

digestate must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.5.7. Item 7: The LCS is a known matrix which has been spiked with known concentration of specific target analyte. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.5.7.1. For solid and tissue samples, the LCS consists of the specified element spiked into clean Teflon chips or glass beads.

14.5.7.2. One LCS is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.5.8. Item 8: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.5.9. Items 9 and 16: Up to 10 sample (including QC check sample and method blank) digestates per batch. Digestates should be sufficiently diluted if concentrations exceed the calibration range. Dilution of digestates will result in increased reporting limits.

14.5.9.1. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.5.10. Items 10 and 17: A CCV is a standard used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily after every batch of 10 samples or portion thereof, and at the end of sequence.

14.5.11. Items 11 and 18: A CCB is an aliquot of reagent water digestate used to monitor contamination. An acceptable CCB is required immediately following CCV.

14.5.12. Item 12: The MS is the actual sample matrix spiked with known concentration of specific target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.5.12.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analyte (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement

is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.5.12.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.5.13. Item 13: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.5.14. Item 14: The dilution test sample is prepared from the five-fold dilution of a high concentration sample post digestion. The high concentration sample is diluted to one-fifth of the original concentration post digestion to confirm that no interference is observed in the original sample.

14.5.14.1. The purpose of the dilution test sample is to assess matrix effects.

14.5.14.2. To comply with client request or project specific DQOs, one dilution test sample is required daily for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.5.15. Item 15: The PDS is the same sample matrix from which the MS/MSD samples were prepared, and is spiked with known concentration of specific target analyte post digestion. The sample which will be spiked for the PDS is processed concurrently with the associated samples. In the processing of the PDS, reagents and procedures identical to those for actual samples are used.

14.5.15.1. The purpose of the PDS is to confirm matrix effects. The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.5.15.2. The number of PDS required is based upon client request or project specific DQOs.

14.5.16. Rinse blanks consisting of 3% HCl solution may be added elsewhere in the sequence to rinse the analytical system.

14.6. Ensure that sufficient amounts of 3% HCl solution and stannous chloride solution are present in the 3% HCl and stannous chloride reservoirs, respectively, and that a sufficient unused volume exists in the waste container at the beginning of the sequence.

14.7. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or on the sequence table printout.

14.7.1. Record the reagent and standard identification numbers on the sequence table printout.

14.8. Initiate the sequence.

14.9. Data Interpretation

14.9.1. Quantitation of a target analyte is based on a reproducible response of the spectrometer within the calibration range and a direct proportionality of the magnitude of response between absorbances in the sample digestate and the calibration standards.

14.9.1.1. Proper quantitation requires the appropriate selection of a wavelength from which the absorbance of an element can be determined.

14.9.1.2. Determine the concentration based on the initial calibration curve.

14.9.1.2.1. The data system is programmed to perform the calculation of concentration via the Beer-Lambert Law.

14.9.1.3. If the instrument response exceeds the calibration range, dilute the digestate and reanalyze.

14.10. Method of Standard Additions (MSA)

14.10.1. The standard addition technique involves adding known amounts of a standard solution to one or more aliquots of a processed sample. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. However, it will not correct for additive interferences which cause a baseline shift.

14.10.1.1. The MSA may be appropriate for analyses of digestates, on analyses submitted as part of a delisting petition, whenever a new sample matrix is being analyzed, and on every batch that fails the post digestion spike addition.

14.10.2. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_s of a standard analyte solution of concentration C_s. To the second aliquot (labeled B) is added the same volume V_s of the digested reagent water. The analytical signals of A and B, S_A and S_B, are measured and corrected for non-analyte signals. The unknown sample concentration C_x is calculated using the formula listed in Section 15.9. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

14.10.3. Improved results can be obtained by employing a series of standard additions. A series of standard solutions containing different known quantities of the analyte are added to equal volumes of the sample, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50% of the expected absorbance from the endogenous analyte in the

sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100% and 150% of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot is shown in Appendix B. A linear regression program may be used to obtain the intercept concentration.

14.10.4. For the results of the MSA technique to be valid, the following limitations must be taken into consideration:

14.10.4.1. The apparent concentrations from the calibration curve must be linear (correlation coefficient of 0.995 or greater) over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve.

14.10.4.2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

14.10.4.3. The determination must be free of spectral interference and corrected for nonspecific background interference.

15. CALCULATIONS

15.1. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{A_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the absorbances for the target analyte.
A_{ave} = mean of the absorbances for the target analyte.

15.2. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent difference.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.

Note: Concentrations must be in equivalent units.

15.3. The recovery of each LCS element is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.4. The recovery of each MS element is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD/PDS).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.6. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_x \times V_x \times D}{W_S}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
C_x = concentration of target analyte in digestate in µg/L.
V_x = volume of digestate in mL.
W_S = mass of solid sample digested in mg.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.7. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_x \times V_x \times D}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
C_x = concentration of target analyte in digestate in µg/L.
V_x = volume of digestate in mL.
W_S = mass of solid sample digested in mg.
C_{ss} = solids content in %.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.8. The target analyte concentration for a tissue sample is calculated as follows:

$$C_T = \frac{C_x \times V_x \times D}{W_T}$$

where: C_T = concentration of target analyte in tissue sample in mg/kg.
C_x = concentration of target analyte in digestate in µg/L.
V_x = volume of digestate in mL.
W_T = mass of tissue sample digested in mg.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration from single-addition method is calculated as follows:

$$C_x = \frac{S_B \times V_s \times C_s}{(S_A - S_B) \times V_x}$$

where: C_x = concentration of target analyte in sample.
S_A = analytical signal (corrected for the blank) of sample aliquot A.
S_B = analytical signal (corrected for the blank) of sample aliquot B.
V_s = volume of target analyte in standard solution.
C_s = concentration of target analyte in standard solution.
V_x = volume of target analyte in sample.

Note: Concentrations and volumes must be in equivalent units.

15.10. All concentrations shall be reported in mg/kg (ppm) for soil and solid waste samples, and mg/kg (ppm) for tissue samples.

15.10.1. Per client request or project specific DQOs, report all concentrations in mg/kg (ppm) on a dry-weight basis for soil and solid waste samples.

15.11. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentration of target analyte in an MB should be less than the respective limit specified in the project specific DQO. In the absence of project specific DQO, the concentration of target analyte in an MB should be less than or equal to one half of the respective RL. If regulatory limit is available, the concentration of target analyte in an MB should be less than 10% of the respective regulatory limit. If the concentration of the target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If the target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD elements vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD element are based upon the historical average recovery ± 3S that is updated at least annually. All LCS/LCSD elements must be within acceptance limits.

18.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.3. The acceptance criteria for MS/MSD elements vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each MS/MSD element are based upon the historical average recovery ± 3S that is updated at least annually.

18.3.1. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.2. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. The acceptance criteria for PDS elements are predetermined. The lower and upper acceptance limits for %REC of each PDS element are 85% and 115%, respectively.

18.4.1. If the %REC of the PDS element and the %REC of the MS/MSD elements are not within the established acceptance limits, matrix effects are confirmed. Perform MSA (see Section 14.10.) on all samples in the same preparation batch.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in mg/kg (ppm) for soil and solid waste samples, and mg/kg (ppm) for tissue samples.

18.7.1. Per client request or project specific DQOs, report all concentrations in mg/kg (ppm) on a dry-weight basis for soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD/PDS: Acceptability of the MS/MSD/PDS recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD/PDS data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported element, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject element is to be reported in samples within that analytical batch, the samples reported with that failed element must be reanalyzed with a valid LCS recovery for the element.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject element is NOT to be reported in the samples within that

analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 7471A, USEPA, Revision 1, September 1994.

22.2. *Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 7471B, USEPA, Revision 2, February 2007.

22.3. *Flame Atomic Absorption Spectrophotometry*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 7000B, USEPA, Revision 2, February 2007.

22.4. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.5. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.6. *Inorganic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Three, USEPA, Revision 4, February 2007.

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Sample Preparation and Digestion Procedures.

23.2. Appendix B: Standard Addition Plot (Example).

23.3. Appendix C: Additional Quality Control Criteria for Department of Defense Project.

23.4. Appendix D: Additional Quality Control Criteria for BP Project.

23.5. ***Appendix E: Multiple Calibration Standard Digestion.***

24. MODIFICATIONS

24.1. The following modifications from EPA Method 7471A Revision 1 are noted.

Calscience SOP M620 Section	Reference Document EPA Method 7471A Section	Summary of Modification
10.2.	5.7, 5.8, and 7.3	Standard preparations are modified.

24.2. The following modifications from EPA Method 7000B Revision 2 are noted.

Calscience SOP M620 Section	Reference Document EPA Method 7000B Section	Summary of Modification
12.8.2.	9.5	Acceptance criteria of method blank are modified.
12.12.2.	9.8.1	Acceptance criteria of post digestion spike are modified.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
3.4	Section 3: Revise reporting limit terminology, and add reference to MDL determination procedure. Section 6: Add LOD/LOQ definitions. Section 9: Update the list of equipment and supplies. Section 12: Clarify quality control criteria. Section 18: Rearrange MB and LCS/LCSD paragraphs.	K. Chang	06/25/12

Revision	Description	Authors(s)	Effective Date
	Appendix A Section 7.1.4: Revise aqua regia solution preparation. Appendix A Section 10: List the modifications in table format. Appendix C Section 5: Revise DoD quality control criteria.		
3.5	Added Appendix E	X. Xu, L. Lem	08/12/13

Appendix A

SAMPLE PREPARATION AND DIGESTION PROCEDURES

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 7471A, Mercury in Solid or Semisolid Waste (Cold-Vapor Technique) – Sample Preparation and Digestion Procedures.

2. SCOPE AND APPLICATION

2.1. The procedure described herein is in addition to the standard procedure.

2.2. This method is restricted to use by or under the supervision of analysts/technicians experienced in the use of the equipment and apparatus required to execute the procedure.

3. METHOD SUMMARY

3.1. EPA Method 7471A provides digestion and cold-vapor atomic absorption conditions for the analysis of mercury in solid or semisolid waste.

4. INTERFERENCES

4.1. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

4.2. Samples high in chlorides require additional permanganate (as much as 25 mL) due to the fact that during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm.

5. SAFETY

5.1. Acids are corrosive. Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of acids and mercury standards.

5.2. All sample preparation activities must be performed in a fume hood vented to the exterior of the laboratory.

5.2.1. All operational fume hoods are to remain energized continuously in order to minimize acidic atmospheric or toxic gas buildup.

5.3. For the safety of the analyst, cracked or broken glassware should be immediately discarded into a broken glassware receptacle. Broken glassware shall not be used in any step of the digestion.

5.4. To ensure the safety of the analyst during any possible emergency situation, it is recommended that chemists do not perform digestions alone. Another chemist should be present during any digestion process.

5.5. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current

version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

5.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

6. EQUIPMENT AND SUPPLIES

6.1. Digestion tubes (vials), 4-oz (120-mL), 90-mm × 43-mm ID, graduated, snap closure, with hinged lids, polypropylene, disposable, Capitol Vial P/N 04HPLS or equivalent.

6.2. Watch glass, ribbed or equivalent, glass, appropriate diameter to cover vial.

6.3. Dispensers, 1–10-mL, 2.5–25-mL, and 5–50-mL, calibrated, adjustable.

6.4. Thermometer, calibrated, capable of accurately measuring at 95°C.

6.5. Block digester, equipped with water bath, capable of maintaining 95°C.

6.6. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

6.7. Spatula, PTFE (preferred) or stainless-steel construction.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Reagent water, interferant free, nano-pure.

7.1.2. Chips, Teflon.

7.1.3. Beads, glass.

7.1.4. ►Diluted aqua regia solution, $HCl/HNO_3/H_2O$, 3:1:4 (v/v/v).

7.1.4.1. Prepare the diluted aqua regia solution by slowly adding ***150 mL*** of concentrated HCl and ***50 mL*** of concentrated HNO_3 to ***150 mL*** of reagent water and dilute to ***400 mL*** with additional reagent water.

7.1.4.2. The diluted aqua regia solution must be ***prepared immediately prior to use***.

7.1.5. Sodium chloride, NaCl, fine white crystals, reagent grade or equivalent.

7.1.6. Hydroxylamine hydrochloride, $H_3NO{\cdot}HCl$, fine white crystalline powder, reagent grade or equivalent.

7.1.7. Sodium chloride-hydroxylamine hydrochloride solution, $NaCl\text{-}H_3NO{\cdot}HCl$.

7.1.7.1. Prepare the sodium chloride-hydroxylamine hydrochloride solution by dissolving 2400 g of NaCl and 2400 g of $H_3NO{\cdot}HCl$ in reagent water and dilute to 20 L with additional reagent water.

7.1.8. Potassium permanganate, $KMnO_4$, dark purple to green crystals, low mercury (≤ 0.05-ppm Hg), reagent grade or equivalent.

7.1.9. Potassium permanganate, $KMnO_4$, 5% (w/v).

7.1.9.1. Prepare the 5% $KMnO_4$ solution by dissolving 1000 g of $KMnO_4$ in 20 L of reagent water.

7.1.10. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

7.2. Standards

7.2.1. Stock Standard Solution

7.2.1.1. Pre-certified stock standard solution, 99.990–99.999% source purity, in sealed polyethylene bottle, containing 1000 ppm of mercury is used to prepare check standards.

7.2.1.2. Prepare the 2.0-ppm mercury working standard solution by diluting 0.2 mL of the mercury stock standard and 5 mL of concentrated HNO_3 to 100 mL with reagent water.

7.2.2. Spike Standard Solution

7.2.2.1. Use the 2.0-ppm mercury working standard solution as the spike standard solution.

7.2.2.2. The spike standard is used to prepare QC check samples such as matrix spikes (MS/MSDs), post digestion spikes (PDSs), and laboratory control samples (LCS/LCSDs).

7.2.2.3. Add 250 µL of the spike standard to each 0.6-g aliquot of solid MS/MSD and LCS/LCSD sample prior to digestion.

7.2.2.4. Add 25 µL of the spike standard to each 10-mL aliquot of PDS sample after digestion.

7.2.3. Unless specified otherwise, all working standards must be replaced after one month or sooner if comparison with check standards indicates a problem.

7.2.4. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

8. CALIBRATION AND STANDARDIZATION

8.1. Top Loading Balance

8.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

8.1.2. Calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If the values are not within these limits, recalibrate the balance.

8.2. Thermometer

8.2.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

8.3. Pipetter

8.3.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

8.4. Dispenser

8.4.1. Calibrate the dispenser according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

9. PROCEDURE

9.1. Solid Sample Preparation

9.1.1. Homogenize a solid, soil, or sediment sample as outlined in the current revision of SOP-M230.

9.1.2. Measure triplicate 0.20-g (wet weight) aliquots (i.e., 0.60-g total) of the homogenized solid sample into a clean digestion tube. Record the mass of sample used to the nearest 0.01 g.

9.1.2.1. For MB/LCS/LCSD, measure 0.60 ± 0.03 g of clean Teflon chips or glass beads. Record the Teflon chip or glass bead identification number.

9.1.2.2. For MS/MSD, measure 0.60 ± 0.03 g of solid sample in each analytical batch selected for spiking.

9.1.3. Add 250 µL of the spike standard solution to all matrix spikes and laboratory control samples.

9.1.4. Proceed to Section 9.6. for digestion procedure.

9.2. Tissue Sample Preparation

9.2.1. Homogenize marine or freshwater tissue sample as outlined in the current revision of SOP-M229.

9.2.2. Measure 1.00 ± 0.05 g (wet weight) of the homogenized tissue sample into a clean digestion tube. Record the mass of sample used to the nearest 0.01 g.

9.2.2.1. For MB/LCS/LCSD, measure 1.00 ± 0.05 g of clean Teflon chips or glass beads. Record the Teflon chip or glass bead identification number.

9.2.2.2. For MS/MSD, measure 1.00 ± 0.05 g of tissue sample in each analytical batch selected for spiking.

9.2.3. Add 250 µL of the spike standard solution to all matrix spikes and laboratory control samples.

9.2.4. Proceed to Section 9.6. for digestion procedure.

9.3. CRQL Check Standard Preparation

9.3.1. Measure 12.5 µL of the 2.0-ppm mercury working standard solution into a clean digestion tube.

9.3.1.1. For lower limit of quantitation, measure 2.5 µL of the 1.0-ppm mercury working standard solution.

9.3.2. Proceed to Section 9.6. for digestion procedure.

9.4. Solid LLOQ Check Sample Preparation

9.4.1. Measure 12.5 µL of the 2.0-ppm mercury working standard solution and 0.60 ± 0.03 g of Teflon chips or glass beads into a clean digestion tube. Record the Teflon chip or glass bead identification number.

9.4.2. Proceed to Section 9.6. for digestion procedure.

9.5. Tissue LLOQ Check Sample Preparation

9.5.1. Measure 12.5 µL of the 2.0-ppm mercury working standard solution and 1.00 ± 0.05 g of Teflon chips or glass beads into a clean digestion tube. Record the Teflon chip or glass bead identification number.

9.5.2. Proceed to Section 9.6. for digestion procedure.

9.6. Digestion

9.6.1. Add 10 mL of the diluted aqua regia solution to the digestion tube.

9.6.2. Place the digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 minutes in the water bath maintained at 95°C.

9.6.3. Remove the digestion tube from the block digester and allow the digestate to cool.

9.6.4. Add 50 mL of reagent water and 15 mL of the 5% $KMnO_4$ solution to the digestion tube.

9.6.5. Add additional portions of the 5% $KMnO_4$ solution to the digestion tube, if necessary, until the purple color persists for at least 15 minutes.

9.6.5.1. Ensure that equal amounts of permanganate are added to standards and blanks.

9.6.6. Mix the contents of the digestion tube thoroughly.

9.6.7. Place the digestion tube in the pre-heated block digester, cover the digestion tube with the same watch glass, and continue to heat for 30 minutes in the water bath maintained at 95°C.

9.6.8. Remove the digestion tube from the block digester and allow the digestate to cool.

9.6.9. Add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digestate to reduce excess permanganate.

9.6.10. Adjust the final volume of the digestate to 100 mL with calibration blank.

9.6.11. Transfer a sufficient volume of the digestate to an autosampler vessel and label appropriately. The digestate may now be analyzed.

9.6.11.1. For post digestion spike addition, add 25 µL of the spike standard to 10.0 mL of digestate designated as PDS.

9.7. Thoroughly document all aspects of the digestion in the Mercury Sample Preparation Logbook. This logbook includes, but is not limited to:

9.7.1. Digestion date, start time, and finish time.

9.7.1.1. The start and stop time of each sample digestion must be accurately recorded in the logbook. If all samples were started and finished at the same time, then an 'arrow down' approach may be used in the logbook. If a batch is open, and a sample is added on after the digestion process of the other batch samples has begun, then the actual start and stop time for each additional sample must be recorded in the logbook.

9.7.1.2. All samples must undergo the entire digestion process regardless when the digestion process was started.

9.7.2. Sample matrix, initial volume, and final volume.

9.7.3. Digestion temperature.

9.7.4. Reagent and supply lot (or identification) numbers.

9.7.5. Standard lot (or identification) number, concentration, and volume added.

9.7.6. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

10. MODIFICATIONS

10.1. ►The following modifications from EPA Method 7471A ***Revision 1*** are noted.

Calscience SOP M620 Appendix A Section	Reference Document EPA Method 7471A Section	Summary of Modification
7.	5.0 and 7.3	Reagent and standard preparations are modified.
9.6.10.	7.1 and 7.2	The final volume of the digestate is modified.

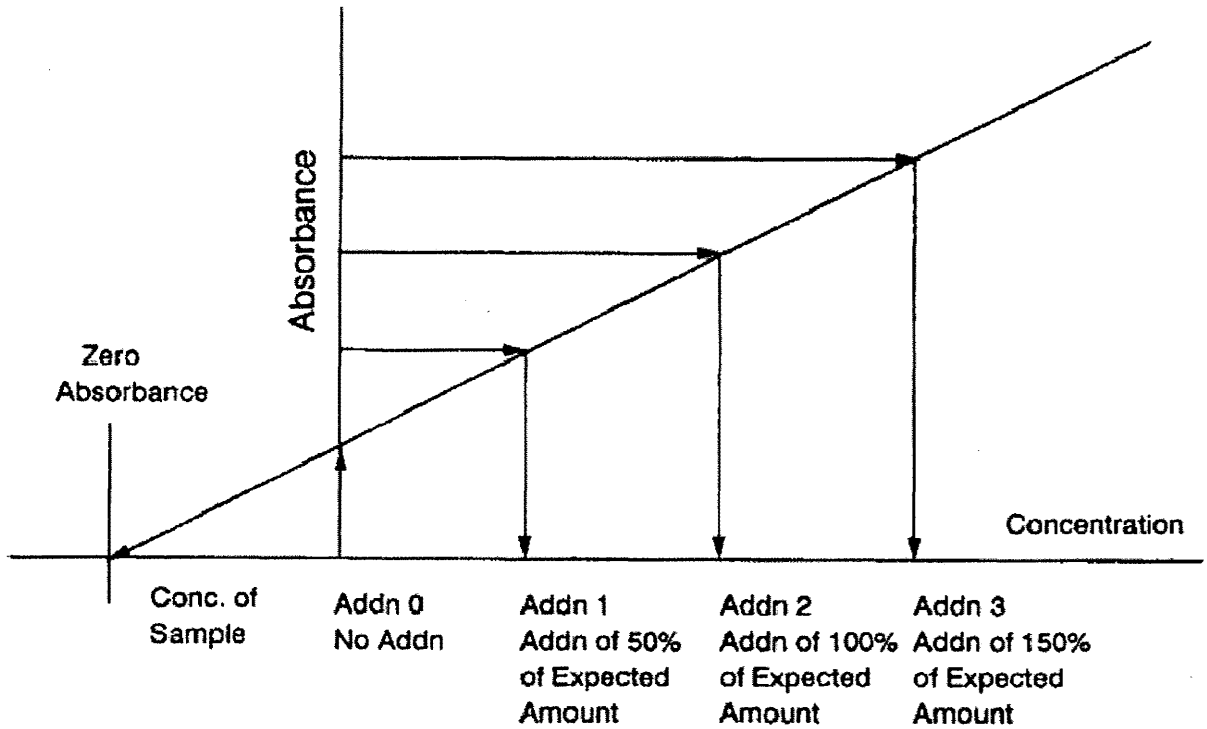
Appendix B

STANDARD ADDITION PLOT (EXAMPLE)

Calscience Environmental Laboratories, Inc.

Appendix B

Standard Addition Plot (Example)



Appendix C

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 7471A, Mercury in Solid or Semisolid Waste (Cold-Vapor Technique) – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, or when a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

5.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification.

5.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.3. No samples shall be analyzed without a valid LOD.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Initial Calibration Blank (ICB)

5.3.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > ***LOD***.

5.3.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and reanalyze the ICB.

5.4. Continuing Calibration Verification (CCV)

5.4.1. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.5. Continuing Calibration Blank (CCB)

5.5.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > LOD.

5.5.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and reanalyze the CCB. Reanalyze all samples since the last acceptable calibration blank.

5.5.2.1. The results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the CCB.

5.6. Event Based Quality Control (MBs and LCS/LCSDs)

5.6.1. Method Blanks (MBs)

5.6.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.6.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, <u>and</u> is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.6.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, <u>and</u> is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.6.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.6.1.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the ***LOD***.

5.6.1.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.6.2. Laboratory Control Samples (LCS/LCSDs)

5.6.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD element in solid matrix are 80% and 120%, respectively.

5.6.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.6.2.3. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control

limit, determine the cause of the problem and effect corrective action.

5.7. Matrix Based Quality Control (MS/MSDs)

5.7.1. Matrix Spikes (MS/MSDs)

5.7.1.1. The lower and upper acceptance limits for %REC of each MS/MSD element in solid matrix are 80% and 120%, respectively. The RPD is ≤ 20%.

5.7.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.7.1.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

6. PROCEDURE

6.1. Standard and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standards
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) Method Blank (MB)
6) Laboratory Control Samples (LCS)
7) Laboratory Control Sample Duplicates (LCSD)
8) Samples (up to 10 per batch, including QC check samples and MBs)
9) Continuing Calibration Verification (CCV)
10) Continuing Calibration Blank (CCB)
11) Matrix Spike (MS)
12) Matrix Spike Duplicate (MSD)
13) Samples (up to 10 per batch, including QC check samples and MBs)
14) Ending CCV
15) Ending CCB

6.1.1. Item 11: The MS is the actual sample matrix spiked with known concentration of specific target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.1.1.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.1.2. Item 12: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess

the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Appendix D

ADDITIONAL QUALITY CONTROL CRITERIA FOR BP PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 7471A, Mercury in Solid or Semisolid Waste (Cold-Vapor Technique) – Additional Quality Control Criteria for BP Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The spike standard solutions shall contain all anticipated target analytes.

3.2. The use of a standard from a second lot as the second source standard is acceptable if written warranties demonstrating that the standards from two different lots are not prepared from the same reference materials are obtained from the manufacturer. "Manufacturer" refers to the producer of the standard, not the vendor.

4. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

4.1. Holding time begins at the date and time the sample is collected as documented on the chain of custody record.

5. QUALITY CONTROL

5.1. Method Detection Limit (MDL)

5.1.1. MDL study should be performed annually for each analyte and matrix.

5.1.2. MDL verification must be performed immediately following an MDL study.

5.1.2.1. MDL verification sample must be spiked at the calculated MDL value.

5.1.2.2. MDL verification is deemed valid if all analytes in the verification sample are recovered.

5.1.3. At a minimum, the MDL study shall be performed on a single instrument, and the calculated MDL value must be confirmed by analyzing an MDL verification sample on all instruments used to analyze BP samples.

5.2. Initial Calibration Blank (ICB)

5.2.1. The absolute value of the concentration of a target analyte in an ICB shall be $\leq 2 \times$ MDL.

5.3. Continuing Calibration Verification (CCV)

5.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily after every 10 analyses or portion thereof, and at the end of sequence.

5.3.2. Documentation for multiple (more than one) injection trials of CCV standards must include the reason for the multiple trials, the corrective action and which trial was used and why.

5.4. Continuing Calibration Blank (CCB)

5.4.1. The absolute value of the concentration of a target analyte in a CCB shall be ≤ 2 × MDL.

5.5. Low-Level Reporting Limit (LLRL) Check

5.5.1. An LLRL check standard must be analyzed daily prior to sample analysis, every 8 hours thereafter during analysis, and at the end of sequence.

5.5.1.1. The concentration of each analyte in the LLRL check solution shall be within 2 × RL.

5.5.2. The low-level reporting limit is validated if the recovery of each analyte is within 50–150%.

5.6. Event Based Quality Control (LCS/LCSDs and MBs)

5.6.1. Method Blanks (MBs)

5.6.1.1. Contamination observed in the MB at a concentration greater than 1/2 of the RL is acceptable if either one of the following conditions is met.

5.6.1.1.1. No contaminant is detected in the associated samples.

5.6.1.1.2. The concentration of the contaminant in the associated samples is greater than 10 times the concentration in the MB.

5.7. Multiple Integrations

5.7.1. Evaluation of %RSD between multiple integrations (replicates) for each sample analysis is required.

5.7.2. Sample with analyte concentration greater than the RL must be reanalyzed if the %RSD is > 20%.

6. PROCEDURE

6.1. All solid samples must undergo a documented thorough sample homogenization (i.e. formal cone and quartering) using inert utensils/mixing platforms that will not interfere with the target analytes.

6.2. Following the establishment of a valid initial calibration, a CCV standard and CCB must be analyzed daily after every 10 analyses or portion thereof, and at the end of sequence. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume.

6.2.1. If a failed CCB is the first of the day, and the concentration of a target analyte in a sample bracketed by the unacceptable ICB or CCB is less than

or equal to 10 times the absolute value of the concentration of the target analyte in the ICB or CCB, reanalyze the sample.

6.2.2. If a failed CCB is <u>not</u> the first of the day, and the concentration of a target analyte in a sample bracketed by the unacceptable CCB is less than or equal to 10 times the absolute value of the concentration of the target analyte in the CCB, reanalyze the sample.

6.3. Standard and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standards
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) LLRL Check
6) Method Blank (MB)
7) Laboratory Control Samples (LCS)
8) Laboratory Control Sample Duplicates (LCSD)
9) Samples (up to 10 analyses, excluding ICV or CCV analyses)
10) Continuing Calibration Verification (CCV)
11) Continuing Calibration Blank (CCB)
12) Matrix Spike (MS)
13) Matrix Spike Duplicate (MSD)
14) Samples (up to 10 analyses, excluding CCV analyses)
15) Ending CCV
16) Ending CCB

6.3.1. Item 5: The LLRL check standard is used to validate the low-level reporting limit. An acceptable LLRL check is required daily prior to sample analysis, every 8 hours thereafter during analysis, and at the end of sequence.

6.3.2. Item 6: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

6.3.2.1. One MB is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation event.

6.3.3. Item 7: The LCS is a known matrix which has been spiked with known concentration of specific target analyte. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

6.3.3.1. One LCS is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation event.

6.3.4. Item 8: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD).

6.3.5. Item 12: The MS is the actual sample matrix spiked with known concentration of specific target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.3.5.1. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently within an 8-hour preparation event.

6.3.5.2. The sample selected for spiking must be one of the samples collected for the specific BP project. If 10 or fewer BP samples are received, and no sample is designated for MS/MSD analyses, then a non-BP sample may be used.

6.3.5.3. Samples identified as trip or field blanks cannot be used for MS/MSD.

6.3.6. Item 13: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Technical Requirements for Environmental Laboratory Analytical Services, BP Laboratory Management Program (LaMP), Revision 09, July 30, 2007.

Appendix E

MULTIPLE CALIBRATION STANDARD DIGESTION

Calscience Environmental Laboratories, Inc.

►*MULTIPLE CALIBRATION STANDARD DIGESTION*

1. ***Initial Calibration Standard Solutions***

1.1. ***Measure 0.01, 0.1, 0.2, 0.5, 1.0 mL of the 1.0-ppm mercury working standard solution and 0.6 g of Teflon® chips into five certified clean digestion tubes. Mix thoroughly.***

1.2. ***Add 10 mL of the diluted aqua regia solution to each digestion tube.***

1.3. ***Place the digestion tubes in the pre-heated block digester, cover the digestion tubes with a clean watch glass, and heat for 2 minutes in the water bath maintained at 95°C.***

1.4. ***Remove the digestion tubes from the block digester and allow the digested standard solutions to cool.***

1.5. ***Add 50 mL of reagent water and 15 mL of the 5% $KMnO_4$ solution to each digestion tube.***

1.6. ***Mix the contents of the digestion tubes thoroughly.***

1.7. ***Place the digestion tubes in the pre-heated block digester, cover the digestion tubes with the same watch glass, and continue to heat for 30 minutes in the water bath maintained at 95°C.***

1.8. ***Remove the digestion tubes from the block digester and allow the digested standard solutions to cool.***

1.9. ***Add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested standard solutions to reduce excess permanganate.***

1.10. ***Adjust the volume of the digested standard solutions to 100 mL with de-ionized water to obtain the 0.1, 1.0, 2.0, 5.0 and 10.0 ppb initial calibration standards.***

1.11. ***Use the following calibration levels as guidance to prepare the initial calibration standards.***

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.10	1000	0.01	100
1.0	1000	0.1	100
2.0	1000	0.2	100
5.0	1000	0.5	100
10.0	1000	1.0	100

1.12. ***Use the following calibration levels as guidance to prepare the initial calibration standards for lower limit of quantitation.***

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.025	100*	0.03	100
0.10	1000	0.0	100
1.0	1000	0.1	100
2.0	1000	0.2	100
5.0	1000	0.5	100
10.0	1000	1.0	100

1.13. **** 100 ppb standard is diluted from 1.0 ppm working standard daily.***

1.14. ***The 2.0-ppb initial calibration standard is also used as the continuing calibration verification solution.***

1.15. ***The initial calibration standard solutions must be prepared fresh daily.***

Title : **EPA METHOD 8015B (M), TOTAL PETROLEUM HYDROCARBONS BY GC/FID**

Document No. : SOP-M507
Revision No. : 1.1
Supersedes : 1.0

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Revision 1.1 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 01/25/13
MANAGEMENT **DATE**

_____ 01-25-13
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA 8015B (M), Total Petroleum Hydrocarbons by GC/FID.

2. APPLICABLE MATRICES

2.1. Aqueous, soil, solids and sludges.

3. DETECTION LIMITS

3.1. Reporting Limits for TPH as Gasoline based on total purgeable hydrocarbons quantitation is 50–100 ug/L for aqueous matrices and 0.5 mg/kg for solid matrices.

3.1.1. Alternate purgeable volatile hydrocarbon types include: Aviation Fuel, Crude Oil.

3.2. Reporting Limits for TPH as Diesel based upon total extractable hydrocarbons quantitation is 50–500 ug/L for aqueous matrices and 5 mg/kg for solid matrices.

3.2.1. Alternate extractable semi-volatile hydrocarbon types include: Crude Oil, Jet A, Jet B, JP4, JP5, Fuel Oil, Generic Fuel Product, Hydraulic Oil, Kerosene, Mineral Oil, Motor Oil, Stoddard Solvent.

3.3. Reporting Limits for Carbon Range analysis based upon total carbon range C7–C36 or C7–C44 quantitation is 50–500 ug/L for aqueous matrices and 5 mg/kg for solid matrices.

3.4. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. This method is used to determine the total concentration of gas chromatographable petroleum-based hydrocarbons in three predominant ranges:

4.1.1. TPH as Gasoline (or other purgeable volatile hydrocarbon) corresponding to a range of hydrocarbons from approximately C4 to C12 and covering a boiling point range of < 50–200°C.

4.1.2. TPH as Diesel (or other extractable semi-volatile hydrocarbon) corresponding to a range of hydrocarbons from approximately C7 to C28 and covering a boiling point range of about 150–430°C.

4.1.3. Carbon Range corresponding to a range of hydrocarbons from approximately C7 to C44 and covering a boiling point range of < 150–430°C.

4.2. Approximate Analytical Time:

4.2.1. Preparation: < 5 minutes/sample for purge & trap.
30 minutes/sample for extraction.

4.2.2. Analysis: 45 minutes/sample.

5. METHOD SUMMARY

5.1. Samples to be analyzed for Gasoline or other purgeable volatile hydrocarbons are introduced into a gas chromatograph via a purge and trap sample concentrator. Samples to be analyzed for Diesel or other extractable semi-volatile hydrocarbons are solvent extracted and portion of the extract injected directly into a gas chromatograph. The gas chromatograph is temperature programmed to separate the hydrocarbons. Detection is achieved by the use of a flame ionization detector (FID). The samples analyzed for Gasoline are reported based on comparison to a gasoline standard or the specified reference hydrocarbon and samples analyzed for Diesel are reported based on comparison to a diesel standard or the specified reference hydrocarbon.

5.2. Samples analyzed for Carbon Range analysis are analyzed similar to Diesel, use Diesel as the calibration and quantitation standard but have additional straight chain alkane marker standards that serve to provide specific retention ranges that allow quantitation within that range.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the

applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: the process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.

6.12. Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality

indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.27. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Performance of this method is restricted to analysts experienced in the use of the instruments and apparatus required to execute this method and interpretation of the

outputs thereof. Each analyst must demonstrate the ability to generate acceptable results with this method and be approved by the applicable Group Leader prior to analyzing billable samples.

7.2. Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment that lead to artifacts and/or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferants under the conditions of the analysis by running laboratory method blanks.

7.3. The use of high purity solvents, reagents and pre-conditioning of disposables (i.e., filter paper, boiling stones, extraction thimbles) that come in contact with the sample or extract help to minimize interference problems.

7.4. Contamination by carryover can occur whenever high and low level samples are analyzed sequentially. Suspected high level samples should be analyzed diluted and at the end of the sequence to prevent carryover contamination. In addition, sample syringes, purging devices, and labware should be thoroughly rinsed with solvent between samples.

7.5. Autosampler positional contamination can also occur and can easily go undetected. For an autosampler position that is suspected to contained sample of unusually high concentration, a blank should be analyzed on that position (and the following position) prior to analyzing other samples.

8. SAFETY

8.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled as a potential health hazard.

8.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current Calscience Health & Safety Manual. In general, safety glasses and lab coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Processes that promote vaporization of volatile chemicals into the work area (e.g., separatory shakeout or sonication) should be performed inside an exhaust hood vented to the exterior of the laboratory.

8.4. Material Safety Data Sheets (MSDS) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. ►EQUIPMENT AND SUPPLIES

9.1. Purge/Trap Gas Chromatograph: Hewlett Packard 5890 Gas Chromatograph, Hewlett Packard 5890 Series II Gas Chromatograph, Agilent 6890N Network Gas Chromatograph, Agilent 7890A Gas Chromatograph, or equivalent configured with a

Tekmar LSC 2000 concentrator and an ALS 2016/2032 autosampler or equivalent instrumentation. The system is configured to allow for on-column injections.

9.2. Purge/Trap Gas Chromatographic Column: J&W Scientific DB-5, 30-m × 0.53-mm ID, 1.5-µm film thickness or equivalent.

9.2.1. Use the following operating parameters as guidance for TPH as gasoline analysis.

- Carrier Gas (***Nitrogen***) flow rate: 8–10 mL/minute
- Makeup Gas (***Nitrogen***) flow rate: 30 mL/minute
- Injector Temperature: No Injector
- Detector Temperature: 220°C (Manufacturer recommended)
- Temperature Program:
  1. Initial Temperature: 45°C, hold 6 minutes
  2. Program: 45°C to 150°C @ 5°C/minute
  3. ***Final Temperature/hold: 150°C, hold 2 minutes***

9.3. Extractable/Direct Injection Gas Chromatograph: Hewlett Packard 6890 Series Gas Chromatograph, Agilent 6890N Network Gas Chromatograph, Agilent 7890A Gas Chromatograph, or equivalent configured with Agilent 7683B Series Autosampler or equivalent instrumentation. The system is configured, specifically, for on-column injections.

9.4. Extractable/Direct Injection Gas Chromatographic Column: J&W Scientific DB-5, 10-m × 0.25-mm ID, 0.5- µm film thickness or equivalent.

9.4.1. Use the following operating parameters as guidance for TPH as diesel analysis.

- Carrier Gas (***Nitrogen***) flow rate: 2–5 mL/minute
- Makeup Gas (***Nitrogen***) flow rate: 20–25 mL/minute
- Injector Temperature: 280–320°C
- Detector Temperature: 280–320°C
- Temperature Program:
  1. Initial Temperature: 40°C, hold 0.3 minutes
  2. Program: 40°C to 320°C @ 60°C/minute
  3. Final Temperature/hold: 320°C, hold 3–6 minute

9.5. Instrument Software

9.5.1. Requires a PC based data system or equivalent.

9.5.2. Agilent GC ChemStation Version A.08.03[847], Agilent GC ChemStation Version A.09.01[1206], Agilent GC ChemStation Version B.03.02[341], or equivalent.

9.6. Instrument Maintenance and Troubleshooting

9.6.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.6.2. Additional information can be found in the user manual or operating guide for the specific instrument

9.7. Gases

9.7.1. High purity helium (as carrier).

9.7.2. Dry grade air.

9.7.3. Purified hydrogen.

9.7.4. High purity nitrogen (for concentration of extract)

9.8. Kuderna-Danish (KD) apparatus.

9.8.1. Concentrator tubes, 10-mL, ground glass joints.

9.8.2. Snyder columns, three ball macro.

9.8.3. Evaporative flasks, 250-mL.

9.8.4. Concentrator tube holder with nitrogen injectors.

9.9. Shakers

9.9.1. Lab-Line Orbit Shaker or equivalent (aqueous)

9.9.2. Lab-Line Dual Action Shaker or equivalent (solids)

9.10. Analytical balance capable of weighing to the nearest 0.1 g.

9.11. Lab-Line Multi-Unit (Six Station) Extraction Heater

9.12. Boiling chips, pre-rinsed with solvent.

9.13. Syringes, 10-µL capacity, 5-mL glass gastight, additional volumes as necessary.

9.14. Purging vessels, as specified for purge and trap unit, cleaned.

9.15. 2000-mL glass beakers

9.16. Vials, 40-mL capacity, equipped with a Teflon-lined screw cap, pre-cleaned.

9.17. Separatory funnels, 1-L and 2-L with Teflon stopcock.

9.18. Fume Hood, exhaust vented from building.

9.19. Ring stands or fume hood hardware to hold separatory funnels.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Methylene Chloride, pesticide grade.

10.1.2. Methanol, purge and trap grade.

10.1.3. Sodium Sulfate, anhydrous, granular.

10.1.4. Silica Gel, 6–12 Mesh (Nominal)

10.1.5. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. ►Refer to the following tables for standard concentrations, alternate spiking levels will be noted where appropriate.

SPIKE CONCENTRATION TABLE

Analyte	Matrix	Stock Conc (ppm)	Volume Added (mL)	Initial Sample Amount	Unit	Final Volume (mL)	On Column (µg)	Final Conc (ppm) In Extract	Final Conc (ppm) In Sample
TPH as Gas	Aqueous	2000	0.005	5.00	mL	5.00	10.0	2.00	2.00
In Methanol (P/T)	Solid	2000	0.005	1.00	g	5.00	10.0	2.00	10.0
TPH as Diesel	Aqueous	20000	0.500	500	mL	25.0	1.20	400	20.0
Extractable in	Solid	20000	0.200	10.0	g	10.0	1.20	400	400
Methylene Chloride	Aqueous	20000	0.100	500	mL	5.00	1.20	400	4.00

SURROGATE CONCENTRATION TABLE

Analyte	Matrix	Stock Conc (ppm)	Volume Added (mL)	Initial Sample Amount	Unit	Final Volume (mL)	On Column (µg)	Final Conc (ppm) In Extract	Final Conc (ppm) In Sample
BFB	Aqueous	500	0.001	5	mL	5.0	0.50	0.1	0.10
In Methanol (P/T)	Solid	500	0.001	1.0	g	5.0	0.50	0.1	0.50
C28	Aqueous	1000	1.25	500.00	mL	25.00	0.15	50.00	2.50
In Methylene Chloride	Solid	1000	0.5	10.00	g	10.00	0.15	50.00	50.0

Note: BFB = 1,4-Bromofluorobenzene; C28 = n-Octacosane

10.2.2. For the previous tables, the following equations apply.

$$\text{Spike Concentration}_{\text{SAMPLE}}\ (\text{ppm}) = \frac{\text{Stock Conc (ppm)} \times \text{Spike Vol (mL)}}{\text{Initial Sample Amount (mL or g)}}$$

$$\text{Spike Concentration}_{\text{EXTRACT}}\ (\text{ppm}) = \frac{\text{Stock Conc (ppm)} \times \text{Spike Vol (mL)}}{\text{Final Extract Volume (mL)}}$$

10.2.3. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

11.1. Holding times are based on generic guidance in EPA SW-846, Chapter 4, Table 4.1, Update III.

11.2. Samples should be collected in Teflon-lined glass containers with minimal headspace.

Analysis	Sample Matrix	Volume	Preservation	Holding Time
Gasoline or other Volatile Fuel	Soil/solid	2 oz	Cool, ≤ 6°C	Analyzed within 14 days.

Analysis	Sample Matrix	Volume	Preservation	Holding Time
Gasoline or other Volatile Fuel	Soil/solid	3 × EnCore®	Cool, ≤ 6°C	Extract within 48 hours, Analyzed within 14 days.
	Water	2 × 40 mL	Cool, ≤ 6°C	Analyzed within 14 days, with HCl to pH < 2.

Analysis	Sample Matrix	Volume	Preservation	Holding Time
Diesel or other Semi-Volatile Fuel	Soil/solid	2 oz	Cool, ≤ 6°C	Extract within 14 days, Analyzed within 40 days.
	Water	500–1000* mL	Cool, ≤ 6°C	Extract within 7 days, Analyzed within 40 days.

* Standard aqueous volume is 500 mL; special projects may require 1000 mL.

11.3. Samples submitted with acid preservation should be designated as such on the chain of custody and containers.

11.4. All samples must be iced or refrigerated from the time of collection until extraction or analysis.

11.5. All samples must be extracted and analyzed prior to expiration of the holding time.

11.6. Additional sample quantities may be required for analysis of matrix-specific QC.

11.7. Additional sample handling information can be found in the Sample Control SOPs.

12. QUALITY CONTROL

12.1. The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control.

12.2. Surrogates shall be added to the QC samples.

12.3. The low concentration standard of the initial multipoint calibration should be at or below the applicable reporting limit. When the low concentration standard is above the reporting limit, a spike at the reporting limit shall be analyzed as part of the initial multipoint calibration and documented. The purpose is to verify that detection and quantitation at the reporting limit is achievable.

12.4. Matrix-Based Quality Control (Surrogates and MS/MSDs)

12.4.1. Matrix-based Quality Control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicates (MS/MSD) and surrogates added to each sample.

12.4.2. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The upper and lower acceptance limits for each surrogate spike compound is the historical average recovery ±3S.

12.4.2.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

12.4.2.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration. This measure alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.4.2.3. By itself, unacceptable surrogate recovery does not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.4.2.3.1. Check the surrogate spiking solutions for degradation and contamination.

12.4.2.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample should be re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.4.2.3.2.1. If, upon re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.4.2.3.2.2. If the MB surrogates are unacceptable, all associated sample data must invalidated and all associated samples re-analyzed.

12.4.3. The acceptance criteria for MS/MSDs are as follows:

12.4.3.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.4.3.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.4.3.2.1. Matrix effects or poor instrument performance/technique typically causes unacceptable % REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.4.3.2.2. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must invalidated and all associated samples re-analyzed.

12.5. Event-Based Quality Control (LCS/LCSDs and MBs)

12.5.1. Event-based quality control consists of QC samples prepared and processed with each batch. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.5.2. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The upper and lower acceptance limits for %REC and RPD of each LCS/LCSD compound are the historical average recovery ±3S. All LCS/LCSD compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, the problem must be identified and corrected. The LCS and all associated samples must then be re-analyzed.

12.5.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

12.5.2.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

12.5.3. Ideally, the concentration of target analytes in a method blank (MB) should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

12.5.3.1. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB without qualification.

12.5.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-analyzed.

12.6. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. EXTRACTABLE/ DIRECT INJECTION CALIBRATION

13.1.1. Prior to the analysis of any samples, the following analytical parameters must be established:

13.1.1.1. A valid five-point initial calibration curve where the %RSD is less than or equal to 20%. The recommended calibration levels are 5, 200, 400, 800, and 1600 ppm, but may vary depending upon the analytical criteria specific to the project at hand.

13.1.1.2. A daily calibration (midpoint) verification (CV) standard with a %D (between the CV and initial calibration RFs) being less than or equal to 15%. The daily CV concentration shall vary on a weekly basis and will be within the calibration range. The RF from the daily CV shall be used for quantitation.

13.1.2. When a new five-point initial calibration curve is generated, it must be confirmed acceptable by the analysis of an external midpoint standard of a separate source. For the initial calibration to be acceptable, the %D between the initial calibration RF and external midpoint standard must be less than or equal to 15%.

13.1.3. If a daily CV does not pass (%D > 15%), it should be reanalyzed. If upon reanalysis, it passes, then the system shall be deemed "in-control" and the analyst may proceed with analysis of samples. If upon reanalysis, it does not pass, the cause should be investigated and a new five-point initial calibration curve must be generated and verified prior to analysis of samples.

13.2. PURGE AND TRAP CALIBRATION

13.2.1. Prior to the analysis of any samples, the following analytical parameters must be established:

13.2.1.1. A valid five-point initial calibration curve where the %RSD is less than or equal to 20%. The recommended calibration levels are 0.05, 1.0, 2.0, 5.0, and 10.0 ppm, but may vary depending upon the analytical criteria specific to the project at hand.

13.2.1.2. A daily calibration (midpoint) verification (CV) standard with a %D (between the CV and initial calibration RFs) being less than

or equal to 15%. The daily CV concentration shall vary on a weekly basis and will be within the calibration range. The average RF from the initial calibration curve shall be used for quantitation.

13.2.1.2.1. When a new five-point initial calibration curve is generated, it must be confirmed acceptable by the analysis of an external midpoint standard of a separate source. For the initial calibration to be acceptable, the %D between the initial calibration RF and external midpoint standard must be less than or equal to 15%.

13.2.1.2.2. If a daily CV does not pass (%D > 15%), it should be reanalyzed.

13.2.1.2.3. If upon reanalysis, it passes, then the system shall be deemed "in-control" and the analyst may proceed with analysis of samples. If upon reanalysis, it does not pass, the cause should be investigated and a new five-point initial calibration curve must be generated and verified prior to analysis of samples.

13.3. RETENTION TIME WINDOWS

13.3.1. Total Petroleum Hydrocarbons (TPH) are distinguished on the basis of the retention time ranges for the characteristic components in each fuel type.

13.3.2. The retention time range for TPH Gasoline and Diesel is equivalent to the range of the reference standard. Typically there will be an overlap of the upper range of Gasoline with the lower range of Diesel. The EPA 8015B (M) method is modeled on the defunct California DHS LUFT method without the established retention time range markers of the EPA 8015B Method.

13.3.3. Other fuel types will use the characteristic retention time range of the reference standard.

13.3.4. Carbon Chain analysis uses a Diesel standard for Calibration and QC samples with additional Alkane range markers, reference Section 13.3.5.

13.3.5. The retention time for each Carbon-Chain Analysis range is defined during initial calibration and is used to quantitate the hydrocarbons found during analysis. Each range is established from the retention times of the following alkane hydrocarbon markers:

- C5 Pentane
- C6 n-Hexane
- C7 n-Heptane
- C8 n-Octane
- C9 n-Nonane
- C10 n-Decane
- C11 n-Undecane
- C12 n-Dodecane

- C13 n-Tridecane
- C14 n-Tetradecane
- C16 n-Hexadecane
- C18 n-Octadecane
- C20 n-Eicodecane
- C22 n-Docosane
- C23 n-Tricosane
- C24 n-Tetracosane
- C28 n-Octacosane
- C32 n-Dotriacontane
- C36 n-Hexatriacontane
- C40 n-Tetracontane
- C44 n-Tetratetracontane

14. PROCEDURE

14.1. EXTRACTION/DIRECT INJECTION METHOD

14.1.1. ►SOLID SAMPLE PREPARATION

14.1.1.1. Take a clean 40-mL vial and label it with aqua tape (aqua tape for methylene chloride) and the appropriate sample identification.

14.1.1.2. Place the vial on a top loading balance and tare the balance to zero.

14.1.1.3. Take the appropriate sample, remove the top layer of sample (about ¼ inch) and weigh out 10-g sample into the vial.

14.1.1.4. Add approximately 2-g sodium sulfate and mix with a clean spatula until the sample is "free-flowing". If additional sodium sulfate is required, repeat with additional 2-g portions (not to exceed 10-g. total) of sodium sulfate until sample becomes "free flowing."

14.1.1.5. **OPTIONAL**: Add 1–2-g Silica Gel to remove polar, non-hydrocarbon oil and greases if required by project requirements.

14.1.1.6. Add 0.5-mL surrogate solution.

14.1.1.7. Add 10-mL of pesticide grade methylene chloride to the vial and tightly cap the vial.

14.1.1.8. Place the vial on shaker machine for 4 minutes. Transfer the methylene chloride layer into clean 40-mL holding vial labeled with the appropriate sample identification.

14.1.1.9. Transfer sufficient concentrated extract into 2-mL autosampler vial for analysis.

14.1.1.10. Store all extracts at 4°C until analysis.

14.1.2. WATER SAMPLE PREPARATION

14.1.2.1. 500-mL Extraction with Partial Concentration

14.1.2.1.1. Take a clean 1-L separatory funnel and label it with aqua tape and the appropriate sample identification.

14.1.2.1.2. Mark sample container to measure amount of sample provided.

14.1.2.1.3. Shake the sample to homogenize and transfer approximately 500 mL into the separatory funnel.

14.1.2.1.4. Add 25 mL of pesticide grade methylene chloride to sample container, cap, shake and pour into separatory funnel.

14.1.2.1.5. Using water, measure volume of sample provided by pouring water into sample container to mark and then pouring water into a graduated cylinder to measure total volume. Record volume in logbook.

14.1.2.1.6. Add 1.25-mL surrogate solution to sample in separatory funnel.

14.1.2.1.7. Cap the separatory funnel and place on shaker machine for 2 minutes, venting periodically into a fume hood.

14.1.2.1.8. Place in ring stand and allow phases to separation.

14.1.2.1.9. Transfer the lower methylene chloride layer into a 250-mL Erlenmeyer flask labeled with aqua tape and the sample identification. Repeat extraction two additional times with 25-mL portions of methylene chloride and collect all extract in the flask.

14.1.2.1.10. Add 5–10-g sodium sulfate to the flask to remove water entrained in the extract. Sodium Sulfate will "clump" when attached to water. Sufficient water is removed when the sodium sulfate added remains dispersed along bottom of flask without clumping.

14.1.2.1.11. **OPTIONAL**: Add 1–2-g silica gel to remove polar, non-hydrocarbon oil and greases if required by project requirements.

14.1.2.1.12. Extract is ready for partial concentration.

14.1.2.1.13. Take entire volume of Methylene Chloride extract and concentrate to 25 mL using a 40-mL glass VOA vial and nitrogen gas injector until level matches reference 25-mL level in second vial used for this purpose.

14.1.2.1.14. Transfer extract into 2-mL autosampler vials labeled with the appropriate sample identification.

14.1.2.1.15. Lower reporting levels will require concentration of extract as follows:

14.1.2.1.15.1. For 100-ppb RL = 2.5-mL extract, concentrate to 0.5 mL with 0.25 mL of surrogate solution, LCS with 0.1-mL solution.

14.1.2.1.15.2. For 50-ppb RL = 5.0-mL extract, concentrate to 0.5 mL with 0.125 mL of surrogate solution, LCS with 0.05-mL solution.

14.1.2.1.15.3. Transfer appropriate amount of extract into a 10-mL K-D concentrator tube labeled with aqua tape and the sample identification.

14.1.2.1.15.4. Place K-D concentrator in nitrogen evaporator apparatus and bubble nitrogen until the proper concentrate volume is achieved. Transfer final extract concentrate in 2-mL autosampler vials labeled with the appropriate sample identification.

14.1.2.2. 1000-mL Extraction with Full Concentration

14.1.2.2.1. Take a clean 2-L separatory funnel and label it with aqua tape and the appropriate sample identification.

14.1.2.2.2. Mark sample container to measure amount of sample provided.

14.1.2.2.3. Shake the sample to homogenize and transfer all the sample (assuming 1000-mL sample container) into the separatory funnel.

14.1.2.2.4. Add 60 mL of pesticide grade methylene chloride to sample container, cap, shake and pour into separatory funnel.

14.1.2.2.5. Using water, measure volume of sample provided by pouring water into sample container to mark and then pouring water into a graduated cylinder to measure total volume Record volume on log book.

14.1.2.2.6. Add 0.2-mL surrogate solution to sample in separatory funnel, LCS add 0.05-mL solution.

14.1.2.2.7. Cap the separatory funnel and place on shaker machine for 2 minutes, venting periodically into a fume hood.

14.1.2.2.8. Place in ring stand and allow phases to separation.

14.1.2.2.9. Transfer the lower methylene chloride layer into a 250-mL Erlenmeyer flask labeled with aqua tape and the sample identification. Repeat extraction two additional times with 60-mL portions of methylene chloride and collect all extract in the flask.

14.1.2.2.10. Add 5–10-g sodium sulfate to the flask to remove water entrained in the extract. Sodium Sulfate will "clump" when attached to water. Sufficient water is removed when the sodium sulfate added remains dispersed along bottom of flask without clumping.

14.1.2.2.11. **OPTIONAL**: Add 1–2-g silica gel to remove polar, non-hydrocarbon oil and greases if required by project requirements.

14.1.2.2.12. Extract is ready for full concentration.

14.1.2.2.13. Take entire volume of Methylene Chloride extract and concentrate using 250-mL KD Evaporator Flask, 10-mL Concentrator Tube and 3-Bubble Snyder Column.

14.1.2.2.14. Place in hot bath using 2000-mL beakers filled with water on heating unit.

14.1.2.2.15. Concentrate to 2 mL.

14.1.2.2.16. Transfer extract into 2-mL autosampler vials labeled with the appropriate sample identification.

14.1.2.3. Store all extracts and concentrates at 4°C until analysis.

14.1.2.4. For projects that have raised reporting limits, difficult matrices, or suspected to contain high analyte levels, the sample amounts and volumes may be modified as appropriate.

14.1.3. SAMPLE ANALYSIS

14.1.3.1. Program the analytical sequence into the data system.

14.1.3.2. Load one of the extract vials for each sample into the autosampler tray according to the sequence entered into the data system and store duplicate vials at 4°C as backup for potential reanalysis.

14.1.3.3. The extracts are analyzed by direct injection into the E/DI gas chromatograph via the autoinjector.

14.1.3.4. For high level samples where detector saturation is of concern, extract should be diluted to achieve a signal within the quantitation range, preferably near mid calibration range.

14.1.3.5. For samples that have been overdiluted (detector response below the low standard), the sample should be reprepared with less of a dilution to achieve a signal within the quantitation range, preferably near mid calibration range.

14.2. PURGE AND TRAP METHOD

14.2.1. SAMPLE PREPARATION

14.2.1.1. The purge and trap procedure involves minimal sample preparation. A portion of the sample is transferred directly to the purge and trap sample concentrator.

14.2.2. SOIL/SOLID SAMPLE ANALYSIS

14.2.2.1. Place a clean purging vessel on a top loading analytical balance and tare the balance to zero.

14.2.2.2. Take the appropriate sample, remove top layer of sample (about ¼ inch), weigh out 1 g into the clean purging vessel, add 5 mL of reagent water, and add surrogate or spiking compounds when required for the project.

14.2.2.3. Attach the vessel to the P/T autosampler minimizing time vessel is open to the environment.

14.2.2.4. Repeat above steps for all samples in batch.

14.2.2.5. Initiate the analytical sequence.

14.2.2.6. For suspected high level samples where detector saturation is of concern, appropriate dilutions should be made by purging a smaller aliquot of sample.

14.2.2.7. For high level samples where further dilution could result in non-representative aliquots, methanolic extraction followed by P/T of the extract should be performed by the following procedure.

14.2.2.7.1. Take the appropriate sample, remove top layer of sample (about ¼ inch), and weigh out 4 g into a clean 40-mL vial.

14.2.2.8. Add 10 mL of purge and trap grade methanol to the vial and tightly cap.

14.2.2.9. Shake the sample for 2 minutes.

14.2.2.9.1. High Level Samples: Transfer the methanol layer into a small vial minimizing headspace. Label with the appropriate sample identification.

14.2.2.9.2. Dispose 40-mL vial and store extract vial at 4°C until analysis.

14.2.2.10. Using a microsyringe, transfer an aliquot of the extract into a cleaned purging vessel containing 5 mL of water containing surrogate, internal, and, if applicable, matrix spiking standards.

14.2.2.11. Attach the vessel to the P/T autosampler minimizing time vessel is open to the environment.

14.2.2.12. Initiate the analytical sequence.

14.2.3. WATER SAMPLE ANALYSIS

14.2.3.1. Using a 5-mL gastight syringe, transfer 5 mL of the sample into a clean purging vessel and add surrogate or spiking compounds.

14.2.3.2. Attach the vessel to the P/T autosampler minimizing time vessel is open to the environment.

14.2.3.3. Repeat above steps for all samples in batch.

14.2.3.4. Initiate the analytical sequence.

14.2.3.5. For medium and high level water samples where detector saturation is of concern, appropriate dilutions should be made by purging a smaller aliquot of sample.

14.3. At the time of sample loading, the pH of each aqueous sample shall be measured with narrow range pH paper to determine if the pH of the sample is < 2 (refer to SOP-T301). The pH range (< 2 or ≥ 2) of each sample shall be documented on the log book.

14.4. The samples are loaded in the following order or in any other acceptable order:

1) Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicates (LCSD)
4) Method Blank (MB)
5) Samples (up to 10 per first portion of batch)
6) Calibration Verification (CV)
7) Samples (up to 10 per second portion of batch)
8) Matrix Spike (MS)
9) Matrix Spike Duplicate (MSD)
10) Ending CCV

14.4.1. Item 1: A CCV is used to verify the acceptance of the initial five point calibration on a continuing basis. An acceptable CCV is required at least every 12 hours and at the end of the sequence.

14.4.1.1. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample re-analyses that would be required in the event of an unacceptable CCV.

14.4.1.2. In establishing the CCV frequency, all samples and dilutions are counted as sample runs.

14.4.2. Item 2: A LCS is a known matrix that has been spiked with a known concentration of all target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the

processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.2.1. For aqueous samples, the LCS consists of the compounds spiked into clean water. For solid samples, the LCS consists of the compounds spiked into washed sea sand.

14.4.2.2. A LCS is required for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.3. Item 3: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCSD, in combination with the LCS, can be used to assess the precision of the analytical process expressed as relative percent difference (RPD).

14.4.4. Item 4: The MB is a known matrix similar to the samples being analyzed that is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (e.g., surrogates, etc.).

14.4.4.1. For aqueous samples, the MB consists of organic free water. For solid samples, the MB consists of washed sea sand.

14.4.4.2. A MB is required with every batch of 20 samples per matrix or portion thereof, whichever is more frequent. It should be noted, however, that as necessary (e.g., after high level samples), additional MBs and instrument blanks may be placed in the sequence.

14.4.5. Item 5: Up to 20 samples per batch. High concentration samples should be sufficiently diluted to ensure that instrumentation is not contaminated. Dilution of samples will result in increased reporting limits.

14.4.6. Item 6: The MS is the actual matrix spiked with known concentrations of all target analytes. The sample that is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.6.1. The purpose of a MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC) of the spiked compounds.

14.4.6.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently. This approach is considered "closed batch" as opposed to "open batch".

14.4.7. Item 7: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MSD, in combination with the MS, can be used to

assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

14.4.8. Item 8: An acceptable CV is required at the completion of every analytical sequence.

14.5. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the run logbook.

14.6. Initiate the sequence.

15. CALCULATIONS

15.1. Analyte quantitation is accomplished by comparison of chromatographic profile and relative retention times between the sample and retention time range previously established in section 13.3.

15.2. For this method, the data system shall be programmed to integrate the total resolved and unresolved peak area within the retention time range for use in the calculations below. The analyst shall verify and ensure proper baseline integration of all chromatographic output.

15.3. The analyst must identify and record the surrogate area peak. This value is subtracted out of the total chromatographic peak area for each output as detailed in calculations below. In addition, this value is used during data entry so that automated calculations can be performed.

15.4. Standards are prepared using the following formula:

$$\text{Standard Concentration (ppm)} = \frac{\text{Standard Material } (\mu g)}{\text{Solvent (mL)}}$$

15.5. The response factor (RF) of the reference standard is calculated using the following formula:

$$\text{Response Factor} = \frac{\text{Area Count}_{(\text{STANDARD})} - \text{Area Count}_{(\text{SURROGATE})}}{\text{Standard Concentration (ppm)}}$$

15.6. The sample concentration shall be calculated against the standard reference material for the analyte requested using the following formula:

$$\text{Sample Concentration (ppm)} = \frac{\text{Area Count}_{(\text{SAMPLE})} - \text{Area Count}_{(\text{SURROGATE})}}{\text{RF}} \times \frac{V_F}{S} \times \text{DF}$$

where: RF = Response factor (AC/ppm)
V_F = Final volume of extract.
S = Amount of sample in mL for liquid (g for solid).
DF = Dilution factor

15.7. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{CF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the average CFs for the target analyte.
CF_{ave} = mean of the 5 initial CFs for the target analyte.

15.8. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|CF_{ave} - CF|}{CF_{ave}} \times 100$$

where: %D = percent difference of target analyte.
CF = target analyte's daily CF.
CF_{ave} = mean of the 5 initial CFs for the target analyte.

15.9. The recovery of LCS compounds is calculated as follows:

$$\%REC_{LCS} = \left(\frac{C_{recovered}}{C_{added}}\right) \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.10. The recovery of the MS compounds is calculated as follows:

$$\%REC_{MS} = \left(\frac{C_{recovered} - C_{sample}}{C_{added}}\right) \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.11. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte recovered in measurement 1.
C_2 = concentration of target analyte recovered in measurement 2.

15.12. Where the chromatographic pattern significantly differs from that of the target standard, the total peak area should be quantitated using the target standard and

result qualified to indicate that chromatographic pattern does not match that of the calibration standard.

15.13. Unless specified otherwise by the client, all TPH concentrations will be reported in µg/L (ppb) for aqueous samples and mg/kg (ppm) for solid samples.

15.14. The data reported shall adhere to the significant figures, rounding and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the

area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The upper and lower acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ±3S. All LCS/LCSD compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, the problem must be identified and corrected.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.3. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The upper and lower acceptance limits for each surrogate spike compound is based upon the historical average recovery ± 3S.

18.3.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

18.3.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual

sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.3. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.3.1. Check the internal standard and surrogate spiking solutions for degradation and contamination.

18.3.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample or extract should be re-analyzed.

18.3.3.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and/or re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-extracted and re-analyzed.

18.3.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSDs are as follows:

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically causes unacceptable % REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the

LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for water samples and µg/kg (ppb) for oil, soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries an MS/MSD data set is does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. REFERENCES

22.1. EPA Method 8000B, Determinative Organic Separations, Revision 2, "Test Methods for Evaluating Solid Waste, Volume 1B, Laboratory Manual", Third Edition, US Environmental Protection Agency, September, 1996.

22.2. EPA Method 8015B, Non-Halogenated Organics using GC/FID, Revision 2, "Test Methods for Evaluating Solid Waste, Volume 1B, Laboratory Manual", Third Edition, US Environmental Protection Agency, September, 1996.

23. TABLES, DIAGRAMS, FLOWCHARTS AND DATA VALIDATION

23.1. Appendix A: Additional Quality Control Criteria for Department of Defense Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8015B Revision 2 are noted.

Calscience SOP M507 Section	Reference Document EPA Method 8015B Section	Summary of Modification
All	All	Revise criteria for various fuel types.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
1.0	Section 3: Revise reporting limits and add reference to detection limits. Section 6: Add LOD/LOQ definitions. Section 9: Update the list of equipment and supplies. Section 10: Revise standard preparation procedure. Section 13: Insert additional hydrocarbon markers. Section 14: Revise solid sample preparation procedure for extraction/direct injection method, and revise CV to CCV. Section 23: Add Appendix A. Section 24: Add modifications. Section 25: Add revision history. Appendix A: Add DoD requirements.	K. Chang	03/30/12
1.1	Section 9: Update instrument parameters and gas supplies. Section 10: Revise standard preparation procedure. Section 14: Revise solid sample preparation procedure for extraction/direct injection method. Section 25: Add revision history.	I. Kwak / S. Tseng	02/01/13

Appendix A

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA 8015B (M), Total Petroleum Hydrocarbons by GC/FID – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

5.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

5.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.3. No samples shall be analyzed without a valid LOD.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Continuing Calibration Verification (CCV)

5.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

5.3.2. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.4. Retention Time Window

5.4.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a low-to-midpoint CCV standard at the beginning of an analytical sequence.

5.4.1.1. When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S.

5.4.1.2. When initial calibration is not performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the low-to-midpoint CCV standard ± 3S.

5.5. Event Based Quality Control (MBs and LCS/LCSDs)

5.5.1. Method Blanks (MBs)

5.5.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.5.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.5.1.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

5.5.1.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.5.2. Laboratory Control Samples (LCS/LCSDs)

5.5.2.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.5.2.1.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.5.2.2. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.6. Matrix Based Quality Control (Surrogates and MS/MSDs)

5.6.1. Surrogates

5.6.1.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall

be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.2. Matrix Spikes (MS/MSDs)

5.6.2.1. The RPD is ≤ 30%.

5.6.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

6. PROCEDURE

6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2. Standard and sample vials are loaded in the following or other logical order:

1) Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicate (LCSD)
4) Method Blank (MB)
5) Samples (up to 10 per batch, excluding QC check samples and MBs)
6) Matrix Spike (MS)
7) Matrix Spike Duplicate (MSD)
8) Ending CCV

6.2.1. Items 1 and 8: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2.2. Item 5: Up to 10 sample (excluding QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

6.2.3. Item 6: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.2.3.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.2.4. Item 7: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 25, 2010.

Title : **EPA 8015B, TOTAL PETROLEUM HYDROCARBONS (GRO/DRO) BY GC/FID**

Document No. : SOP-M505
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Revision 1.2 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 08/09/12
MANAGEMENT **DATE**

_____ 08-09-12
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 8015B, Total Petroleum Hydrocarbons (GRO/DRO) by GC/FID.

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous matrices, soils, solids and sludges.

3. DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for this method are as follows:

	Solid	Aqueous
GRO (C_6 – C_{10})	0.5 mg/kg	50 mg/L
DRO (C_{10} – C_{28})	5 mg/kg	100 mg/L

3.2. The EQLs will be proportionally higher for samples which require dilution or reduced sample size.

4. SCOPE AND APPLICATION

4.1. EPA Method 8015B is used to determine the total concentrations of petroleum hydrocarbons in two separate ranges.

4.1.1. Gasoline range organics (GROs) correspond to the range of alkanes from C_6 to C_{10} and cover a boiling point range of approximately 60–170°C.

4.1.2. Diesel range organics (DROs) correspond to the range of alkanes from C_{10} to C_{28} and cover a boiling point range of approximately 170–430°C.

4.2. The approximate preparation and analysis times are as follows:

	Purge-and-Trap	Solvent Extraction
Preparation	< 5 min/sample	30 min/sample
Analysis	45 min/sample	45 min/sample

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of purge-and-trap system and gas chromatograph (GC), and skilled in the interpretation of gas chromatograms.

5. METHOD SUMMARY

5.1. EPA Method 8015B describes chromatographic procedures that will allow for the identification of gasoline and diesel range organics in the extract and their qualitative and quantitative analysis by gas chromatography. Detection is achieved using a flame ionization detector (FID).

5.2. Prior to performing this procedure for the analysis of gasoline range organics (GROs), the appropriate sample introduction technique must be performed on each sample. Acceptable introductory methods include the following:

Type of Sample Preparation/Introduction	EPA Method No.	SOP No.
Purge and Trap	5030B	SOP-M212
Closed System Purge and Trap	5035	SOP-M213

5.3. ►Prior to performing this procedure for the analysis of diesel range organics (DROs), the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory methods include the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510C	SOP-M200
Ultrasonic Extraction	3550B	SOP-M202
Orbital Shaker Apparatus		

5.4. The samples analyzed for GROs are reported based on comparison to a gasoline standard, and the samples analyzed for DROs are reported based on comparison to a diesel standard.

5.5. Fused silica capillary columns are necessary for the analysis of petroleum hydrocarbons.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. ►***Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.***

6.13. ►***Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.***

6.14. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.15. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.16. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.17. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.18. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.19. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.20. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.21. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.22. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.23. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.24. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.26. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.27. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.28. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination. In addition, sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

7.2.1. The use of high purity solvents and reagents, and the pre-conditioning of disposables (i.e., filter paper, boiling stones, and extraction thimbles) that come in contact with the sample or extract help to minimize interferences.

7.3. Autosampler positional contamination can also occur and can easily go undetected. For an autosampler position that is suspected to contain sample of unusually high concentration, a solvent blank should be analyzed on that position (and the following position) prior to analyzing other samples.

8. SAFETY

8.1. Extraction must be performed in a fume hood vented to the exterior of the laboratory.

8.2. Methylene chloride creates excessive pressure very rapidly. Extreme care must be taken when methylene chloride is added to the sample bottle and to the separatory funnel. In each case, after adding methylene chloride, vent often to avoid pressure build-up and possible explosion.

8.3. For the safety of the analyst, cracked or broken glassware should be immediately discarded into a broken glassware receptacle. Broken glassware shall not be used in any step of the extraction.

8.4. To ensure the safety of the analyst during any possible emergency situation, chemists shall not perform extractions alone. Another chemist must be present during any extraction process.

8.5. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Hewlett-Packard 5890 Series II Gas Chromatograph configured with a low dead volume glass lined injector and PC based data system or equivalent.

9.1.1. Purge-and-Trap Concentrator: Teledyne Tekmar-Dohrmann 3100 or equivalent.

9.1.2. Purge-and-Trap Autosampler: Teledyne Tekmar, Varian Archon, Hewlett-Packard, OI Analytical DPM-16, or equivalent.

9.1.3. Direct Injection Autosampler: Hewlett-Packard 7673 or equivalent.

9.2. ►***Instrument Software***

9.2.1. ***Agilent GC ChemStation Version A.09.01[1206], Agilent GC ChemStation Version B.04.02[98], or equivalent.***

9.3. ►***Instrument Maintenance and Troubleshooting***

9.3.1. ***Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.***

9.4. Primary Detection Channel

9.4.1. Detector: Flame ionization detector (FID).

9.4.1.1. Carrier and Makeup Gas: High purity helium.

9.4.1.2. Reduction and FID Fuel Gas: High purity hydrogen.

9.4.1.3. Oxidation and FID Combustion gas: High purity air.

9.4.2. Column: 30-m × 0.53-mm ID, 1.5-µm film thickness, capillary, fused silica, J&W Scientific DB-5 or equivalent.

9.5. Purge Gas: High purity helium.

9.6. Extract Concentration Gas: High purity nitrogen.

9.7. pH indicator paper, narrow range (0.0 – 3.0).

9.8. Purge vessel, vial (1" diameter, 40-mL capacity) or tube (¾" diameter, 30-mL capacity), glass, disposable.

9.9. Balance, top loading, capable of accurately weighing to the nearest 0.01 g.

9.10. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with N.I.S.T. Traceable Certification.

9.11. Syringes, 5-mL, gastight, Teflon Luer Lock (TLL) termination, Hamilton 1000 Series or equivalent with N.I.S.T. Traceable Certification.

9.12. Refer to the specific SOPs of the purge-and-trap or solvent extraction methods for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Hydrochloric acid (HCl), 1:1 (v/v). Prepare the solution by diluting concentrated HCl (ACS grade or equivalent) with reagent water.

10.1.4. Sodium bisulfate, $NaHSO_4$, anhydrous, ACS grade or equivalent.

10.1.5. Methylene chloride, CH_2Cl_2, pesticide grade or equivalent.

10.1.6. Methanol, CH_3OH, purge and trap grade or equivalent.

10.1.7. Silica gel, anhydrous, 6–12-mesh (nominal).

10.1.8. Refer to the specific SOPs of the purge-and-trap or solvent extraction methods for additional reagents.

10.1.9. All reagents must be inspected and documented prior to use.

10.2. ►Standards

10.2.1. Pre-certified stock standard solutions or solids, each in sealed glass ampules or bottles, containing various concentrations gasoline compounds, diesel compounds, and surrogates are used to prepare calibration and check standards.

10.2.2. Gasoline calibration standard solutions containing 2000 ppm of gasoline compounds and 100 ppm of 1,4-bromofluoro-benzene (BFB) surrogate in methanol are used to prepare gasoline calibration standards.

10.2.2.1. The gasoline calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppm)				
Gasoline	0.05	1.0	2.0	5.0	10.0
BFB	0.02	0.05	0.1	0.3	0.5

10.2.2.2. The ***2.0-ppm*** standard is also used as the gasoline continuing calibration verification solutions.

10.2.3. Diesel calibration standard solution containing 20000 ppm of diesel compounds and 1000 ppm of ***n-octacosane*** surrogate in methylene chloride is used to prepare diesel calibration standards.

10.2.3.1. The diesel calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppm)				
Diesel	5	200	400	800	1600
n-Octacosane	0.625	25	50	100	200

10.2.3.2. The ***400-ppm*** standard is also used as the diesel continuing calibration verification solutions.

10.2.4. Gasoline initial calibration verification (ICV) solution containing 2.0 ppm of gasoline compounds, and 50 ppm of BFB surrogate in methanol. The gasoline ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.5. Diesel initial calibration verification (ICV) solution containing 400 ppm of diesel compounds, and 50 ppm of ***n-octacosane*** surrogate in methylene chloride. The diesel ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.6. Gasoline continuing calibration verification (CCV) solution containing mid-range concentrations of gasoline compounds and BFB surrogate in methanol. The gasoline CCV solutions are of a source same as that used for the initial five-point calibration.

10.2.6.1. The gasoline CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
Gasoline	2.0
BFB	0.1

10.2.7. Diesel continuing calibration verification (CCV) solutions containing mid-range concentrations of diesel compounds and ***n-octacosane*** surrogate in methylene chloride. The diesel CCV solutions are of a source same as that used for the initial five-point calibration.

10.2.7.1. The diesel CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
Diesel	400
n-Octacosane	50

10.2.8. Surrogate standard solution for GRO analysis containing 100 ppm of 1,4-bromofluoro-benzene (BFB) in methanol, and for DRO analysis containing 1000 ppm of ***n-octacosane*** in methylene chloride.

10.2.8.1. Add 5 µL of the BFB surrogate standard to each gasoline sample including the quality control (QC) check samples and method blanks prior to purge and trap.

10.2.8.2. Add 1.25 mL of the ***n-octacosane*** surrogate standard to each aqueous diesel sample including the quality control (QC) check samples and method blanks prior to extraction if the final extract volume is 25 mL.

10.2.8.3. Add 0.25 mL of the ***n-octacosane*** surrogate standard to each aqueous diesel sample including the quality control (QC) check

samples and method blanks prior to extraction if the final extract volume is 5 mL.

10.2.8.4. Add 0.5 mL of the ***n-octacosane*** surrogate standard to each solid diesel sample including the quality control (QC) check samples and method blanks prior to extraction.

10.2.9. Spike standard solution for GRO analysis containing 2000 ppm of gasoline compounds in methanol, and for DRO analysis containing 20000 ppm of diesel compounds in methylene chloride. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.9.1. The standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

10.2.9.2. Add 5 µL of the gasoline spike standard to each gasoline MS/MSD and LCS/LCSD sample prior to purge and trap.

10.2.9.3. Add 500 µL of the diesel spike standard to each aqueous diesel MS/MSD and LCS/LCSD sample prior to extraction if the final extract volume is 25 mL.

10.2.9.4. Add 100 µL of the diesel spike standard to each aqueous diesel MS/MSD and LCS/LCSD sample prior to extraction if the final extract volume is 5 mL.

10.2.9.5. Add 200 µL of the diesel spike standard to each solid diesel MS/MSD and LCS/LCSD sample prior to extraction.

10.2.10. All working standards must be replaced after three months or sooner if comparison with check standards indicates a problem.

10.2.11. All stock standards must be inspected and documented prior to use.

11. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

11.1. Aqueous gasoline samples should be collected in 40-mL pre-cleaned amber VOA vials with Teflon-lined closures. Collect all gasoline samples in triplicate. Aqueous diesel samples should be collected in 500-mL pre-cleaned amber glass containers with Teflon-lined closures.

11.1.1. Adjust the pH of the aqueous gasoline sample to < 2 by adding 1:1 HCl solution while stirring.

11.2. Solid gasoline samples should be collected in 4-oz pre-cleaned clear glass wide-mouth jars with Teflon-lined closures. Solid gasoline samples for EPA Method 5035 closed system purge-and-trap process should be collected in EnCore™ samplers. Collect all gasoline samples in triplicate. Solid diesel samples should be collected in 4-oz pre-cleaned clear glass wide-mouth jars with Teflon-lined closures.

11.3. Samples should be maintained in a chilled state (≤ 4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.4. Upon receipt, the samples are stored in a 4°C cooler.

11.4.1. Aqueous gasoline samples with acid preservation must be analyzed within 14 days of collection.

11.4.2. Aqueous diesel samples must be extracted within 7 days of collection. All extracted samples are then stored under dark and refrigerated (4°C) conditions and must be analyzed within a 40-day period post extraction.

11.4.3. Solid gasoline samples must be analyzed within 14 days of collection.

11.4.4. Solid gasoline samples collected in EnCore™ samplers must be transferred to a soil sample vial containing a stirring bar, preserved with 0.2 g of anhydrous sodium bisulfate per 1.0 g of sample within 48 hours of collection, and analyzed within 14 days of collection (or analyzed within 48 hours of collection without sodium bisulfate preservation).

11.4.5. Solid diesel samples must be extracted within 14 days of collection. All extracted samples are then stored under dark and refrigerated (4°C) conditions and must be analyzed within a 40-day period post extraction.

12. QUALITY CONTROL

12.1. Initial Calibration (IC)

12.1.1. The initial five-point calibration must be established prior to the processing of samples or sample extracts.

12.1.2. The IC is deemed valid if the %RSD for each analyte is ≤ 20%.

12.1.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2. Initial Calibration Verification (ICV)

12.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.2.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Investigate, effect corrective action, which may include re-preparation of standard solutions, and recalibrate, if necessary.

12.3. Continuing Calibration Verification (CCV)

12.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof, and at the end of sequence.

12.3.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.3.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Reanalyze the CCV. If the CCV criteria remain unacceptable, effect corrective action and reanalyze the CCV and/or recalibrate.

12.4. Retention Time Window

12.4.1. Establishment of retention time window width is accomplished by making three injections of mid-range CCV standards throughout the course of a 72-hour period. Serial injections over a shorter period of time may result in narrow retention time window width that does not accurately account for variations over several days.

12.4.1.1. Retention time window width is ± 3S (where S is the standard deviation of the three retention times for that analyte/surrogate).

12.4.2. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a mid-range CCV standard at the beginning of an analytical sequence.

12.4.2.1. Absolute retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S.

12.4.2.2. Daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the mid-range CCV standard ± 3S.

12.4.3. Retention time window for each analyte/surrogate is verified as follows:

12.4.3.1. The retention time of the first daily CCV standard must fall within the absolute retention time window.

12.4.3.2. All succeeding CCV standards throughout the course of a 24-hour period must fall within the daily retention time window established by the first CCV standard.

12.4.3.3. If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and position.

12.5. Event Based Quality Control (LCS/LCSDs and MBs)

12.5.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.5.2. The acceptance criteria for LCS/LCSD elements are as follows:

12.5.2.1. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.5.2.2. All LCS/LCSD elements must be within acceptance limits.

12.5.3. Ideally, the concentration of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.5.3.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

12.5.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-extracted and/or re-analyzed.

12.6. Matrix Based Quality Control (Surrogates, Internal Standards, and MS/MSDs)

12.6.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD), surrogates added to each sample, and internal standards added to each sample.

12.6.2. The acceptance criteria for surrogate spike compound recoveries are as follows:

12.6.2.1. The lower and upper acceptance limits for %REC of each surrogate spike compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.2.2. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

12.6.2.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration or a problem may have occurred during extraction. The data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.6.2.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.6.2.4.1. Check the surrogate spiking solutions for degradation and contamination.

12.6.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal

the cause of the unacceptable surrogate(s) recovery, the same extract should be re-analyzed.

12.6.2.4.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.2. If the MB surrogates are unacceptable, all associated sample data must invalidated and all associated samples re-extracted and re-analyzed.

12.6.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

12.6.3. The acceptance criteria for MS/MSDs compounds are as follows:

12.6.3.1. The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.3.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.6.3.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.4. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the

analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.7. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-extracted and re-analyzed.

12.8. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Initial Calibration

13.1.1. Establish an acceptable five-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.1.2. After obtaining an acceptable five-point calibration curve and prior to processing environmental or QC samples, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.2.

13.1.3. The initial five-point calibration and ICV should include all anticipated target analytes for the duration of the use of the initial calibration.

13.2. Retention time window width for each analyte/surrogate is generated by running three mid-range CCV standards over a 72-hour period. Retention time window width determination shall be performed at method set-up, following column changes, after major instrument maintenance or when a significant retention time shift is suspected.

13.2.1. GROs and DROs are distinguished on the basis of the ranges of retention times for characteristic components in each fuel type. The first eluting component sets the lower limit of the retention time window, and the last eluting component sets the upper limit of the retention time window.

13.2.2. For GROs, the compounds 2-methylpentane and 1,2,4-trimethylbenzene are used to define the GRO retention time window range.

13.2.3. For DROs, the compounds n-decane (C_{10}) and n-octocosane (C_{28}) are used to define the DRO retention time window range.

13.3. Top Loading Balance

13.3.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

13.3.2. Calibration shall be within ± 2% at 1 g (± 0.02 g) and at 100 g (± 2 g). If the values are not within these limits, recalibrate the balance.

14. PROCEDURE

14.1. Instrument Setup

14.1.1. Purge-and-Trap Setup

14.1.1.1. The trap should be heated (conditioned) for at least 10 minutes at 180°C with backflushing prior to sample analysis.

14.1.1.2. The purge-and-trap autosampler and concentrator are set for a purge time of 11.0 ± 0.1 minutes and a desorb time of 4.0 minutes.

14.1.1.3. Adjust the purge gas (helium) flow rate to 40 mL/min.

14.1.1.4. Use 5-mL purge volume for daily environmental and QC sample analysis.

14.1.2. Use the following GC operating conditions as guidance to establish the GC temperature program and flow rate necessary to separate the analytes of interest.

Description	GC Operating Condition	
	GRO Analysis	DRO Analysis
Carrier gas flow rate	8~10 mL/min	8~10 mL/min
Makeup gas flow rate	30.0 mL/min	30.0 mL/min
Injector temperature	n/a	250°C
Detector temperature	220°C	320°C
Initial temperature	45°C, hold 6.00 min	35°C, hold 4.00 min
Temperature program	45°C to 150°C at 5.00°C/min	35°C to 320°C at 8.00°C/min
Final temperature	150°C, hold 2.00 min	320°C, hold 3.00 min

14.2. Refer to the specific SOPs of the introductory/preparatory methods for sample introduction/preparation (Section 5.2. and Section 5.3.).

14.2.1. Measure 5.00 mL of aqueous gasoline sample for purge-and-trap process. Record the volume to the nearest 0.05 mL.

14.2.1.1. The MB/LCS/LCSD sample consists of clean reagent water, and the MS/MSD sample consists of aqueous gasoline sample in each analytical batch selected for spiking.

14.2.2. Measure 1.00 g of solid gasoline sample for purge-and-trap process. Record the mass to the nearest 0.01 g.

14.2.2.1. The MB/LCS/LCSD sample consists of washed sea sand, and the MS/MSD consists of solid gasoline sample in each analytical batch selected for spiking.

14.2.3. Measure 500 or 1000 mL of aqueous diesel sample for solvent extraction process. Record the volume to the nearest 1 mL.

14.2.3.1. The MB/LCS/LCSD sample consists of clean reagent water, and the MS/MSD sample consists of aqueous diesel sample in each analytical batch selected for spiking.

14.2.4. Measure 10.0 g of solid gasoline sample for solvent extraction process. Record the mass to the nearest 0.1 g.

14.2.4.1. The MB/LCS/LCSD sample consists of washed sea sand, and the MS/MSD consists of solid diesel sample in each analytical batch selected for spiking.

14.2.5. Add the surrogate standard solution listed in Section 10.2.8. to all samples, matrix spikes, laboratory control samples, and method blanks prior to purge and trap or solvent extraction.

14.2.6. Add the spike standard solution listed in Section 10.2.9. to all matrix spikes and laboratory control samples prior to purge and trap or solvent extraction.

14.2.7. Purge-and-Trap Procedure

14.2.7.1. Transfer 5.00 mL of an aqueous gasoline sample to a clean purge vessel and purge via EPA Method 5030B.

14.2.7.2. Transfer 1.00 g of a solid gasoline sample and 5.00 mL of reagent water to a clean purge vessel and purge via EPA Method 5030B/5035.

14.2.7.3. Transfer 1.00 g of a high-level solid gasoline sample to a clean purge vessel and dilute to 5.00 mL with methanol and purge via EPA Method 5030B/5035.

14.2.7.4. After loading samples for purge-and-trap extraction and prior to GC analysis, the pH condition of each aqueous sample must be measured with narrow range pH paper to determine whether the pH of the sample is < 2. The pH range (< 2 or ≥ 2) of each sample shall be documented in the appropriate location on the raw data sheet and the instrument run logbook.

14.2.7.4.1. Measure the pH of the aqueous sample remained in the sample container.

14.2.8. Solvent Extraction Procedure

14.2.8.1. Extract 500 mL of an aqueous diesel sample via EPA Method 3510C with three 25-mL aliquots of methylene chloride, and concentrate the methylene chloride extract to 25 mL for extraction with partial concentration. 1−2 g of silica gel may be added to remove polar, non-hydrocarbon oil and greases if required by project requirements.

14.2.8.2. Extract 1000 mL of an aqueous diesel sample via EPA Method 3510C with three 60-mL aliquots of methylene chloride, and concentrate the methylene chloride extract to 5 mL for extraction with full concentration. 1−2 g of silica gel may be added to remove polar, non-hydrocarbon oil and greases if required by project requirements.

14.2.8.3. ►***For 5-ppm or higher RL requirement, extract 10.0 g of a solid diesel sample via EPA Method 3550B with one 10-mL aliquot of methylene chloride, and concentrate the methylene chloride extract to 10 mL.***

14.2.8.4. ***►For projects requiring lower RL, extract 10.0 g of a solid diesel sample via EPA Method 3550B with three 10-mL aliquots of methylene chloride, and concentrate the methylene chloride extract to 10 mL.***

14.3. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof, and at the end of sequence. If the QC and retention time window criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.3. and Section 12.4.3.

14.3.1. If a failed CCV is the first of the day, corrective action must be effected prior to analyzing any samples.

14.4. Sample purge vessels or vials are loaded in the following or other logical order:

1) Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicate (LCSD)
4) Method Blank (MB)
5) Samples (up to 10 per batch)
6) Matrix Spike (MS)
7) Matrix Spike Duplicate (MSD)
8) Middle CCV
9) Samples (up to 10 per batch)
10) Ending CCV

14.4.1. Items 1, 8, and 10: A CCV is used to verify the acceptance of the initial five-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, every batch of 10 samples or portion thereof, and at the end of sequence.

14.4.2. Item 2: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.2.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid samples, the LCS consists of the specified compounds spiked into washed sea sand.

14.4.2.2. One LCS is required for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.3. Item 3: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is

expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.4.4. Item 4: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (e.g., surrogates, etc.).

14.4.4.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of washed sea sand. For diluted high-level solid samples, the MB consists of washed sea sand and appropriate amount of methanol.

14.4.4.2. An MB is required for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. It should be noted, however, that as necessary (e.g., after high level samples), additional MBs may be placed in the sequence.

14.4.5. Items 5 and 9: Up to 10 samples per batch. High concentration samples should be sufficiently diluted to ensure that instrument is not contaminated. Dilution of samples will result in increased reporting limits.

14.4.6. Item 6: The MS is an actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.6.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.5.

14.4.6.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently. This approach is considered "closed batch" as opposed to "open batch."

14.4.7. Item 7: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.5. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the run logbook.

14.6. Initiate the sequence.

14.7. Data Interpretation

14.7.1. Establish the retention time window range for each fuel type and surrogate (Section 12.4. and Section 13.2.).

14.7.1.1. Tentative identification of a fuel occurs when the peaks of the first and last eluting components from a sample falls within the retention time window range.

14.7.1.2. Tentative identification of a surrogate occurs when the peak of the surrogate from a sample or extract falls within the retention time window.

14.7.1.3. Use the CCV standards analyzed during the sequence to evaluate retention time stability. If characteristic analyte(s) or surrogate in the CCV standard fall outside of their retention time window(s), determine the cause of the problem and effect appropriate corrective action.

14.7.1.3.1. If any characteristic analyte(s) or surrogate in the CCV standard fall outside of their retention time window(s), then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.

14.7.2. Quantitation of a target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample or extract and the calibration standards.

14.7.2.1. ►***Proper quantitation requires the appropriate selection of a baseline from which the total area of the resolved and unresolved peak(s) can be determined. Baseline should be drawn same way for all the runs including QC, MB and samples. We base that on MB baseline integration.***

14.7.2.2. Determine the concentration based on the initial calibration curve.

14.7.2.2.1. Calculate the concentration of each target analyte in a sample or extract using the average of the initial RFs and the total area of the resolved and unresolved peaks (excluding the surrogate peak).

14.7.2.3. If the instrument response exceeds the calibration range, dilute the sample or extract and reanalyze.

14.7.3. Qualitative confirmation by a second GC column is generally not required for determining petroleum hydrocarbons, but is required when analytical interferences are indicated.

14.7.4. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

15. CALCULATIONS

15.1. The response factor is calculated as follows:

$$RF = \frac{A_x}{C_x}$$

where: RF = response factor for target analyte being measured.
A_x = area of the characteristic peak(s) for target analyte being measured.
C_x = concentration of target analyte being measured in µg/L.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RF_{ave} - RF_{daily}|}{RF_{ave}} \times 100$$

where: %D = percent difference.
RF_{daily} = daily RF for the target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.4. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a diesel sample extract is calculated as follows:

$$C_{ex} = \frac{A_x}{RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in mg/L.
A_x = area of the characteristic peaks for target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.8. The target analyte concentration for an aqueous gasoline sample is calculated as follows:

$$C_A = \frac{A_x}{RF_{ave}} \times \frac{V_p}{V_A} \qquad D = \frac{V_p}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in mg/L.
A_x = area of the characteristic peak(s) for target analyte.
V_p = purge volume in mL. For daily environmental and QC sample analysis, $V_p = 5$.
RF_{ave} = mean of the 5 initial RFs for the target analyte.
V_A = volume of aqueous sample purged in mL.
D = dilution factor.

15.9. The target analyte concentration for a solid gasoline sample without dilution prior to purge-and-trap is calculated as follows:

$$C_S = \frac{A_x}{RF_{ave}} \times \frac{V_p}{W_S} \qquad D = \frac{V_p}{W_S}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
A_x = area of the characteristic peak(s) for target analyte.
V_p = purge volume in mL. For daily environmental and QC sample analysis, $V_p = 5$.
RF_{ave} = mean of the 5 initial RFs for the target analyte.
W_S = weight of solid sample purged in g.
D = dilution factor.

15.10. The target analyte concentration for a solid gasoline sample with dilution prior to purge-and-trap is calculated as follows:

$$C_S = \frac{A_x}{RF_{ave}} \times \frac{V_p \times V_m}{W_S \times V_S} \qquad D = \frac{V_p \times V_m}{W_S \times V_S}$$

where:
- C_S = concentration of target analyte in solid sample in mg/kg.
- A_x = area of the characteristic peak(s) for target analyte.
- V_p = purge volume in mL. For daily environmental and QC sample analysis, $V_p = 5$.
- V_m = volume of dilution solvent (methanol) in mL.
- RF_{ave} = mean of the 5 initial RFs for the target analyte.
- W_S = weight of solid sample diluted in g.
- V_S = volume of diluted solid sample purged in mL.
- D = dilution factor.

15.11. The target analyte concentration for an aqueous diesel sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A}$$

where:
- C_A = concentration of target analyte in aqueous sample in mg/L.
- C_{ex} = concentration of target analyte in extract in mg/L.
- V_{ex} = volume of extract in mL.
- V_A = volume of aqueous sample extracted in mL.
- D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.12. The target analyte concentration for a solid diesel sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S}$$

where:
- C_S = concentration of target analyte in solid sample in mg/kg.
- C_{ex} = concentration of target analyte in extract in mg/L.
- V_{ex} = volume of extract in mL.
- W_S = weight of solid sample extracted in g.
- D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.13. All concentrations shall be reported in mg/L (ppm) for aqueous samples and mg/kg (ppm) for soil and solid waste samples.

15.14. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S. All LCS/LCSD compounds must be within acceptance limits.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.3. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The lower and upper acceptance limits for %REC of each surrogate spike compound are based upon the historical average recovery ± 3S.

18.3.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

18.3.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.3. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.3.1. Check the surrogate spiking solutions for degradation and contamination.

18.3.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable

surrogate(s) recovery, the same sample or extract should be re-analyzed.

18.3.3.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and/or re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-extracted and re-analyzed.

18.3.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S.

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in mg/L (ppm) for aqueous samples and mg/kg (ppm) for soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action

employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary

collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Nonhalogenated Organics Using GC/FID*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8015B, USEPA, Revision 2, December 1996.

22.2. *Determinative Chromatographic Separations*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000C, USEPA, Revision 3, March 2003.

22.3. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.4. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, November 2000.

22.5. *Organic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, November 2000.

23. TABLES, DIAGRAMS, FLOWCHARTS AND DATA VALIDATION

23.1. ►Appendix A: Additional Quality Control Criteria for ***Department of Defense*** Project.

24. ►MODIFICATIONS

24.1. ***The following modifications from EPA Method 8015B Revision 2 are noted.***

Calscience SOP M505 Section	Reference Document EPA Method 8015B Section	Summary of Modification
14.2.8.3	7.1.1.2	Use of Orbital Shaker for DRO soil extraction.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
1.2	Section 5: Add reference to the use of Orbital Shaker for diesel extraction. Section 6: Add LOD and LOQ. Section 9: Insert instrument software version & maintenance information. Section 10: Replace surrogate for DRO from DCB to n-Octacosane. Revise CCV solution preparation. Section 14: Change DRO extraction for soil procedure. Update quantitation procedure. Section 23: Revise Appendix A title. Section 24: Add modifications. Section 25: Add revision history. Appendix A: Update DoD quality control requirements and criteria.	Y. Patel / K. Chang	08/15/12

Appendix A

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. ►EPA Method 8015B, Total Petroleum Hydrocarbons (GRO/DRO) by GC/FID – Additional Quality Control Criteria for ***Department of Defense (DoD)*** Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. ►STANDARDS

3.1. ***The spike standard solution shall contain all anticipated target analytes.***

3.2. ***The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.***

4. ►QUALITY CONTROL

4.1. ***Limit of Detection (LOD)***

4.1.1. ***LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.***

4.1.2. ***LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.***

4.1.2.1. ***LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.***

4.1.2.2. ***LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., pattern recognition, etc.).***

4.1.2.2.1. ***For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.***

4.1.2.3. ***If these criteria are not met, perform either one of the following tasks.***

4.1.2.3.1. ***Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.***

4.1.2.3.2. ***Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.***

4.1.3. ***No samples shall be analyzed without a valid LOD.***

4.2. ***Limit of Quantitation (LOQ)***

4.2.1. ***LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.***

4.2.1.1. ***The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.***

4.2.1.2. ***The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.***

4.2.2. ***LOQ verification must be performed quarterly to verify precision and bias at the LOQ.***

4.2.2.1. ***LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.***

4.2.2.2. ***LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.***

4.3. ***Initial Calibration Verification (ICV)***

4.3.1. ***The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.***

4.4. ***Continuing Calibration Verification (CCV)***

4.4.1. ***Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.***

4.4.2. ***The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.***

4.4.3. ***The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.***

4.5. Retention Time Window

4.5.1. ***Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration,***

and by using a low-to-midpoint CCV standard at the beginning of an analytical sequence.

4.5.1.1. ***When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S.***

4.5.1.2. ***When initial calibration is <u>not</u> performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the low-to-midpoint CCV standard ± 3S.***

4.5.2. ***Retention time for each analyte/surrogate in the calibration verification standard is verified as follows:***

4.5.2.1. ***When initial calibration is performed, the ICV standard and all CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the midpoint calibration standard.***

4.5.2.2. ***When initial calibration is <u>not</u> performed, all succeeding CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the first CCV standard.***

4.5.2.3. ***If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and/or position, if necessary.***

4.6. Event Based Quality Control (MBs ***and LCS/LCSDs***)

4.6.1. Method Blanks (MBs)

4.6.1.1. ***The MB is considered to be contaminated if one of the following conditions is met.***

4.6.1.1.1. ***The concentration of any target analyte in the MB exceeds 1/2 the RL, <u>and</u> is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).***

4.6.1.1.2. ***The concentration of any common laboratory contaminant in the MB exceeds RL, <u>and</u> is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).***

4.6.1.1.3. ***The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).***

4.6.1.2. ***If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.***

4.6.1.2.1. If ***insufficient*** sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

4.6.2. ***Laboratory Control Samples (LCS/LCSDs)***

4.6.2.1. ***Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.***

4.6.2.1.1. ***Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.***

4.6.2.2. ***All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.***

5. ►PROCEDURE

5.1. ***An acceptable CCV is required daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.***

5.2. ***The sample selected for spiking must be one of the samples collected for the specific DoD project.***

6. REFERENCES

6.1. ►Department of Defense Quality Systems Manuals for Environmental Laboratories, Version ***4.2, October 25, 2010***.

Title : **EPA METHOD 8081A, ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY**

Document No. : SOP-M400
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Revision 5.0 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 01/02/13
MANAGEMENT **DATE**

_____ 01-02-13
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 8081A, Organochlorine Pesticides by Gas Chromatography.

2. APPLICABLE MATRICES

2.1. ►This method is applicable to water, oil, soil, and solid wastes. ***It is also applicable to marine and freshwater tissues as a modified method.***

3. ►DETECTION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

	Water	Soil	***Sediment***
Pesticides	0.1 µg/L	5 µg/kg (wet-weight)	***1 µg/kg (wet-weight)***
Chlordane	1.0 µg/L	50 µg/kg (wet-weight)	***10 µg/kg (wet-weight)***
Toxaphene	2.0 µg/L	100 µg/kg (wet-weight)	***20 µg/kg (wet-weight)***

	Oil	Wipe/Filter	Tissue
Pesticides	100 µg/kg	0.1 µg/sample	2 µg/kg
4,4'-Dichlorobenzophenone		***0.5 µg/sample***	
Chlordane	1000 µg/kg	1.0 µg/sample	***20 µg/kg***
Toxaphene	2000 µg/kg	2.0 µg/sample	***40 µg/kg***

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution or cleanup.

3.3. ***Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.***

4. ►SCOPE AND APPLICATION

4.1. EPA Method 8081A is used to determine the concentrations of a number of common organochlorine pesticides in various matrices. The method is used to quantitate organochlorine pesticides without derivitization.

4.2. The following compounds ***are routinely*** determined by this method.

aldrin
α-BHC
β-BHC
γ-BHC (lindane)
δ-BHC
α-chlordane
γ-chlordane
chlordane
4,4'-DDD
4,4'-DDE
4,4'-DDT
dieldrin
endosulfan I
endosulfan II
endosulfan sulfate
endrin
endrin aldehyde
endrin ketone
heptachlor
heptachlor epoxide
hexachlorobenzene
methoxychlor
toxaphene

4.3. ***The following compounds may also be determined by this method.***

chlorobenzilate
2,4'-DDD (o,p'-DDD)
2,4'-DDE (o,p'-DDE)
2,4'-DDT (o,p'-DDT)
diallate
4,4'-dichlorobenzophenone (4,4'-DCBP)
hexachlorocyclopentadiene
kepone
mirex
cis-nonachlor
trans-nonachlor
oxychlorodane

4.4. Upon client request, additional target analytes may be added to this analysis. However, it needs to be demonstrated that any added compounds lend themselves to EPA Method 8081A determination, either by regulatory reference or validation studies.

4.5. Extracts suitable for analysis by this method may also be analyzed for EPA Method 8141, organophosphorus pesticides.

4.6. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph (GC) and skilled in the interpretation of gas chromatograms.

5. ►METHOD SUMMARY

5.1. EPA Method 8081A describes chromatographic procedures that will allow for the separation of organochlorine pesticide compounds in the extract and their qualitative and quantitative analysis by gas chromatography. Detection is achieved using an electron capture detector (ECD).

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample.

5.2.1. Aqueous samples are extracted via EPA Methods 3510 or 3520 at neutral pH using methylene chloride exchanged into hexane.

5.2.2. Solid samples are extracted via EPA Methods 3540, 3545, or 3550 using methylene chloride-acetone (1:1) exchanged into hexane, or via EPA Method 3545 using methylene chloride exchanged into hexane.

5.2.3. Solid samples for TCLP, SPLP, or STLC analysis are prepared using the appropriate mobility extraction method, and the resulting mobility-procedure extracts (leachates) are extracted via EPA Methods 3510 or 3520 at neutral pH using methylene chloride exchanged into hexane.

5.2.4. Oil samples are prepared in accordance with EPA Method 3580 using hexane as the diluent.

5.2.5. ***Tissue samples are extracted via EPA Methods 3540 or 3545 using methylene chloride exchanged into hexane.***

5.2.6. A variety of cleanup procedures may be applied to the extracts, depending on the nature of the target analytes and the matrix interferences.

5.3. Acceptable preparatory methods include, but are not limited to, the following:

Type of Sample Preparation	Method	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510	SOP-M200

Type of Sample Preparation (Cont.)	Method	SOP No.
Continuous Liquid-Liquid Extraction	3520	SOP-M201
Soxhlet Extraction	3540	SOP-M203
Pressurized Fluid Extraction	3545	SOP-M204
Ultrasonic Extraction	3550	SOP-M202
Waste Dilution	3580	SOP-M205
Cleanup	3600(M)	SOP-M234
Gel-Permeation Cleanup	3640	SOP-M233
Marine Tissue Preparation and Cleanup	***CEL Proprietary***	***SOP-M236***
TCLP	1311	SOP-M226
SPLP	1312	SOP-M227
STLC (California Code of Regulations)	CCR T22.11.5.A-II	SOP-M228

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. ***Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.***

6.12. ***Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.***

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.27. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. ►INTERFERENCES

7.1. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.2. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially.

7.2.1. Sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2.2. ***Analysis of a suspected high level sample should be followed by an analysis of solvent blank to check for cross-contamination. In addition***, suspected high level samples ***may*** be diluted and then analyzed at the end of the sequence to prevent carryover contamination.

7.3. Interference can also occur when "dirty" samples leave residue in the analytical column. To minimize this effect, guard columns should be used and cut frequently or replaced. In addition, the analytical column can be "baked" after such samples. Other maintenance procedures include cleaning the inlet or replacing injection liner and seal.

7.4. Endrin and 4,4'-DDT are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated with high boiling residue from sample injection or when the injector contains metal fittings.

7.4.1. Endrin and 4,4'-DDT breakdown to endrin aldehyde, endrin ketone, 4,4'-DDD, or 4,4'-DDE.

7.4.2. When such breakdown is observed, the corrective action may include, but is not limited to 1) cleaning and deactivating the injection port, 2) replacing the injection port liner, or 3) clipping the guard column.

7.5. Phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations.

7.5.1. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

7.5.2. Exhaustive cleanup of solvents, reagents and glassware may be necessary to eliminate background phthalate ester contamination.

7.6. The presence of sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples. EPA Method 3660, Sulfur Cleanup, should be employed for sulfur removal prior to analysis.

7.6.1. The recovery of endrin aldehyde is drastically reduced when using the TBA procedure in EPA Method 3660; hence, this compound must be determined prior to sulfur cleanup when it is an analyte of interest and the TBA procedure is to be used for cleanup.

7.6.2. The use of copper powder technique in EPA Method 3660 may adversely affect the recoveries of some organochlorine compounds and many organophosphorus compounds.

7.7. Waxes, lipids, and other high molecular weight materials can be removed by EPA Method 3640, Gel-Permeation Cleanup.

7.8. Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides.

7.8.1. Certain co-eluting organophosphorus pesticides may be eliminated by the pesticide option of EPA Method 3640.

7.8.2. Co-eluting chlorophenols may be eliminated by EPA Methods 3630 (Silica Gel Cleanup), 3620 (Florisil Cleanup), or 3610 (Alumina Cleanup).

7.9. Polychlorinated biphenyls (PCBs) may interfere with the analysis of the organochlorine pesticides. The problem may be most severe for the analysis of multiple-component analytes such as chlordane and toxaphene. If PCBs are known or expected to occur in samples, consult EPA Methods 3620 and 3630 to separate the pesticides from the PCBs.

7.10. ***Kepone extracted from samples or in standards exposed to water or methanol may produce peaks with broad tails that elute later than the standard by up to one minute. This shift is presumably the result of the formation of a hemi-acetal from the ketone functionality and may seriously affect the ability to identify this compound on the basis of its retention time. As a result, this method is not recommended for determining kepone. EPA Method 8270 may be more appropriate for the analysis of kepone.***

8. ►SAFETY

8.1. Compounds covered by this method have been tentatively classified as known or suspected human carcinogens. Primary standards of these compounds must be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when analysts handle high concentrations of these compounds.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

8.4. ***Refer to the preparatory methods for additional safety issues.***

9. ►EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Agilent 6890N Gas Chromatograph, Agilent 7890A Gas Chromatograph, or equivalent configured with the following components:

9.1.1. Autoinjector, Agilent 7683 Series, Agilent 7683B Series, or equivalent.

9.2. ***Instrument Software***

9.2.1. ***Agilent GC ChemStation Version B.03.01[317], Agilent GC ChemStation Version B.03.02[341], or equivalent.***

9.3. ***Instrument Maintenance and Troubleshooting***

9.3.1. ***Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.***

9.4. Primary Detection Channel

9.4.1. Detector: Electron capture detector (ECD).

9.4.2. Analytical Column: 30-m × 0.32-mm ID, 0.50-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides or equivalent.

9.5. Confirmation Detection Channel

9.5.1. Detector: Electron capture detector (ECD).

9.5.2. Analytical Column: 30-m × 0.32-mm ID, 0.25-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides2 or equivalent.

9.6. Guard Column: 5-m × 0.32-mm ID, intermediate-polarity deactivated, uncoated fused-silica, Restek IP Deactivated Guard Column or equivalent.

9.7. Carrier Gas: ***Nitrogen, N_2, high purity (99.998%)***, compressed, Praxair ***4.8*** grade or equivalent.

9.8. ***Carrier Gas: Hydrogen, H_2, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.***

9.9. ***Makeup Gas: Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent.***

9.10. Makeup Gas: Methane, CH_4, 5%, and argon, Ar, 95%, compressed, Praxair P-5 Mixture or equivalent.

9.11. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.12. Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

9.13. Autoinjector vials, 12-mm × 32-mm (2-mL capacity), crimp top, clear glass, with aluminum crimp caps and Teflon-lined septa, disposable.

9.14. ***Vial inserts, 300–µL, clear glass, with conical bottom and spring.***

9.15. ***Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.***

9.16. ***Refer to the specific SOPs of the preparatory methods for additional equipment and supplies.***

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Sodium thiosulfate, $Na_2S_2O_3$, anhydrous, white solid, reagent grade or equivalent.

10.1.4. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v).

10.1.4.1. Prepare the 10% $Na_2S_2O_3$ solution by dissolving 200 g of anhydrous $Na_2S_2O_3$ in reagent water and dilute to 2 L with additional reagent water.

10.1.5. Methylene chloride (or dichloromethane), CH_2Cl_2, clear colorless liquid, pesticide grade or equivalent.

10.1.6. Hexane, C_6H_{14}, clear colorless liquid, pesticide grade or equivalent.

10.1.7. Acetone, CH_3COCH_3, clear colorless liquid, pesticide grade or equivalent.

10.1.8. ***Refer to the specific SOPs of the preparatory methods for additional reagents.***

10.1.9. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing ***various concentrations*** of single-component ***and multi-component*** pesticide target analyte, and 200 ppm of each surrogate are used to prepare calibration and check standards.

10.2.1.1. Prepare each working standard solution by diluting the appropriate volumes of the stock standards to ***the specified volumes*** with hexane.

10.2.1.2. The ***routine single-component pesticide*** working standards are prepared as follows:

Routine Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
OC pesticides	2000	8.0	4.0	4.0
hexachlorobenzene	100	160		
surrogates	200	160	8.0	

Routine Analyte	Initial Conc. (ppm)	Initial Volume (µL)	Final Conc. (ppm)	Final Volume (mL)
OC pesticides	200	80	4.0	4.0
hexachlorobenzene	100	160		
surrogates	200	160	8.0	

10.2.1.3. ***The non-routine single-component pesticide working standards are prepared as follows:***

Non-Routine Analyte	Initial Conc. (ppm)	Initial Volume (µL)	Final Conc. (ppm)	Final Volume (mL)
2,4'-DDD	100	160	2.0	8.0
2,4'-DDE	100		2.0	
2,4'-DDT	100		2.0	
mirex	100		2.0	
cis-nonachlor	100		2.0	
trans-nonachlor	100		2.0	
oxychlordane	100		2.0	
4,4'-DCBP	500	160	10	
kepone	1000	8.0	2.0	4.0
chlorobenzilate	1000	8.0	2.0	4.0
diallate	1000		2.0	
hexachlorocyclopentadiene	1000		2.0	
surrogates	200	80	4.0	

Non-Routine Analyte	Initial Conc. (ppm)	Initial Volume (µL)	Final Conc. (ppm)	Final Volume (mL)
2,4'-DDD	100	160	2.0	8.0
2,4'-DDE	100		2.0	
2,4'-DDT	100		2.0	
mirex	100		2.0	
cis-nonachlor	100		2.0	
trans-nonachlor	100		2.0	
oxychlordane	100		2.0	
4,4'-DCBP	500	160	10	
kepone	100	80	2.0	4.0
chlorobenzilate	100	80	2.0	4.0
diallate	100		2.0	
hexachlorocyclopentadiene	100		2.0	
surrogates	200	80	4.0	

10.2.1.4. ***The multi-component pesticide working standards are prepared as follows:***

Analyte	Initial Conc. (ppm)	Initial Volume (µL)	Final Conc. (ppm)	Final Volume (mL)
chlordane	1000	400	100	4.0
toxaphene	1000	400	100	4.0

10.2.2. ***Pre-certified stock standard solution, in sealed glass ampule, containing 200 ppm each of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) is used to prepare surrogate working standard.***

10.2.2.1. ***Prepare the 2.0-ppm surrogate working standard solution by diluting 10 mL of the 200-ppm surrogate stock standard to 1.0 L with acetone or other acetone miscible solvent.***

10.2.3. ***Pre-certified stock standard solutions, each in sealed glass ampules, containing various concentrations of target analytes are used to prepare spike working standards.***

10.2.3.1. ***Prepare each 1.0-ppm spike working standard solution by diluting the appropriate volumes of the stock standards to the specified volumes with acetone or other acetone miscible solvent.***

10.2.3.2. ***The 1.0-ppm spike working standards are prepared as follows:***

Routine Analyte	Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume (mL)
OC pesticides	200	1.0	1.0	200
hexachlorobenzene	1000	0.2		

Non-Routine Analyte	Initial Conc. (ppm)	Initial Volume (µL)	Final Conc. (ppm)	Final Volume (mL)
2,4'-DDD	100	100	1.0	10
2,4'-DDE	100		1.0	
2,4'-DDT	100		1.0	
mirex	100		1.0	
cis-nonachlor	100		1.0	
trans-nonachlor	100		1.0	
oxychlordane	100		1.0	
4,4'-DCBP	500	100	5.0	
kepone	100	100	1.0	10
chlorobenzilate	100	100	1.0	10
diallate	100		1.0	
hexachlorocyclopentadiene	100		1.0	

10.2.4. Degradation test stock standard solution containing 500 ppm each of 4,4'-DDT and endrin in methanol.

10.2.4.1. Prepare the 500-ppb degradation test working standard solution by diluting ***10*** µL of the 500-ppm degradation test stock standard to ***10*** mL with hexane.

10.2.4.2. Prepare the 50-ppb degradation test working standard solution by diluting 4.0 mL of the 500-ppb degradation test working standard to 40 mL with hexane.

10.2.4.3. Inject 2.0 µL of the 50-ppb degradation test working standard for degradation test.

10.2.5. Calibration standard solutions containing various concentrations of target analytes and surrogates in hexane.

10.2.5.1. Dilute the appropriate volumes of the working ***and stock*** standards to ***the specified volumes*** with hexane for initial calibration.

10.2.5.2. ***Use the following calibration levels as guidance to prepare the routine single-component pesticide calibration standards.***

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A1	S	A1 + S	A1 + S	A1 + S
10	20	4.0 + 8.0	10	4.0
20	40	4.0 + 8.0	20	4.0
40	80	4.0 + 8.0	40	4.0
60	120	4.0 + 8.0	60	4.0
80	160	4.0 + 8.0	80	4.0

Note: A1 = Routine Single-Component Analyte; S = Surrogate

10.2.5.3. ***Use the following calibration levels as guidance to prepare the non-routine single-component pesticide calibration standards.***

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A2	A3	A2 + A3	A2 + A3	A2 + A3
10	50	2.0 + 10	40	8.0
20	100	2.0 + 10	80	8.0
40	200	2.0 + 10	160	8.0
60	300	2.0 + 10	240	8.0
80	400	2.0 + 10	320	8.0

Note: A2 = Non-Routine Single-Component Analyte; A3 = 4,4'-DCBP

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A4	S	A4 + S	A4 + S	C
10	20	2.0 + 4.0	20	4.0
20	40	2.0 + 4.0	40	4.0
40	80	2.0 + 4.0	80	4.0
60	120	2.0 + 4.0	120	4.0
80	160	2.0 + 4.0	160	4.0

Note: A4 = Kepone, Chlorobenzilate, Diallate, or Hexachlorocyclopentadiene
S = Surrogate

10.2.5.4. ***Use the following calibration levels as guidance to prepare the multi-component pesticide calibration standards.***

Calibration Level (ppb)		Initial				Final	
		Concentration (ppm)		Volume (µL)		Volume (mL)	
C	T	C	T	C	T	C	T
100	200	100	100	4.0	8.0	4.0	4.0
250	500	100	100	10	20	4.0	4.0
500	1000	100	100	20	40	4.0	4.0
750	1500	100	100	30	60	4.0	4.0
2000	4000	100	100	80	160	4.0	4.0

Note: C = Chlordane; T = Toxaphene

10.2.5.5. The ***midpoint*** standards are also used as the continuing calibration verification solutions.

10.2.5.6. ***The calibration levels for the initial calibration of a non-routine target analyte may be established differently per client request or project specific DQOs.***

10.2.6. Initial calibration verification (ICV) solutions containing ***the appropriate concentrations*** of each target analyte and surrogate in hexane. The ICV solution must be of a source differing from that used for the initial ***multi-point*** calibration. If it is of the same source, then it must be of different lot.

10.2.6.1. Dilute the appropriate volumes of the second source working ***and stock*** standards to ***the specified volumes*** with hexane for initial calibration verification.

10.2.6.2. ***Use the following calibration level as guidance to prepare the routine single-component pesticide ICV solution.***

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A1	S	A1 + S	A1 + S	A1 + S
40	80	4.0 + 8.0	40	4.0

Note: A1 = Routine Single-Component Analyte; S = Surrogate

10.2.6.3. ***Use the following calibration levels as guidance to prepare the non-routine single-component pesticide ICV solutions.***

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A2	A3	A2 + A3	A2 + A3	A2 + A3
40	200	2.0 + 10	160	8.0

Note: A2 = Non-Routine Single-Component Analyte; A3 = 4,4'-DCBP

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A4	S	A4 + S	A4 + S	C
40	80	2.0 + 4.0	80	4.0

Note: A4 = Kepone, Chlorobenzilate, Diallate, or Hexachlorocyclopentadiene
S = Surrogate

10.2.6.4. ***Use the following calibration levels as guidance to prepare the multi-component pesticide ICV solutions.***

Calibration Level (ppb)		Initial				Final	
		Concentration (ppm)		Volume (µL)		Volume (mL)	
C	T	C	T	C	T	C	T
500	1000	100	100	20	40	4.0	4.0

Note: C = Chlordane; T = Toxaphene

10.2.6.5. ***The calibration level for the initial calibration verification of a non-routine target analyte may be established differently per client request or project specific DQOs.***

10.2.7. Continuing calibration verification (CCV) solutions containing ***the appropriate*** concentrations of each target analyte and surrogate in hexane. The CCV solution is of a source same as that used for the initial ***multi-point*** calibration.

10.2.7.1. Dilute the appropriate volumes of the working ***and stock*** standards to ***the specified volumes*** with hexane for continuing calibration verification.

10.2.7.2. ***Use the following calibration level as guidance to prepare the routine single-component pesticide CCV solution.***

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A1	S	A1 + S	A1 + S	A1 + S
40	80	4.0 + 8.0	400	40

Note: A1 = Routine Single-Component Analyte; S = Surrogate

10.2.7.3. ***Use the following calibration levels as guidance to prepare the non-routine single-component pesticide CCV solutions.***

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A2	A3	A2 + A3	A2 + A3	A2 + A3
40	200	2.0 + 10	160	8.0

Note: A2 = Non-Routine Single-Component Analyte; A3 = 4,4'-DCBP

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A4	S	A4 + S	A4 + S	C
40	80	2.0 + 4.0	80	4.0

Note: A4 = Kepone, Chlorobenzilate, Diallate, or Hexachlorocyclopentadiene
S = Surrogate

10.2.7.4. ***Use the following calibration levels as guidance to prepare the multi-component pesticide CCV solutions.***

Calibration Level (ppb)		Initial				Final	
		Concentration (ppm)		Volume (µL)		Volume (mL)	
C	T	C	T	C	T	C	T
500	1000	100	100	200	400	40	40

Note: C = Chlordane; T = Toxaphene

10.2.7.5. ***The calibration level for the continuing calibration verification of a non-routine target analyte may be established differently per client request or project specific DQOs.***

10.2.8. Surrogate ***working*** standard solution containing ***2.0*** ppm each of deca-chlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) in acetone ***or other acetone miscible solvent***.

10.2.8.1. Add 500 µL of the 2.0-ppm surrogate working standard to each sample including ***each*** quality control (QC) check samples and method blank prior to ***solvent*** extraction.

10.2.8.2. ***Add 500 µL of the 2.0-ppm surrogate working standard to each mobility-procedure extract including each mobility-procedure extract designated as QC check sample and method blank prior to solvent extraction.***

10.2.9. Spike ***working*** standard solutions containing ***various concentrations*** of target analytes in acetone or other acetone miscible solvent. The spike standard solution must be of a source differing from that used for the initial ***multi-point*** calibration. If it is of the same source, then it must be of different lot.

10.2.9.1. ***Use the 1.0-ppm spike working standard solutions as the single-component pesticide spike working standard solutions. Use the 1000-ppm chlordane stock standard solution and the 1000-ppm toxaphene stock standard solution as the multi-component pesticide spike working standard solutions.***

10.2.9.2. The ***spike*** standards are used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

10.2.9.3. Add 500 µL of the single-component pesticide spike working standard to each MS/MSD and LCS/LCSD sample prior to ***solvent*** extraction.

10.2.9.4. ***Per client request or project specific data quality objectives (DQOs)***, add 5.0 µL of the chlordane spike working standard to each MS/MSD and LCS/LCSD sample prior to ***solvent*** extraction.

10.2.9.5. ***Per client request or project specific DQOs***, add 10 µL of the toxaphene spike working standard to each MS/MSD and LCS/LCSD sample prior to ***solvent*** extraction.

10.2.9.6. Add 500 µL of the single-component pesticide spike working standard to each mobility-procedure extract designated as MS/MSD and LCS/LCSD prior to ***solvent*** extraction.

10.2.9.7. ***Per client request or project specific DQOs, add 5.0 µL of the chlordane spike working standard to each mobility-procedure extract designated as MS/MSD and LCS/LCSD prior to solvent extraction.***

10.2.9.8. ***Per client request or project specific DQOs, add 10 µL of the toxaphene spike working standard to each mobility-procedure extract designated as MS/MSD and LCS/LCSD prior to solvent extraction.***

10.2.10. All working standards must be replaced after six months (unless specified otherwise) or sooner if ***routine QC or*** comparison with check standards indicates a problem.

10.2.10.1. ***Store all working standards under dark and refrigerated condition.***

10.2.11. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2.11.1. ***Evaluate the toxaphene stock standards carefully. Some toxaphene components, particularly the more heavily chlorinated components, are subject to dechlorination reactions. As a result, the toxaphene stock standards from different manufacturers may exhibit marked differences which could lead to possible false negative results or to large differences in quantitative results.***

10.2.11.2. ***Check all opened stock standards frequently for signs of degradation or evaporation.***

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1-L pre-cleaned amber glass containers with Teflon-lined closures. Collect all samples in duplicate.

11.1.1. If the aqueous sample ***is known or suspected to contain*** residual chlorine, add 4 mL of the 10% $Na_2S_2O_3$ solution per 1 L of sample. The 10% $Na_2S_2O_3$ solution may be added to the sample container prior to sample collection.

11.1.2. ***If MS/MSD analyses for single-component pesticide target analytes are required, collect one sample in quadruplicate.***

11.1.3. ***If MS/MSD analyses for multi-component pesticide target analytes are required, collect one sample in quadruplicate, or collect two samples in quadruplicate each.***

11.1.4. ***If MS/MSD analyses for single-component and multi-component pesticide target analytes are required, collect two samples in quadruplicate each, or collect three samples in quadruplicate each.***

11.2. Solid samples should be collected in 4-oz or 8-oz pre-cleaned clear glass wide-mouth jars, or 6-in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.3. Oil, wipe, and filter samples should be collected in 40-mL pre-cleaned amber glass or clear glass VOA vials with Teflon-lined closures.

11.4. Tissue samples should be collected in 4-oz (or other appropriate capacity) pre-cleaned clear glass or quartz wide-month jars with Teflon or aluminum foil-lined closures. Refer to SOP-M229 for additional information on sample collection, preservation, and containers.

11.5. Mobility-procedure extracts should be collected in 500-mL pre-cleaned amber glass containers with Teflon-lined closures.

11.5.1. If the mobility-procedure extract ***is known or suspected to contain residual chlorine***, add 2 mL of the 10% $Na_2S_2O_3$ solution per 500 mL of mobility-procedure extract.

11.5.2. Completely fill and hermetically seal the sample container with minimum headspace.

11.6. Aqueous ***and non-aqueous (except tissue)*** samples shall be maintained in a chilled state post sample collection until received at the laboratory. Aqueous ***and non-aqueous (except tissue)*** samples should not be frozen (e.g., do not use dry ice as the refrigerant). Tissue samples shall be maintained in a frozen state post sample collection until received at the laboratory.

11.6.1. ***For additional information on aqueous and non-aqueous (except tissue) sample collection and preservation, refer to Code of Federal Regulations (CFR), Title 40, Part 136 (§136.3).***

11.6.2. ***For additional information on sample collection and preservation, refer to SOP-M229 and EPA Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Third Edition, Volume 1, Section 6.3.***

11.7. Upon receipt, the aqueous ***and non-aqueous (except tissue)*** samples are stored in a 0~6°C cooler. Tissue samples are stored in a −10~−20°C freezer.

11.7.1. Aqueous samples must be solvent extracted within 7 days of sample collection.

11.7.2. Non-aqueous samples must be solvent extracted within 14 days of sample collection.

11.7.3. Mobility-procedure extracts must be solvent extracted within 7 days post mobility extraction.

11.7.3.1. Mobility-procedure extracts shall be stored in a 0~6°C cooler post mobility extraction if solvent extraction is not to be performed within 24 hours.

11.7.4. All solvent extracts are then stored under dark and refrigerated (0~6°C) conditions and must be analyzed within 40 days post ***solvent*** extraction.

12. ►QUALITY CONTROL

12.1. Degradation Test

12.1.1. Prior to running the calibration standards, the degradation test standard solution must be analyzed and meet the ***defined*** acceptance criteria.

12.1.2. The ***following*** criteria must be demonstrated every 12 hours.

12.1.2.1. The degradation (or percent breakdown) of 4,4'-DDT and endrin shall be ≤ 15% for each compound. The formula for calculating %B is listed in Section 15.14.

12.1.3. If these criteria are not met, then the analytical system is deemed unacceptable for sample analysis to begin. Effect corrective action, rerun the degradation test, ***perform injector maintenance***, and recalibrate.

12.2. Initial Calibration (IC)

12.2.1. The initial ***multi-point*** calibration must be established prior to the processing of sample extracts.

12.2.1.1. The calibration curve is established with ***a minimum of*** five calibration standards, ***but may contain six or seven calibration standards***.

12.2.2. The IC is deemed valid if the %RSD for each analyte is ≤ 20%.

12.2.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.3.1. ***If the RSD of any analyte is unacceptable, review the results (e.g., proper identification, area count, response factor, etc.) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards.***

12.2.3.2. If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis ***to rule out problems due to random chance***.

12.2.3.2.1. ***In some cases, replace the calibration standard may be necessary.***

12.2.3.3. ***If a calibration standard is replaced and/or reanalyzed, recalculate the RSD, and document the rationale for re-analysis.***

12.3. Initial Calibration Verification (ICV)

12.3.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.3.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective action, which may include re-preparation of standard solutions or instrument maintenance, and recalibrate.

12.4. Continuing Calibration Verification (CCV)

12.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.4.1.1. For EPA Region 9 requirement, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.4.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.4.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.5. Retention Time Window

12.5.1. Establishment of retention time window width is accomplished by making three injections of CCV standards throughout the course of a 72-hour period. Serial injections over a shorter period of time may result in narrow retention time window width that does not accurately account for variations over several days.

12.5.1.1. Retention time window width is ± 3S (where S is the standard deviation of the three retention times for that analyte/surrogate) or ± 0.030 minute, whichever is greater.

12.5.1.1.1. ***For each multi-component analyte (i.e., chlordane and toxaphene), calculate the standard deviation for each one of the five major characteristic peaks.***

12.5.2. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a CCV standard at the beginning of an analytical sequence.

12.5.2.1. When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S or ± 0.030 minute, whichever is greater.

12.5.2.2. When initial calibration is <u>not</u> performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the CCV standard ± 3S or ± 0.030 minute, whichever is greater.

12.5.3. Retention time for each analyte/surrogate in the calibration verification standard is verified as follows:

12.5.3.1. When initial calibration is performed, the ICV standard and all CCV standards throughout the course of an analytical sequence

within a 12-hour shift must fall within the daily retention time window established by the midpoint calibration standard.

12.5.3.2. When initial calibration is not performed, all succeeding CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the first CCV standard.

12.5.3.3. If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and/or position, if necessary.

12.6. Event Based Quality Control (MBs and LCS/LCSDs)

12.6.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB) and a laboratory control sample and laboratory control sample duplicate (LCS/LCSD).

12.6.2. ***The acceptance criteria for MBs are as follows:***

12.6.2.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

12.6.2.2. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.6.2.3. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples ***re-processed*** and/or re-analyzed.

12.6.3. The acceptance criteria for LCS/LCSD compounds are as follows:

12.6.3.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 50% and 135%, respectively. The RPD is ≤ 25%.

12.6.3.1.1. ***If historical data is available, the lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.***

12.6.3.2. All LCS/LCSD compounds must be within acceptance limits. However, if a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside of control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Lower and

upper marginal exceedance (ME) limits can be established to determine when corrective action is necessary.

12.6.3.3. ME is defined as being beyond the LCS control limit (3 standard deviations), but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean.

12.6.3.4. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than 11 analytes.

12.6.3.5. The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number of Analytes Allowed in ME of the LCS Control Limit
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

12.6.3.6. Marginal exceedances must be random. If the same analyte exceeds the LCS control limit 2 out of 3 consecutive LCS, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

12.7. Matrix Based Quality Control (Surrogates and MS/MSDs)

12.7.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and surrogates added to each sample.

12.7.2. The acceptance criteria for surrogate compounds are as follows:

12.7.2.1. The lower and upper acceptance limits for %REC of each surrogate compound in an aqueous sample are 50% and 135%, respectively. The lower and upper acceptance limits for %REC of each surrogate compound in a non-aqueous sample are 50% and 130%, respectively.

12.7.2.1.1. ***If historical data is available, the lower and upper acceptance limits for %REC of each surrogate compound are based upon the historical average recovery ± 3S that is updated at least annually.***

12.7.2.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each surrogate compound are 60% and 150%, respectively.

12.7.2.2. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

12.7.2.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration or a problem may have occurred during extraction or cleanup. The data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.7.2.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.7.2.4.1. Check the surrogate standard solutions for degradation and contamination.

12.7.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recoveries, the same extract should be re-analyzed.

12.7.2.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be ***re-processed*** and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.7.2.4.3.1. If, upon ***re-processing*** and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.7.2.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all

associated samples ***re-processed*** and re-analyzed.

12.7.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

12.7.3. The acceptance criteria for MS/MSD compounds are as follows:

12.7.3.1. The lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 25%.

12.7.3.1.1. ***If historical data is available, the lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.***

12.7.3.1.2. ***For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 30%.***

12.7.3.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.7.3.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.7.4. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.8. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples ***re-processed*** and re-analyzed.

12.9. Additional information regarding internal quality control checks is provided in SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. ***Analytical Balance***

13.1.1. ***Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.***

13.1.2. ***If control limits are not specified, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.***

13.2. ***Chromatograph Degradation Test***

13.2.1. Prior to ***initial calibration and*** the analysis of field or QC sample extracts, the GC system must be shown to be resistant to the breakdown of 4,4'-DDT and endrin. The acceptance criteria for the degradation test are listed in Sections 12.1.

13.3. ***Chromatograph*** Initial Calibration

13.3.1. Establish an acceptable ***multi-point*** calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.2.

13.3.1.1. Because of the sensitivity of the electron capture detector, always clean the injection port and column prior to performing the initial calibration.

13.3.1.2. Recalibration is required for the following maintenance procedures.

13.3.1.2.1. Change, replace, or reverse the analytical column.

13.3.2. After obtaining an acceptable ***multi-point*** calibration curve and prior to processing field or QC sample extracts, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.3.

13.3.3. The initial ***multi-point*** calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

13.4. ***Retention Time Window***

13.4.1. Retention time window width for each analyte/surrogate is generated by running three CCV standards over a 72-hour period. Retention time window width determination shall be performed at method set-up, following column changes, after major instrument maintenance or when a significant retention time shift is suspected.

13.4.2. Document the serial number of the analytical column associated with the retention time window study.

13.4.3. Record the retention time in minutes for each analyte/surrogate to three decimal places.

14. ►PROCEDURE

14.1. Instrument Setup

14.1.1. Use the following GC operating conditions as guidance to establish the GC temperature program and flow rate necessary to separate the analytes of interest.

Description	GC Operating Condition
Inlet mode	pulsed splitless
Inlet temperature	220°C
Inlet pressure	21.579 psi
Total flow rate	90.5 mL/min
Septum purge flow	3 mL/min
Injection pulse pressure	50 psi until 0.3 min
Purge flow to split vent	82.9 mL/min at 2 min
Carrier gas flow rate	4.6 mL/min
Makeup gas flow rate	30 mL/min
Detector temperature	300°C
Initial temperature	120°C
Temperature program	120°C to 200°C at 45°C/min 200°C to 230°C at 12.5°C/min 230°C to 330°C at 20°C/min
Final temperature	330°C, hold 1.9 min

14.1.2. Autoinjector is set to inject 2 µL of field or QC sample extract.

14.1.3. ***Once established, the same operating conditions must be applied for all subsequent standard, sample, and blank analyses.***

14.2. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence. If the QC and retention time criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.4. and Section 12.5.3.

14.2.1. For EPA Region 9 requirement, refer to Section 12.4.1.1. for CCV frequency.

14.2.2. If a failed CCV is the first of the day, effect corrective action prior to analyzing any samples.

14.2.3. If a failed CCV is <u>not</u> the first of the day, effect corrective action and reanalyze all samples since the last acceptable CCV.

14.3. Following extraction by one of the methods specified in Section 5.2., the extracts for the QC and actual environmental samples are received in autoinjector vials. The autoinjector vials are then loaded onto the GC sample tray.

14.4. Standard and sample vials are loaded in the following or other logical order:

1) Degradation Test
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)

5) Method Blank (MB)
6) Samples (up to 20 per batch, including QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

14.4.1. Item 1: An acceptable degradation test demonstrates that the chromatographic system is not causing breakdown of thermally labile compounds due to active sites (e.g., the injection port is contaminated or contains catalytic active sites). A degradation test meeting the acceptance criteria is required daily prior to sample analysis and every 12 hours thereafter during analysis.

14.4.2. Items 2 and 9: A CCV is used to verify the acceptance of the initial ***multi-point*** calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

14.4.2.1. For EPA Region 9 requirement, refer to Section 12.4.1.1. for CCV frequency.

14.4.2.2. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample extract re-analyses that would be required in the event of an unacceptable CCV.

14.4.3. Item 3: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.3.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid and oil samples, the LCS consists of the specified compounds spiked into washed sea sand. For wipe samples, the LCS consists of the specified compounds spiked into unused gauze pad. For filter samples, the LCS consists of the specified compounds spiked into unused filter paper. ***For tissue samples, the LCS consists of the specified compounds spiked into a tissue matrix substitute (e.g., washed sea sand, worms, clams, or certified organic chicken meat).*** For mobility-procedure extracts, the LCS consists of the specified compounds spiked into the mobility-procedure extract designated as LCS.

14.4.3.2. One LCS is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.4. Item 4: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.4.5. Item 5: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (e.g., surrogates, etc.).

14.4.5.1. For aqueous samples, the MB consists of clean reagent water. For solid and oil samples, the MB consists of washed sea sand. For wipe samples, the MB consists of unused gauze pad. For filter samples, the MB consists of unused filter paper. ***For tissue samples, the MB consists of a tissue matrix substitute (e.g., washed sea sand, worms, clams, or certified organic chicken meat).*** For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB.

14.4.5.2. One MB is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.5.3. When samples that are processed together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of hexane must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.4.6. Item 6: Up to 20 sample (including QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

14.4.6.1. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.4.7. Item 7: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.7.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.5.

14.4.7.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently. This approach is considered "closed batch" as opposed to "open batch."

14.4.8. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.4.9. Solvent blanks may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration sample extracts), to check for potential carryover or cross-contamination.

14.5. Ensure that a sufficient amount of hexane is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles at the beginning of the sequence.

14.6. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or on the sequence table printout.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. Establish the daily retention time window for each analyte/surrogate (see Section 12.5.2.1. and Section 12.5.2.2.).

14.8.1.1. Tentative identification of an analyte/surrogate occurs when a peak from a sample extract falls within the daily retention time window.

14.8.1.1.1. For ***each multi-component analyte (i.e., chlordane and toxaphene)***, choose a minimum of 5 characteristic peaks that are at least 25% of the height of the largest characteristic peak for the ***analyte***, and determine the retention time window of each characteristic peak.

14.8.1.2. Use the succeeding CCV standards analyzed throughout the course of an analytical sequence within a 12-hour shift to evaluate retention time stability (see Section 12.5.3.). If any analyte(s)/surrogate(s) in the CCV standard fall outside of their daily retention time window(s), determine the cause of the problem and effect appropriate corrective action.

14.8.1.2.1. If any analyte(s)/surrogate(s) in the single-component pesticide CCV standard fall outside of their daily retention time window(s), then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.

14.8.1.2.2. If ***any major characteristic peak(s)/surrogate(s)*** in the ***multi-component pesticide*** CCV standard fall outside of their daily retention time window(s), then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.

14.8.2. Quantitation of a target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample extract and the calibration standards.

14.8.2.1. ***Multi-component analyte may be quantitated from the total area between the first and last eluting component (total area approach), or the area of 5 or more major characteristic peaks (subset peak approach).***

14.8.2.1.1. ***Total area approach is recommended if the area of the unresolved peaks contributes a significant portion of the area of the total response.***

14.8.2.1.2. ***The reasons for applying total area approach on sample quantitation and the problems associated with sample matrix should be fully documented.***

14.8.2.2. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak(s) can be determined.

14.8.2.2.1. For ***multi-component analyte*** quantitation, a forced baseline or baseline-to-baseline integration across the entire target range is required to ensure the appropriate integration of ***analyte*** response.

14.8.2.3. Determine the concentration based on the initial calibration curve.

14.8.2.3.1. Calculate the concentration of each single-component pesticide target analyte in a sample extract using the average of the initial RFs and the area of the characteristic peak. The formula for calculating concentration is listed in Section 15.7.

14.8.2.3.2. Calculate the concentration of ***each multi-component pesticide target analyte*** in a sample extract using the average of the initial RFs and the total area of the five predetermined peaks. The formula for calculating concentration is listed in Section 15.7.

14.8.2.3.3. Refer to Appendix A for examples of the predetermined peaks ***of each multi-component analyte***.

14.8.2.3.4. The data system is programmed to perform the calculation of concentration.

14.8.2.4. If the instrument response exceeds the calibration range, dilute the extract and reanalyze.

14.8.3. Tentative identification of a target analyte occurs when a peak from a sample extract falls within the analyte's retention time window. Confirmation is necessary when the composition of samples is not well characterized. Qualitative confirmation techniques are by second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors.

14.8.4. Second column confirmation is made on a "confirmation" channel configured with a column of dissimilar stationery phase and a second detector. The principle is that the retention time of the target analyte will differ between the primary and confirmation column and, unless the detected compound is the particular target analyte, it will not be observed within both retention time windows.

14.8.4.1. Report the higher result between the primary and confirmation column. The RPD between results must be ≤ 40%.

14.8.4.1.1. If one result is significantly higher (e.g., > 40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are observed, examine the baseline parameters established by the instrument data system (or operator) during peak integration. A rising baseline may cause the mis-integration of the peak for the lower result.

14.8.4.1.2. If no anomalies are observed, review the chromatographic conditions. If there is no evidence of chromatographic problems, then it may be appropriate to report the lower result.

14.8.4.1.3. The data user must be advised of the disparity between the results on the two columns. Under some circumstances, including those involving in monitoring compliance with an action level or

regulatory limit, further cleanup of the sample or additional analyses may be required when the two results in question span the action level or regulatory limit.

14.8.4.2. In cases where a peak is not observed in the confirmation column's retention time window, the analyte is reported as "ND."

14.8.4.3. A calibration curve and retention time window for each analyte/surrogate are also established and maintained for the confirmation channel. The calibration and quality control requirements for the confirmation channel are identical to those of the primary channel.

14.8.5. GC/MS confirmation is more reliable than second column confirmation. In this case, where confirmation is required by project requirements, the sample is re-analyzed on GC/MS. When GC/MS results indicate that a target analyte is not present, the GC result is reported as "ND."

14.8.6. Confirmation is required for all positive results unless the samples meet all of the following requirements:

14.8.6.1. All samples (***aqueous***, solid, or oil, or ***tissue***) come from the same source (e.g., same monitoring well). However, samples of the same matrix from the same site but from differing sources (e.g., different monitoring wells) are not exempted.

14.8.6.2. All chemical parameters have been previously analyzed, identified, and confirmed by a second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors. Documentation of such must be maintained.

14.8.6.3. The resulting chromatograms are relatively simple and do not contain complex or overlapping peaks.

14.8.6.4. Chromatograms are largely unchanged from those for which confirmation was carried out.

14.8.7. Qualitative confirmation by a second GC column is not required for determining chlordane and toxaphene.

14.8.8. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

14.8.8.1. ***When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.***

14.8.8.2. ***When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially***

integrating a peak, etc.), manual integrations performed by the analyst are necessary.

14.8.8.3. ***Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.***

14.9. Recommended Instrument Maintenance

14.9.1. Perform the following tasks to remedy the column adsorption problem.

14.9.1.1. Inject an 800-ppb single-component pesticide standard solution to prime (or deactivate) the column.

14.9.1.2. Run one or more solvent blanks consisting of hexane until no carryover is observed prior to analyzing any standards or samples.

14.9.2. Perform the following tasks to eliminate the degradation problem.

14.9.2.1. For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter.

14.9.2.2. Break off the first few centimeters (up to 30 cm) of the injection port side of the column.

14.9.2.3. Check the injector temperature and lower it to 205°C, if necessary.

14.9.2.4. Remove the columns and solvent backflush according to the manufacturer's instructions.

14.9.2.5. If all else fail, it may be necessary to deactivate the metal injector body and/or replace the columns.

14.9.3. Perform the following tasks to rinse the analytical column.

14.9.3.1. Depending on the nature of the residues expected, the first rinse might be reagent water, followed by methanol and acetone, with methylene chloride as the final rinse. In some cases, methylene chloride may be the only solvent necessary.

14.9.3.2. After the final rinse, the analytical column should be filled with methylene chloride and remained flooded overnight to allow materials within the stationary phase to migrate into the solvent.

14.9.3.3. The analytical column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen passing through the column.

15. ►CALCULATIONS

15.1. The response factor is calculated as follows:

$$RF = \frac{A_x}{C_x}$$

where: RF = response factor for target analyte being measured.
A_x = area of the characteristic peak(s) for target analyte being measured.
C_x = concentration of target analyte being measured in µg/L.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.
RF_{ave} = mean of the 5, ***6, or 7*** initial RFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RF_{ave} - RF_{daily}|}{RF_{ave}} \times 100$$

where: %D = percent difference.
RF_{daily} = daily RF for the target analyte.
RF_{ave} = mean of the 5, ***6, or 7*** initial RFs for the target analyte.

15.4. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x}{RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in µg/L.
A_x = area of the characteristic peak(s) for target analyte.
RF_{ave} = mean of the 5, ***6, or 7*** initial RFs for the target analyte.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
V_A = volume of aqueous sample solvent extracted in mL.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration for a solid (oil, ***or tissue***) sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S}$$

where: C_S = concentration of target analyte in solid (oil, ***or tissue***) sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid (oil, ***or tissue***) sample solvent extracted in g.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.10. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid sample solvent extracted in g.
C_{ss} = solids content in %.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.11. The target analyte concentration for a wipe (or filter) sample is calculated as follows:

$$C_W = C_{ex} \times V_{ex} \times D$$

where: C_W = concentration of target analyte in wipe (or filter) sample in µg/sample.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in L.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.12. The target analyte concentration for a mobility-procedure extract is calculated as follows:

$$C_{MP} = \frac{C_{ex} \times V_{ex} \times D}{V_{MP}}$$

where: C_{MP} = concentration of target analyte in mobility-procedure extract in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
V_{MP} = volume of mobility-procedure extract solvent extracted in mL. Unless specified otherwise, V_{MP} = 100.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.13. The percent breakdown is calculated as follows:

15.13.1. The percent breakdown of DDT is calculated as follows:

$$\%B_{DDT} = \frac{A_{DDD} + A_{DDE}}{A_{DDT} + A_{DDD} + A_{DDE}} \times 100$$

where: $\%B_{DDT}$ = percent breakdown of DDT.
A_{DDD} = degradation peak area of DDD.
A_{DDE} = degradation peak area of DDE.
A_{DDT} = peak area of DDT.

15.13.2. The percent breakdown of endrin is calculated as follows:

$$\%B_{endrin} = \frac{A_{aldehyde} + A_{ketone}}{A_{endrin} + A_{aldehyde} + A_{ketone}} \times 100$$

where: $\%B_{endrin}$ = percent breakdown of endrin.
$A_{aldehyde}$ = degradation peak area of aldehyde.
A_{ketone} = degradation peak area of ketone.
A_{endrin} = peak area of endrin.

15.14. Refer to the preparatory method(s) for additional calculations.

15.15. All concentrations shall be reported in µg/L (ppb) for aqueous samples, µg/kg (ppb) for oil, soil and solid waste, ***or tissue*** samples, and µg/sample for wipe and filter samples.

15.15.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

15.16. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples ***re-processed*** and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 50% and 135%, respectively. The RPD is ≤ 25%. All LCS/LCSD compounds must be within acceptance limits (see Section ***12.6.3.*** for additional information).

18.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.3. The acceptance criteria for surrogate compound recoveries are predetermined. The lower and upper acceptance limits for %REC of each surrogate compound in an

aqueous sample are 50% and 135%, respectively. The lower and upper acceptance limits for %REC of each surrogate compound in a non-aqueous sample are 50% and 130%, respectively.

18.3.1. For EPA Region 9 requirement, refer to Section ***12.7.2.1.2.*** for acceptance criteria.

18.3.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

18.3.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.4.1. Check the surrogate standard solutions for degradation and contamination.

18.3.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same extract should be re-analyzed.

18.3.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be ***re-processed*** and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.4.3.1. If, upon ***re-processing*** and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples ***re-processed*** and re-analyzed.

18.3.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD compounds are predetermined. The lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 25%.

18.4.1. ***For EPA Region 9 requirement, refer to Section 12.7.3.1.2. for acceptance criteria.***

18.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for aqueous samples, µg/kg (ppb) for oil, soil and solid waste, ***or tissue*** samples, and µg/sample for wipe and filter samples.

18.7.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a

result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained

are within acceptance criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Organochlorine Pesticides by Gas Chromatography*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8081A, USEPA, Revision 1, December 1996.

22.2. ►***Determinative Chromatographic Separations, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000B, USEPA, Revision 2, December 1996.***

22.3. *Determinative Chromatographic Separations*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000C, USEPA, Revision 3, March 2003.

22.4. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.5. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.6. *Organic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, February 2007.

22.7. *Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs)*, SW-846 Method 8081 or 8080, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Quantitation Peaks for Single-Component and ***Multi-Component*** Target Compounds.

23.2. ***Appendix B: Procedure for Low Limit of Quantitation.***

23.3. Appendix ***C***: Additional Quality Control Criteria for Department of Defense Project.

23.4. Appendix ***D***: Control Limits for Department of Defense Project.

24. MODIFICATIONS

24.1. ►***The following modifications from EPA Method 8081A Revision 1 are noted.***

Calscience SOP M400 Section	Reference Document EPA Method 8081A Section	Summary of Modification
All	All	None.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
5.0	Section 2: Add tissue matrix. Section 3: Update terminology for RL, and add reference to the determinations of DL and RL. Section 4: Revise the scope to indicate routine and non-routine analytes. Update EPA method numbers. Section 5: Update method summary. Section 6: Add LOD and LOQ definitions. Section 7: Update interferences. Section 9: Update the list of equipment and supplies. Section 10: Revise reagent and standard preparations. Section 11: Revise the requirements on collection and preservation. Section 12: Revise quality control criteria. Section 13: Add calibration procedures. Section 14: Update procedures. Section 15: Revise formulas to apply additional calibration levels and add reference to tissue matrix. Section 18: Update section references, and add EPA Region 9 requirements. Section 23: Rearrange the order of appendices. Section 24: Revise modifications. Section 25: Add revision history. Appendix B: Revise the whole appendix for lower limit of quantitation. Appendix C: Update DoD quality control requirements and criteria.	J. Kang / K. Chang	01/04/13

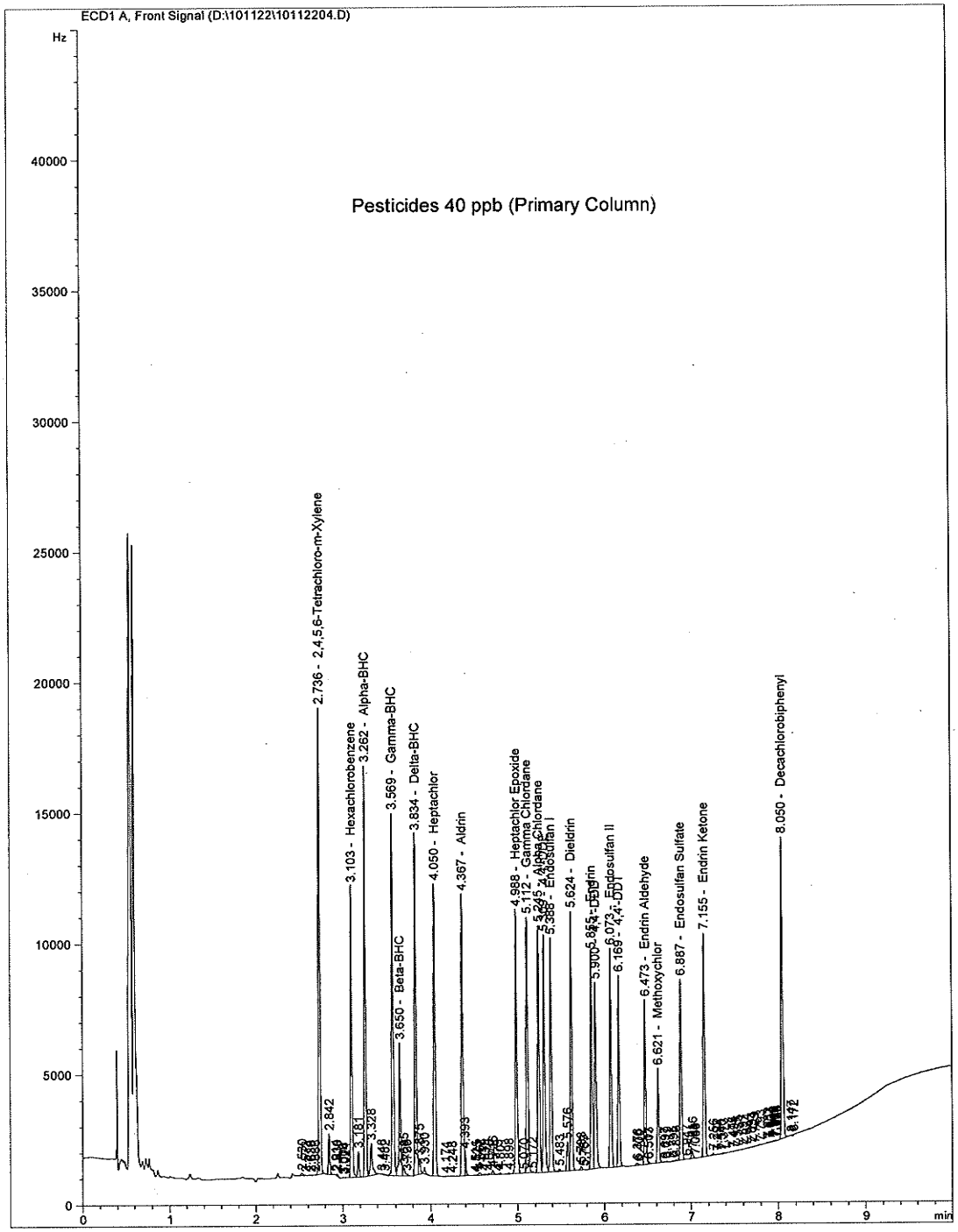
Appendix A

QUANTITATION PEAKS FOR SINGLE-COMPONENT AND MULTI-COMPONENT TARGET COMPOUNDS

Calscience Environmental Laboratories, Inc.

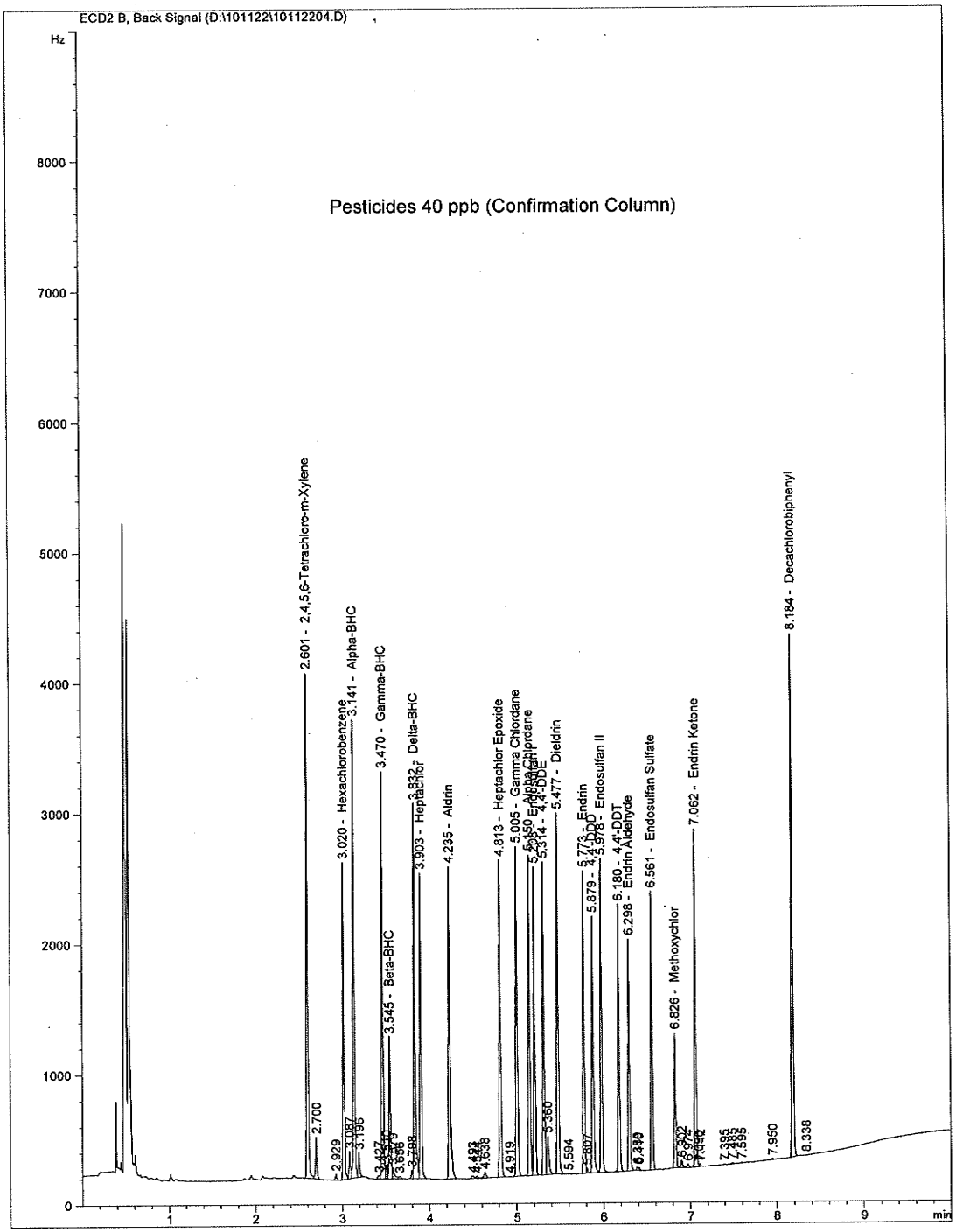
Appendix A

Quantitation Peaks for Single-Component Target Compounds



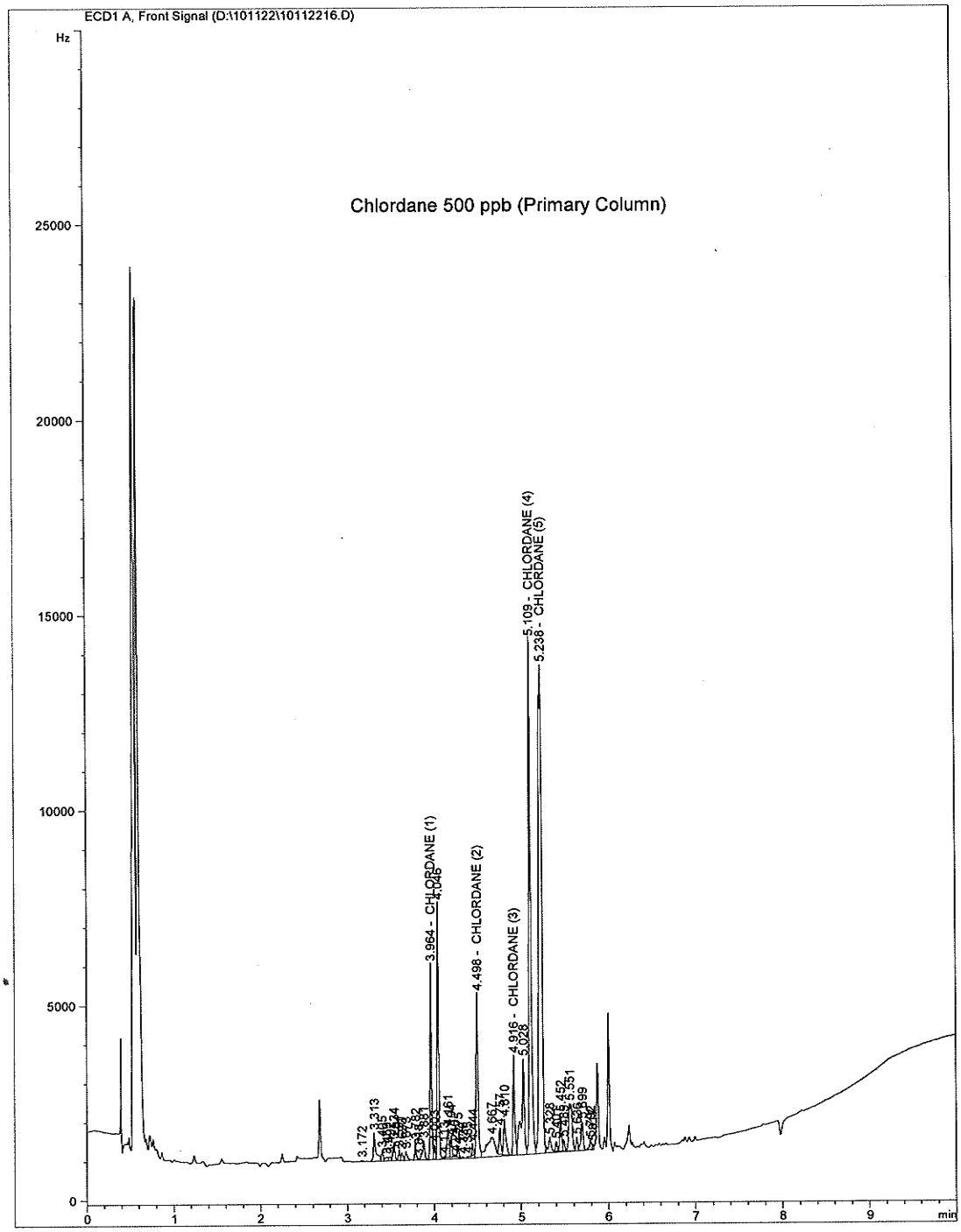
Appendix A

Quantitation Peaks for Single-Component Target Compounds (Cont.)



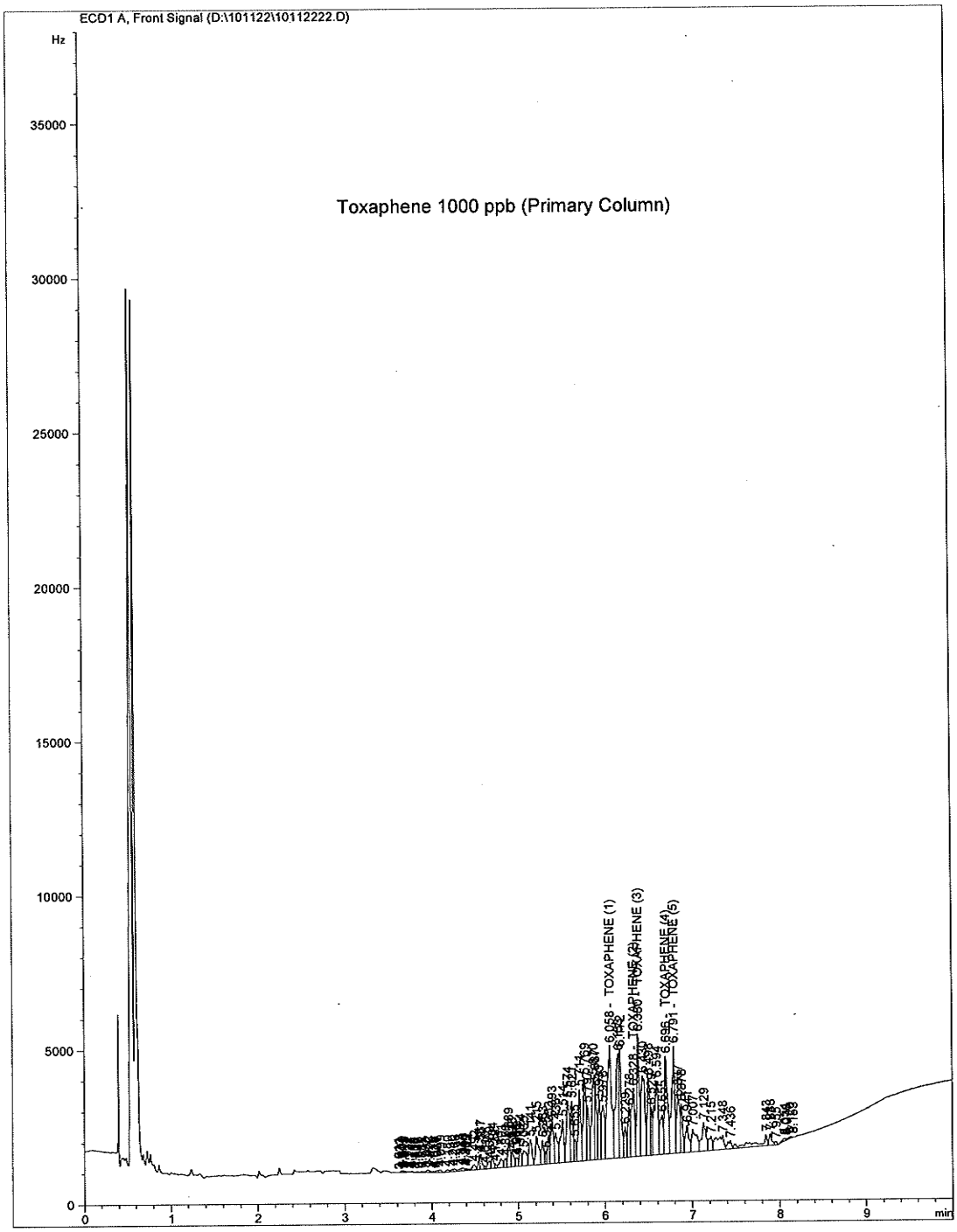
Appendix A

Quantitation Peaks for Multi-Component Target Compounds



Appendix A

Quantitation Peaks for Multi-Component Target Compounds (Cont.)



Appendix B

PROCEDURE FOR LOWER LIMIT OF QUANTITATION

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8081A, Organochlorine Pesticides by Gas Chromatography – Procedure for Lower Limit of Quantitation.

2. APPLICABLE MATRICES

2.1. This method is applicable to water, soil, and solid wastes.

3. DETECTION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

	Water	Soil
Pesticides	0.010 µg/L	0.2 µg/kg (wet-weight)
Chlordane	0.025 µg/L	0.5 µg/kg (wet-weight)
Toxaphene	0.125 µg/L	2.5 µg/kg (wet-weight)

4. SCOPE AND APPLICATION

4.1. The procedure described herein either supersedes or is in addition to the standard procedure.

5. STANDARDS

5.1. Calibration standard solutions containing various concentrations of target analytes and surrogates in hexane.

5.1.1. Dilute the appropriate volumes of the working and stock standards to the specified volumes with hexane for initial calibration.

5.1.2. Use the following calibration levels as guidance to prepare the routine single-component pesticide calibration standards for lower limit of quantitation.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A1	S	A1 + S	A1 + S	A1 + S
0.5	1.0	4.0 + 8.0	0.5	4.0
2.0	4.0	4.0 + 8.0	2.0	4.0
10	20	4.0 + 8.0	10	4.0
40	80	4.0 + 8.0	40	4.0
60	120	4.0 + 8.0	60	4.0
80	160	4.0 + 8.0	80	4.0

Note: A1 = Routine Single-Component Analyte; S = Surrogate

5.1.3. Use the following calibration levels as guidance to prepare the non-routine single-component pesticide calibration standards for lower limit of quantitation.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A2	A3	A2 + A3	A2 + A3	A2 + A3
2.0	10	2.0 + 10	8.0	8.0
10	50	2.0 + 10	40	8.0
40	200	2.0 + 10	160	8.0
60	300	2.0 + 10	240	8.0
80	400	2.0 + 10	320	8.0

Note: A2 = Non-Routine Single-Component Analyte; A3 = 4,4'-DCBP

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A4	S	A4 + S	A4 + S	C
2.0	4.0	2.0 + 4.0	4.0	4.0
10	20	2.0 + 4.0	20	4.0
40	80	2.0 + 4.0	80	4.0
60	120	2.0 + 4.0	120	4.0
80	160	2.0 + 4.0	160	4.0

Note: A4 = Kepone, Chlorobenzilate, Diallate, or Hexachlorocyclopentadiene
S = Surrogate

5.1.4. Use the following calibration levels as guidance to prepare the multi-component pesticide calibration standards for lower limit of quantitation.

Calibration Level (ppb)		Initial				Final	
		Concentration (ppm)		Volume (µL)		Volume (mL)	
C	T	C	T	C	T	C	T
5.0		100		0.2		4.0	
10	25	100	100	0.4	1.0	4.0	4.0
100	200	100	100	4.0	8.0	4.0	4.0
500	1000	100	100	20	40	4.0	4.0
750	1500	100	100	30	60	4.0	4.0
2000	4000	100	100	80	160	4.0	4.0

Note: C = Chlordane; T = Toxaphene

5.1.5. The midpoint standards are also used as the continuing calibration verification solutions.

5.1.6. The calibration levels for the initial calibration of a non-routine target analyte may be established differently per client request or project specific DQOs.

5.2. Initial calibration verification (ICV) solutions containing the appropriate concentrations of each target analyte and surrogate in hexane. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

5.2.1. Dilute the appropriate volumes of the second source working and stock standards to the specified volumes with hexane for initial calibration verification.

5.2.2. Use the following calibration level as guidance to prepare the routine single-component pesticide ICV solution for lower limit of quantitation.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A1	S	A1 + S	A1 + S	A1 + S
40	80	4.0 + 8.0	40	4.0

Note: A1 = Routine Single-Component Analyte; S = Surrogate

5.2.3. Use the following calibration levels as guidance to prepare the non-routine single-component pesticide ICV solutions for lower limit of quantitation.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A2	A3	A2 + A3	A2 + A3	A2 + A3
40	200	2.0 + 10	160	8.0

Note: A2 = Non-Routine Single-Component Analyte; A3 = 4,4'-DCBP

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A4	S	A4 + S	A4 + S	C
40	80	2.0 + 4.0	80	4.0

Note: A4 = Kepone, Chlorobenzilate, Diallate, or Hexachlorocyclopentadiene
S = Surrogate

5.2.4. Use the following calibration levels as guidance to prepare the multi-component pesticide ICV solutions for lower limit of quantitation.

Calibration Level (ppb)		Initial				Final	
		Concentration (ppm)		Volume (µL)		Volume (mL)	
C	T	C	T	C	T	C	T
500	1000	100	100	20	40	4.0	4.0

Note: C = Chlordane; T = Toxaphene

5.2.5. The calibration level for the initial calibration verification of a non-routine target analyte may be established differently per client request or project specific DQOs.

5.3. Continuing calibration verification (CCV) solutions containing the appropriate concentrations of each target analyte and surrogate in hexane. The CCV solution is of a source same as that used for the initial multi-point calibration.

5.3.1. Dilute the appropriate volumes of the working and stock standards to the specified volumes with hexane for continuing calibration verification.

5.3.2. Use the following calibration level as guidance to prepare the routine single-component pesticide CCV solution for lower limit of quantitation.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A1	S	A1 + S	A1 + S	A1 + S
40	80	4.0 + 8.0	400	40

Note: A1 = Routine Single-Component Analyte; S = Surrogate

5.3.3. Use the following calibration levels as guidance to prepare the non-routine single-component pesticide CCV solutions for lower limit of quantitation.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A2	A3	A2 + A3	A2 + A3	A2 + A3
40	200	2.0 + 10	160	8.0

Note: A2 = Non-Routine Single-Component Analyte; A3 = 4,4'-DCBP

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A4	S	A4 + S	A4 + S	C
40	80	2.0 + 4.0	80	4.0

Note: A4 = Kepone, Chlorobenzilate, Diallate, or Hexachlorocyclopentadiene
S = Surrogate

5.3.4. Use the following calibration levels as guidance to prepare the multi-component pesticide CCV solutions for lower limit of quantitation.

Calibration Level (ppb)		Initial				Final	
		Concentration (ppm)		Volume (µL)		Volume (mL)	
C	T	C	T	C	T	C	T
500	1000	100	100	200	400	40	40

Note: C = Chlordane; T = Toxaphene

5.3.5. The calibration level for the continuing calibration verification of a non-routine target analyte may be established differently per client request or project specific DQOs.

5.4. Surrogate working standard solution containing 2.0 ppm each of deca-chlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) in acetone or other acetone miscible solvent.

5.4.1. Add 250 µL of the 2.0-ppm surrogate working standard to each sample including each quality control (QC) check sample and method blank prior to solvent extraction.

5.5. Spike working standard solutions containing various concentrations of target analytes in acetone or other acetone miscible solvent. The spike standard solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

5.5.1. Use the 1.0-ppm spike working standard solutions as the single-component pesticide spike working standard solutions. Use the 1000-ppm chlordane stock standard solution and the 1000-ppm toxaphene stock standard solution as the multi-component pesticide spike working standard solutions.

5.5.2. Add 250 µL of the single-component pesticide spike working standard to each MS/MSD and LCS/LCSD sample prior to solvent extraction.

5.5.3. Per client request or project specific data quality objectives (DQOs), add 2.5 µL of the chlordane spike working standard to each MS/MSD and LCS/LCSD sample prior to solvent extraction.

5.5.4. Per client request or project specific DQOs, add 5.0 µL of the toxaphene spike working standard to each MS/MSD and LCS/LCSD sample prior to solvent extraction.

6. PROCEDURE

6.1. Aqueous Sample Preparation and Extraction via EPA Method 3510

6.1.1. Prepare and extract an aqueous sample as outlined in SOP-M200 with the following modification on final extract volume.

6.1.1.1. Adjust the final extract volume to 5.0 mL.

6.2. Solid Sample Preparation and Extraction via EPA Method 3545

6.2.1. Prepare and extract a solid sample as outlined in SOP-M204 with the following modifications on sample mass and final extract volume.

6.2.1.1. Measure 50.0 ± 2.5 g of a homogenized solid sample into a clean, pre-assembled extraction cell. Record the mass to the nearest 0.1 g.

6.2.1.1.1. For MB/LCS/LCSD, measure exactly 50.0 g of washed sea sand. Record the washed sea sand identification number.

6.2.1.1.2. For MS/MSD, measure exactly 50.0 g of solid sample in each analytical batch selected for spiking.

6.2.1.2. Adjust the final extract volume to 5.0 mL.

6.3. Instrument Setup

6.3.1. Use the following GC operating conditions as guidance to establish the GC temperature program and flow rate necessary to separate the analytes of interest.

Description	GC Operating Condition
Inlet mode	pulsed splitless
Inlet temperature	220°C
Inlet pressure	21.579 psi
Total flow rate	90.5 mL/min
Septum purge flow	3 mL/min
Injection pulse pressure	50 psi until 0.3 min
Purge flow to split vent	82.9 mL/min at 2 min
Carrier gas flow rate	4.6 mL/min
Makeup gas flow rate	30 mL/min
Detector temperature	300°C
Initial temperature	120°C
Temperature program	120°C to 200°C at 45°C/min 200°C to 230°C at 12.5°C/min 230°C to 330°C at 20°C/min
Final temperature	330°C, hold 1.9 min

Appendix C

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. ►EPA Method 8081***A***, Organochlorine Pesticides by Gas Chromatography – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. ►QUALITY CONTROL

5.1. ***Limit of Detection (LOD)***

5.1.1. ***LOD determination*** shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, ***and following*** a change in instrumentation that affects the sensitivity of the analysis ***thereafter***.

5.1.2. ***LOD*** verification must be performed immediately following an ***LOD determination*** and quarterly thereafter ***to verify method sensitivity***.

5.1.2.1. ***LOD*** verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for ***a single-analyte standard***, or greater than 1 to 4 times the detection limit for ***a multi-analyte standard***.

5.1.2.2. ***LOD*** verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

5.1.2.2.1. ***For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.***

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the ***LOD determination*** and verification at a higher concentration. Set the ***LOD*** at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive ***LOD*** verifications at a higher concentration. Set the ***LOD*** at the higher concentration.

5.1.3. No samples shall be analyzed without a valid ***LOD***.

5.2. ***Limit of Quantitation (LOQ)***

5.2.1. ***LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.***

5.2.1.1. ***The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.***

5.2.1.2. ***The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.***

5.2.2. ***LOQ verification must be performed quarterly to verify precision and bias at the LOQ.***

5.2.2.1. ***LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.***

5.2.2.2. ***LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.***

5.3. Continuing Calibration Verification (CCV)

5.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 ***field*** samples or portion thereof within a 12-hour shift, and at the end of sequence.

5.3.2. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.4. Retention Time Window

5.4.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a low-to-midpoint CCV standard at the beginning of an analytical sequence.

5.4.1.1. When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S.

5.4.1.2. When initial calibration is not performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the low-to-midpoint CCV standard ± 3S.

5.5. Event Based Quality Control (MBs and LCS/LCSDs)

5.5.1. Method Blanks (MBs)

5.5.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.5.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.5.1.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the ***LOD***.

5.5.1.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.5.2. Laboratory Control Samples (LCS/LCSDs)

5.5.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound in aqueous and solid matrices are listed in Appendix ***D***.

5.5.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.5.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.5.2.3. All project-specific analytes of concern must be within control limits. No marginal exceedance is allowed for any project-specific analyte of concern. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.6. Matrix Based Quality Control (Surrogates and MS/MSDs)

5.6.1. Surrogates

5.6.1.1. The lower and upper acceptance limits for %REC of each surrogate compound in aqueous and solid matrices are listed in Appendix ***D***.

5.6.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.2. Matrix Spikes (MS/MSDs)

5.6.2.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous and solid matrices are listed in Appendix ***D***. The RPD is ≤ 30%.

5.6.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

6. ►PROCEDURE

6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 ***field*** samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2. Standard and sample vials are loaded in the following or other logical order:

1) Degradation Test
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 10 per batch, excluding QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

6.2.1. Items 2 and 9: A CCV is used to verify the acceptance of the initial ***multi-point*** calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 10 ***field*** samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2.2. Item 6: Up to 10 sample (excluding QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not

contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

6.2.3. Item 7: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.2.3.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.2.4. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

6.3. Data Interpretation

6.3.1. The flagging criteria and data reporting procedure for second column confirmation are as follows:

6.3.1.1. If RPD is > 40%, apply the appropriate data qualifier (J-flag) and document in the case narrative.

6.3.1.2. Follow project-specific reporting requirements when reporting data.

6.3.1.2.1. If project-specific reporting requirements are unavailable, apply method-specific reporting requirements.

6.3.1.2.2. If method-specific reporting requirements are unavailable, report the results from the primary column or detector, unless there is a scientifically valid and documented reason for not doing so.

6.3.2. Identify unconfirmed results with the appropriate data qualifiers and document in the case narrative.

7. REFERENCES

7.1. ►Department of Defense Quality Systems Manual for Environmental Laboratories, Version ***4.2, October 25, 2010***.

Appendix D

CONTROL LIMITS FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

Appendix D

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Aqueous Matrix

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
4,4'-DDD	25	150	10	170
4,4'-DDE	35	140	15	160
4,4'-DDT	45	140	30	155
Aldrin	25	140	10	155
α-BHC	60	130	50	140
α-Chlordane	65	125	55	135
β-BHC	65	125	55	135
δ-BHC	45	135	30	150
Dieldrin	60	130	50	140
Endosulfan I	50	110	40	120
Endosulfan II	30	130	10	150
Endosulfan sulfate	55	135	40	150
Endrin	55	135	45	145
Endrin aldehyde	55	135	40	150
Endrin ketone	75	125	70	135
γ-BHC	25	135	10	155
γ-Chlordane	60	125	50	135
Heptachlor	40	130	30	145
Heptachlor epoxide	60	130	50	140
Methoxychlor	55	150	40	165

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix D

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Solid Matrix

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
4,4'-DDD	30	135	10	155
4,4'-DDE	70	125	60	135
4,4'-DDT	45	140	30	155
Aldrin	45	140	30	155
α-BHC	60	125	50	135
α-Chlordane	65	120	55	130
β-BHC	60	125	50	135
δ-BHC	55	130	45	145
Dieldrin	65	125	55	135
Endosulfan I	15	135	10	155
Endosulfan II	35	140	20	160
Endosulfan sulfate	60	135	50	145
Endrin	60	135	50	145
Endrin aldehyde	35	145	20	165
Endrin ketone	65	135	55	145
γ-BHC	60	125	50	135
γ-Chlordane	65	125	55	135
Heptachlor	50	140	35	155
Heptachlor epoxide	65	130	55	140
Methoxychlor	55	145	45	155

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix D

DoD Control Limits of Surrogate Compounds in Aqueous Matrix

Analyte	Control Limit	
	Lower	Upper
Decachlorobiphenyl	30	135
TMX	25	140

DoD Control Limits of Surrogate Compounds in Solid Matrix

Analyte	Control Limit	
	Lower	Upper
Decachlorobiphenyl	55	130
TMX	70	125

Title : **EPA METHOD 8082, POLYCHLORINATED BIPHENYLS (PCBs) AS AROCLORS BY GAS CHROMATOGRAPHY**

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Revision 4.0 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 01/22/13
MANAGEMENT **DATE**

_____ 01-22-13
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 8082, Polychlorinated Biphenyls (PCBs) as Aroclors by Gas Chromatography.

2. APPLICABLE MATRICES

2.1. ►This method is applicable to water, oil, soil, and solid wastes. ***It is also applicable to marine and freshwater tissues as a modified method.***

3. ►DETECTION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

	Water	Soil	***Sediment***
PCBs as Aroclors	1.0 µg/L	50 µg/kg ***(wet-weight)***	***10 µg/kg (wet-weight)***

	Oil	Wipe/Filter	***Tissue***
PCBs as Aroclors	1000 µg/kg	1.0 µg/sample	***10 µg/kg***
Aroclor 1221			***25 µg/kg***

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution or cleanups.

3.3. ***Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.***

4. ►SCOPE AND APPLICATION

4.1. EPA Method 8082 is used to determine the concentrations of polychlorinated biphenyls (PCBs) ***as Aroclors in extracts from*** various matrices, ***using*** a gas chromatographic system configured with a fused-silica capillary column coated with a slightly polar silicone.

4.1.1. ***Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns compared to those of Aroclor standards.***

4.2. The following ***compounds are routinely*** determined by this method.

Aroclor-1016	Aroclor-1242	Aroclor-1260
Aroclor-1221	Aroclor-1248	Aroclor-1262
Aroclor-1232	Aroclor-1254	Aroclor-1268

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph (GC) and skilled in the interpretation of gas chromatograms.

5. ►METHOD SUMMARY

5.1. EPA Method 8082 describes chromatographic procedures that will allow for the identification of Aroclors in the extract and their qualitative and quantitative analysis by gas chromatography. Detection is achieved using an electron capture detector (ECD).

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample.

5.2.1. ***Aqueous*** samples are extracted via EPA Methods 3510 or 3520 at neutral pH using methylene chloride exchanged into hexane.

5.2.2. Solid samples are extracted via EPA Methods 3540, ***3545***, or 3550 using methylene chloride-acetone (1:1) exchanged into hexane, or via EPA Method 3545 using methylene chloride exchanged into hexane.

5.2.3. Solid samples for TCLP, SPLP, or STLC analysis are ***prepared*** using the appropriate ***mobility extraction method, and the resulting mobility-procedure extracts (leachates) are extracted via EPA Methods 3510 or 3520 at neutral pH using methylene chloride exchanged into hexane***.

5.2.4. Oil samples are prepared in accordance with EPA Method 3580 using hexane as the diluent.

5.2.5. ***Tissue samples are extracted via EPA Methods 3540 or 3545 using methylene chloride exchanged into hexane.***

5.2.6. ***A variety of cleanup procedures may be applied to the extracts, depending on the nature of the target analytes and the matrix interferences.***

5.3. Acceptable preparatory methods include, ***but are not limited to***, the following:

Type of Sample Preparation	Method	SOP No.
Separatory Funnel Liquid-Liquid Extraction	EPA 3510	SOP-M200
Continuous Liquid-Liquid Extraction	EPA 3520	SOP-M201
Soxhlet Extraction	EPA 3540	SOP-M203
Pressurized Fluid Extraction	EPA 3545	SOP-M204
Ultrasonic Extraction	EPA 3550	SOP-M202
Waste Dilution	EPA 3580	SOP-M205
Cleanup	***EPA 3600(M)***	***SOP-M234***
Gel-Permeation Cleanup	***EPA 3640***	***SOP-M233***
Marine Tissue Preparation and Cleanup	***CEL Proprietary***	***SOP-M236***
TCLP	EPA 1311	SOP-M226
SPLP	EPA 1312	SOP-M227
STLC (***California Code of Regulations***)	***CCR T22.11.5.A-II***	SOP-M228

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. ***Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.***

6.12. ***Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.***

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche

copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.27. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. ►INTERFERENCES

7.1. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.2. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially.

7.2.1. Sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2.2. ***Analysis of a suspected high level sample should be followed by an analysis of solvent blank to check for cross-contamination. In addition***, suspected high level samples ***may*** be diluted and then analyzed at the end of the sequence to prevent carryover contamination.

7.3. Interference can also occur when "dirty" samples leave residue in the analytical column. To minimize this effect, a guard column should be used and cut frequently or replaced. In addition, the analytical column can be "baked" after such samples. Other maintenance procedures include cleaning the inlet or replacing injection liner and seal.

7.4. Phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.

7.4.1. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters can best be minimized by

avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

7.4.2. Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

7.4.3. ***Phthalate ester interferences may be removed using EPA Method 3665 (Sulfuric Acid/Permanganate Cleanup) prior to analysis.***

7.5. Sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur can be removed through the use of EPA Method 3660 ***(Sulfur Cleanup)***.

8. ►SAFETY

8.1. ***Compounds covered by this method*** have been tentatively classified as known or suspected human carcinogens. Primary standards of these ***compounds*** must be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when analysts handle high concentrations of these ***compounds***.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

8.4. ***Refer to the preparatory methods for additional safety issues.***

9. ►EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Agilent 6890 ***Series*** Gas Chromatograph, ***Agilent 7890A Gas Chromatograph***, or equivalent configured with ***the following components***.

9.1.1. Autoinjector, Agilent 7680 Series, Agilent 7683 Series, ***or equivalent***.

9.2. ***Instrument Software***

9.2.1. ***Agilent GC ChemStation Version A.09.01[1206], Agilent GC ChemStation Version B.04.02[98], or equivalent.***

9.3. ***Instrument Maintenance and Troubleshooting***

9.3.1. ***Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.***

9.4. Primary Detection Channel

9.4.1. Detector: Electron capture detector (ECD).

9.4.2. Analytical Column: 30-m × 0.32-mm ID, 0.50-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek ***Rtx®-CLPesticides2*** or equivalent.

9.5. ***Confirmation Detection Channel***

9.5.1. ***Detector: Electron capture detector (ECD).***

9.5.2. ***Analytical Column: 15-m × 0.32-mm ID, 0.50-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides or equivalent.***

9.6. Guard Column: 5-m × 0.32-mm ID, intermediate-polarity deactivated, uncoated fused silica, Restek IP Deactivated Guard Column or equivalent.

9.7. Carrier Gas: ***Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent.***

9.8. ***Carrier Gas: Hydrogen, H_2, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.***

9.9. ***Makeup Gas: Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent.***

9.10. Makeup Gas: ***Methane, CH_4, 5%, and argon, Ar, 95%, compressed, Praxair P-5 Mixture or equivalent.***

9.11. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certificate ***or equivalent documentation***.

9.12. ***Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.***

9.13. ***Autoinjector vials, 12-mm × 32-mm (2-mL capacity), crimp top, clear glass, with aluminum crimp caps and Teflon-lined septa, disposable.***

9.14. ***Vial inserts, 300−µL, clear glass, with conical bottom and spring.***

9.15. ***Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.***

9.16. ***Refer to the specific SOPs of the preparatory methods for additional equipment and supplies.***

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. ***Sodium thiosulfate, $Na_2S_2O_3$, anhydrous, white solid, reagent grade or equivalent.***

10.1.4. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v).

10.1.4.1. Prepare the 10% ***$Na_2S_2O_3$*** solution by dissolving ***200 g of anhydrous*** $Na_2S_2O_3$ in reagent water ***and dilute to 2 L with additional reagent water***.

10.1.5. Methylene chloride ***(or dichloromethane)***, CH_2Cl_2, ***clear colorless liquid***, pesticide grade or equivalent.

10.1.6. Hexane, C_6H_{14}, ***clear colorless liquid***, pesticide grade or equivalent.

10.1.7. Acetone, CH_3COCH_3, ***clear colorless liquid***, pesticide grade or equivalent.

10.1.8. ***Refer to the specific SOPs of the preparatory methods for additional reagents.***

10.1.9. All reagents must be inspected and documented ***in the Chemicals and Supplies Verification Logbook*** prior to use.

10.2. Standards

10.2.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 100/1000 ppm of each target analyte, and 200 ppm of each surrogate are used to prepare calibration and check standards.

10.2.1.1. ***Prepare each working standard solution by diluting the appropriate volumes of the stock standards to the specified volumes with hexane.***

10.2.1.2. ***The 20-ppm working standards are prepared as follows:***

Analyte	Initial Conc. (ppm)	Initial Volume (µL)	Final Conc. (ppm)	Final Volume (mL)
Aroclor 1016	100	800	20	4.0
Aroclor 1260	100	800		
surrogates	200	80	4.0	

Analyte	Initial Conc. (ppm)	Initial Volume (µL)	Final Conc. (ppm)	Final Volume (mL)
Aroclor 1016	1000	80	20	4.0
Aroclor 1260	1000	80		
surrogates	200	80	4.0	

Analyte	Initial Conc. (ppm)	Initial Volume (µL)	Final Conc. (ppm)	Final Volume (mL)
Aroclor 1221	100	800	20	4.0
Aroclor 1254	100	800	20	4.0
Aroclor 1232	100	800	20	4.0
Aroclor 1262	100	800	20	4.0
Aroclor 1248	100	800	20	4.0
Aroclor 1268	100	800	20	4.0
Aroclor 1242	100	800	20	4.0
surrogates	200	80	4.0	4.0

10.2.1.3. ***The 500-ppb working standard is prepared as follows:***

Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppb)	Volume (mL)
Aroclor 1221	100	20	500	4.0
Aroclor 1254	100	20		
Aroclor 1232	100	20	500	4.0
Aroclor 1262	100	20		
Aroclor 1248	100	20	500	4.0
Aroclor 1268	100	20		
Aroclor 1242	100	20	500	4.0

10.2.2. ***Pre-certified stock standard solution, in sealed glass ampule, containing 200 ppm each of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) is used to prepare surrogate working standard.***

10.2.2.1. ***Prepare the 2.0-ppm surrogate working standard solution by diluting 10 mL of the 200-ppm surrogate stock standard to 1.0 L with acetone or other acetone miscible solvent.***

10.2.3. ***Pre-certified stock standard solutions, each in sealed glass ampules, containing 100/1000 ppm of each target analyte are used to prepare spike working standards.***

10.2.3.1. ***Prepare each 10-ppm spike working standard solution by diluting the appropriate volumes of the stock standards to the specified volumes with acetone or other acetone miscible solvent.***

10.2.3.2. ***The 10-ppm spike working standards are prepared as follows:***

Analyte	Initial		Final	
	Conc. (ppm)	Volume (mL)	Conc. (ppm)	Volume (mL)
Aroclor 1016	1000	2.0	10	200
Aroclor 1260	1000	2.0		
Aroclor 1221	100	1.0	10	10
Aroclor 1254	100	1.0	10	10
Aroclor 1232	100	1.0	10	10
Aroclor 1262	100	1.0	10	10
Aroclor 1248	100	1.0	10	10
Aroclor 1268	100	1.0	10	10
Aroclor 1242	100	1.0	10	10

10.2.4. Calibration standard solution containing ***various concentrations of target analytes and surrogates*** in hexane.

10.2.4.1. ***Dilute the appropriate volumes of the 20-ppm working standards to the specified volumes with hexane for initial calibration.***

10.2.4.2. ***Use the following calibration levels as guidance to prepare the calibration standards.***

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A	S	A + S	A + S	A + S
100	20	20 + 4.0	20	4.0
250	50	20 + 4.0	50	4.0
500	100	20 + 4.0	1000	40
750	150	20 + 4.0	150	4.0
2000	400	20 + 4.0	400	4.0

Note: A = Aroclor; S = Surrogate

10.2.4.3. The ***midpoint*** standard is also used as the continuing calibration verification solution.

10.2.5. Initial calibration verification (ICV) solution containing 500 ppb of ***each target analyte*** and 100 ppb of each surrogate in hexane. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.5.1. ***Dilute 100 µL of the second source 20-ppm working standard to 4.0 mL with hexane for initial calibration verification.***

10.2.5.2. ***Use the following calibration level as guidance to prepare the ICV solution.***

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A	S	A + S	A + S	A + S
500	100	20 + 4.0	100	4.0

Note: A = Aroclor; S = Surrogate

10.2.6. Continuing calibration verification (CCV) solution containing ***500 ppb of each target analyte and 100 ppb of each surrogate*** in hexane. The CCV solution is of a source same as that used for the initial five-point calibration.

10.2.6.1. ***Dilute 1000 µL of the 20-ppm working standard to 40 mL with hexane for continuing calibration verification.***

10.2.6.2. ***Use the following calibration level as guidance to prepare the CCV solution.***

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A	S	A + S	A + S	A + S
500	100	20 + 4.0	1000	40

Note: A = Aroclor; S = Surrogate

10.2.7. Surrogate ***working*** standard solution containing 2.0 ppm each of deca-chlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) in acetone or ***other acetone miscible solvent***.

10.2.7.1. Add 500 µL of the ***2.0-ppm*** surrogate ***working*** standard to each sample including ***each*** quality control (QC) check sample and method blank prior to ***solvent*** extraction.

10.2.7.2. ***Add 500 µL of the 2.0-ppm surrogate working standard to each mobility-procedure extract including each mobility-procedure extract designated as QC check sample and method blank prior to solvent extraction.***

10.2.8. Spike ***working*** standard solution containing 10 ppm of each target analyte in acetone or ***other acetone miscible solvent***. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.8.1. ***Use the 10-ppm spike working standard solution containing only Aroclor 1016 and Aroclor 1260 if samples are not expected to contain any Aroclor. Use the 10-ppm spike working standard solution containing the specific Aroclor(s) if samples are expected to contain these Aroclor(s).***

10.2.8.2. The ***spike*** standards are used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

10.2.8.3. Add 200 µL of the spike ***working*** standard ***containing only Aroclor 1016 and Aroclor 1260*** to each MS/MSD and LCS/LCSD sample prior to ***solvent*** extraction.

10.2.8.4. ***Per client request or project specific data quality objectives (DQOs), add 200 µL of the spike working standard containing the specific Aroclor(s) to each MS/MSD and LCS/LCSD sample prior to solvent extraction.***

10.2.8.5. ***Add 200 µL of the spike working standard containing only Aroclor 1016 and Aroclor 1260 to each mobility-procedure extract designated as MS/MSD and LCS/LCSD prior to solvent extraction.***

10.2.8.6. ***Per client request or project specific DQOs, add 200 µL of the spike working standard containing the specific***

Aroclor(s) to each mobility-procedure extract designated as MS/MSD and LCS/LCSD prior to solvent extraction.

10.2.9. All working standards must be replaced after six months ***(unless specified otherwise)*** or sooner if ***routine QC or*** comparison with check standards indicates a problem.

10.2.9.1. ***Store all working standards under dark and refrigerated condition.***

10.2.10. All stock standards must be inspected and documented ***in the Chemicals and Supplies Verification Logbook*** prior to use.

10.2.10.1. ***Check all opened stock standards frequently for signs of degradation or evaporation.***

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1-L pre-cleaned amber glass containers with Teflon-lined closures. ***Collect all samples in duplicate.***

11.1.1. ***If the aqueous sample is known or suspected to contain residual chlorine, add*** 4 mL of the 10% $Na_2S_2O_3$ solution per 1 L of sample. ***The 10% $Na_2S_2O_3$ solution may be added to the sample container prior to sample collection.***

11.1.2. ***If MS/MSD analyses are required, collect one sample in quadruplicate.***

11.2. Solid samples should be collected in 4-oz ***or 8-oz*** pre-cleaned clear glass wide-mouth jars, ***or 6-in decontaminated stainless steel or brass sleeves*** with Teflon-lined closures.

11.3. Oil, wipe, or filter samples should be collected in 40-mL ***pre-cleaned amber glass or clear glass*** VOA vials with Teflon-lined closures.

11.4. ***Tissue samples should be collected in 4-oz (or other appropriate capacity) pre-cleaned clear glass or quartz wide-month jars with Teflon or aluminum foil-lined closures. Refer to SOP-M229 for additional information on sample collection, preservation, and containers.***

11.5. ***Mobility-procedure extracts should be collected in 500-mL pre-cleaned amber glass containers with Teflon-lined closures.***

11.5.1. ***If the mobility-procedure extract is known or suspected to contain residual chlorine, add 2 mL of the 10% $Na_2S_2O_3$ solution per 500 mL of mobility-procedure extract.***

11.5.2. ***Completely fill and hermetically seal the sample container with minimum headspace.***

11.6. ***Aqueous and non-aqueous (except tissue)*** samples shall be maintained in a chilled state post sample collection until received at the laboratory. ***Aqueous and non-aqueous (except tissue)*** samples should not be frozen (e.g., do not use dry ice

as the refrigerant). ***Tissue samples shall be maintained in a frozen state post sample collection until received at the laboratory.***

11.6.1. ***For additional information on aqueous and non-aqueous (except tissue) sample collection and preservation, refer to Code of Federal Regulations (CFR), Title 40, Part 136 (§136.3).***

11.6.2. ***For additional information on sample collection and preservation, refer to SOP-M229 and EPA Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Third Edition, Volume 1, Section 6.3.***

11.7. Upon receipt, the ***aqueous and non-aqueous (except tissue)*** samples are stored in a ***0~6°C*** cooler. ***Tissue samples are stored in a −10~−20°C freezer.***

11.7.1. Aqueous samples must be ***solvent*** extracted within 7 days of ***sample*** collection.

11.7.2. ***Non-aqueous samples must be solvent extracted within 14 days of sample collection.***

11.7.3. ***Mobility-procedure extracts must be solvent extracted within 7 days post mobility extraction.***

11.7.3.1. ***Mobility-procedure extracts shall be stored in a 0~6°C cooler post mobility extraction if solvent extraction is not to be performed within 24 hours.***

11.7.4. All ***solvent extracts*** are then stored under dark and refrigerated ***(0~6°C)*** conditions and must be analyzed within 40 days post ***solvent*** extraction.

12. ►QUALITY CONTROL

12.1. Initial Calibration (IC)

12.1.1. The initial five-point calibration must be established prior to the processing of sample extracts.

12.1.1.1. ***The calibration curve is established with a minimum of five calibration standards.***

12.1.1.1.1. ***A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other Aroclor mixtures. Hence, it is not necessary to establish the initial five-point calibration for each of the other Aroclors.***

12.1.1.1.2. ***In situations where only a few Aroclors are of interest for a specific project, it will be necessary to establish the initial five-point calibration for each Aroclor of interest.***

12.1.1.2. ***If the calibration curve is not established for each Aroclor other than Aroclor 1016 and Aroclor 1260, analyze the 500-ppb working standards for pattern recognition.***

12.1.1.2.1. ***The 500-ppb working standards may also be used to determine the single-point calibration factor for each Aroclor if both of the following conditions are met.***

12.1.1.2.1.1. ***The linearity of the detector response is demonstrated using the calibration standards containing only Aroclor 1016 and Aroclor 1260.***

12.1.1.2.1.2. ***The calibration option is linear least squares regression and the regression is forced through zero.***

12.1.2. The IC is deemed valid if the %RSD for each analyte is ≤ 20%.

12.1.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.1.3.1. ***If the RSD of any analyte is unacceptable, review the results (e.g., proper identification, area count, response factor, etc.) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards.***

12.1.3.2. ***If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis to rule out problems due to random chance.***

12.1.3.2.1. ***In some cases, replace the calibration standard may be necessary.***

12.1.3.3. ***If a calibration standard is replaced and/or reanalyzed, recalculate the RSD, and document the rationale for re-analysis.***

12.2. Initial Calibration Verification (ICV)

12.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.2.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). ***Document the unacceptable result and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable,***

investigate, effect corrective action, which may include re-preparation of standard solutions ***or instrument maintenance***, and recalibrate.

12.3. Continuing Calibration Verification (CCV)

12.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.3.1.1. For EPA Region 9 requirement, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.3.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.3.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. ***Document the unacceptable result*** and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, ***effect corrective action and*** recalibrate.

12.4. Retention Time Window

12.4.1. Establishment of retention time window width is accomplished by making three injections of CCV standards throughout the course of a 72-hour period. Serial injections over a shorter period of time may result in narrow retention time window width that does not accurately account for variations over several days.

12.4.1.1. Retention time window width is ± 3S (where S is the standard deviation of the three retention times for that analyte/surrogate) ***or ± 0.030 minute, whichever is greater***.

12.4.1.1.1. ***For each multi-component analyte (i.e., Aroclor), calculate the standard deviation for each one of the five major characteristic peaks.***

12.4.2. Establishment of retention time window position is accomplished by using ***the midpoint calibration standard once per initial calibration, and*** by using a CCV standard at the beginning of an analytical sequence.

12.4.2.1. ***When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S or ± 0.030 minute, whichever is greater.***

12.4.2.2. ***When initial calibration is <u>not</u> performed***, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the CCV standard ± 3S ***or ± 0.030 minute, whichever is greater***.

12.4.3. Retention time for each analyte/surrogate ***in the calibration verification standard*** is verified as follows:

12.4.4. Retention time window for each analyte/surrogate is verified as follows:

12.4.4.1. ***When initial calibration is performed, the ICV standard and all CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the midpoint calibration standard.***

12.4.4.2. ***When initial calibration is <u>not</u> performed***, all succeeding CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the first CCV standard.

12.4.4.3. If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and/or position, if necessary.

12.5. Event Based Quality Control (MBs and LCS/LCSDs)

12.5.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB) and a laboratory control sample and laboratory control sample duplicate (LCS/LCSD).

12.5.2. ***The acceptance criteria for MBs are as follows:***

12.5.2.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

12.5.2.2. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.5.2.3. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples ***re-processed*** and/or re-analyzed.

12.5.3. The acceptance criteria for LCS/LCSD compounds are as follows:

12.5.3.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 50% and 135%, respectively. The RPD is ≤ 25%.

12.5.3.1.1. ***If historical data is available, the lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.***

12.5.3.2. All LCS/LCSD compounds must be within acceptance limits. ***If one or more LCS/LCSD compounds are not acceptable,***

determine the cause of the problem and effect corrective action.

12.6. Matrix Based Quality Control (Surrogates and MS/MSDs)

12.6.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and surrogates added to each sample.

12.6.2. The acceptance criteria for surrogate compounds are as follows:

12.6.2.1. The lower and upper acceptance limits for %REC of each surrogate compound ***in an aqueous sample*** are 50% and 135%, respectively. ***The lower and upper acceptance limits for %REC of each surrogate compound in a non-aqueous sample are*** 50% and 130%, respectively.

12.6.2.1.1. ***If historical data is available, the lower and upper acceptance limits for %REC of each surrogate compound are based upon the historical average recovery ± 3S that is updated at least annually.***

12.6.2.1.2. ***For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each surrogate compound are 60% and 150%, respectively.***

12.6.2.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

12.6.2.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration or a problem may have occurred during extraction or cleanup. The data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.6.2.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.6.2.4.1. Check the surrogate ***standard*** solutions for degradation and contamination.

12.6.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate

recoveries, the same extract should be re-analyzed.

12.6.2.4.3. If incorrect procedures or degraded/contaminated ***standard*** solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be ***re-processed*** and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.1. If, upon ***re-processing*** and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples ***re-processed*** and re-analyzed.

12.6.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

12.6.3. The acceptance criteria for MS/MSD compounds are as follows:

12.6.3.1. The lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 25%.

12.6.3.1.1. ***If historical data is available, the lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.***

12.6.3.1.2. ***For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 30%.***

12.6.3.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The

MS/MSD data shall be reported with the corresponding sample data.

12.6.3.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.4. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.7. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples ***re-processed*** and re-analyzed.

12.8. Additional information regarding internal quality control checks is provided in SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. ***Analytical Balance***

13.1.1. ***Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.***

13.1.2. ***If control limits are not specified, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.***

13.2. ***Chromatograph*** Initial Calibration

13.2.1. Establish an acceptable five-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.2.1.1. ***Because of the sensitivity of the electron capture detector, always clean the injection port and column prior to performing the initial calibration.***

13.2.1.2. ***Recalibration is required for the following maintenance procedures.***

13.2.1.2.1. ***Change, replace, or reverse the analytical column.***

13.2.2. After obtaining an acceptable five-point calibration curve and prior to processing ***field*** or QC sample extracts, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.2.

13.2.3. The initial five-point calibration and ICV ***shall*** include all anticipated target analytes for the duration of the use of the initial calibration.

13.3. ***Retention Time Window***

13.3.1. Retention time window width for each analyte/surrogate is generated by running three CCV standards over a 72-hour period. Retention time window width determination shall be performed at method set-up, following column changes, after major instrument maintenance or when a significant retention time shift is suspected.

13.3.2. Document the serial number of the analytical column associated with the retention time window study.

13.3.3. ***Record the retention time in minutes for each analyte/surrogate to three decimal places.***

14. ►PROCEDURE

14.1. Instrument Setup

14.1.1. Use the following GC operating conditions as guidance to establish the GC temperature program and flow rate necessary to separate the analytes of interest.

Description	GC Operating Condition
Inlet mode	splitless
Inlet temperature	220°C
Inlet pressure	6.2041 psi
Total flow rate	87.6 mL/min
Carrier gas flow rate	1.7 mL/min
Makeup gas flow rate	30 mL/min
Detector temperature	300°C
Initial temperature	120°C
Temperature program	120°C to 300°C at 15°C/min
Final temperature	300°C, hold 15 min

14.1.2. Autoinjector is set to inject 2 µL of ***field*** or QC sample extract.

14.1.3. ***Once established, the same operating conditions must be applied for all subsequent standard, sample, and blank analyses.***

14.2. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence. If the QC and retention time criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.3. and Section 12.4.3.

14.2.1. For EPA Region 9 requirement, refer to Section 12.3.1.1. for CCV frequency.

14.2.2. If a failed CCV is the first of the day, effect corrective action prior to analyzing any samples.

14.2.3. If ***a failed CCV is <u>not</u> the first of the day***, effect corrective action and reanalyze all samples since the last acceptable CCV.

14.3. Following extraction by one of the methods specified in Section 5.2., the extracts for the QC and actual environmental samples are received in autoinjector vials. The autoinjector vials are then loaded onto the GC sample tray.

14.4. ***Standard and*** sample vials are loaded in the following or other logical order:

1) Instrument Blank (IB)
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 20 per batch, ***including QC check samples and MBs***)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

14.4.1. Item 1: The IB is a vial of hexane used to determine ***whether*** the GC system is free of interferants. Additional instrument blanks may also be added elsewhere in the sequence, as necessary (i.e., after suspected high level samples). IB is optional.

14.4.2. Items 2 and 9: A CCV is used to verify the acceptance of the initial five-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

14.4.2.1. For EPA Region 9 requirement, refer to Section 12.3.1.1. for CCV frequency.

14.4.2.2. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample extract re-analyses that would be required in the event of an unacceptable CCV.

14.4.3. Item 3: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.3.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid and oil samples, the LCS consists of the specified compounds spiked into washed sea sand. For wipe samples, the LCS consists of the specified compounds spiked into unused gauze pad. For filter samples, the LCS consists of the specified compounds

spiked into unused filter paper. ***For tissue samples, the LCS consists of the specified compounds spiked into a tissue matrix substitute (e.g., washed sea sand, worms, clams, or certified organic chicken meat). For mobility-procedure extracts, the LCS consists of the specified compounds spiked into the mobility-procedure extract designated as LCS.***

14.4.3.2. One LCS is required every day ***preparatory methods (i.e., extractions, cleanups, etc.)*** are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.4. Item 4: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.4.5. Item 5: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (i.e., surrogates, etc.).

14.4.5.1. For aqueous samples, the MB consists of clean reagent water. For solid and oil samples, the MB consists of washed sea sand. For wipe samples, the MB consists of unused gauze pad. For filter samples, the MB consists of unused filter paper. ***For tissue samples, the MB consists of a tissue matrix substitute (e.g., washed sea sand, worms, clams, or certified organic chicken meat). For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB.***

14.4.5.2. One MB is required every day ***preparatory methods (i.e., extractions, cleanups, etc.)*** are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.5.3. When samples that are ***processed*** together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of hexane must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.4.6. Item 6: Up to 20 sample ***(including QC check sample and method blank)*** extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not

contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

14.4.6.1. ***All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.***

14.4.7. Item 7: The MS is an actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.7.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.5.

14.4.7.2. One MS is required for every batch of 20 samples per matrix or portion thereof ***processed*** concurrently. This approach is considered "closed batch" as opposed to "open batch."

14.4.8. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.4.9. ***Solvent blanks may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration sample extracts), to check for potential carryover or cross-contamination.***

14.5. Ensure that a sufficient amount of hexane is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles at the beginning of the sequence.

14.6. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook ***or on the sequence table printout***.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. Establish the daily retention time window for each analyte/surrogate (see Section 12.4.2.1. ***and Section 12.4.2.2.***).

14.8.1.1. Tentative identification of an ***analyte/surrogate*** occurs when a peak from a sample extract falls within the daily retention time window.

14.8.1.1.1. For each ***multi-component analyte (i.e., Aroclor)***, choose a minimum of ***5*** characteristic peaks that

are at least 25% of the height of the largest characteristic peak for the ***analyte***, and determine the retention time window of each characteristic peak.

14.8.1.1.2. The set of peaks for each Aroclor should include at least one peak that is unique to that Aroclor.

14.8.1.1.2.1. ***For Aroclor 1016 and Aroclor 1260, none of the peaks chosen should be found in both of these Aroclors.***

14.8.1.2. Use the succeeding CCV standards analyzed throughout the course of an analytical sequence within a 12-hour shift to evaluate retention time stability (see Section 12.4.3.). If any ***analyte(s)/surrogate(s)*** in the CCV standard fall outside of their daily retention time window(s), determine the cause of the problem and effect appropriate corrective action.

14.8.1.2.1. If any ***major characteristic peak(s)/surrogate(s)*** in the CCV standard fall outside of their daily retention time window(s), then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.

14.8.1.3. For Aroclors other than Aroclor 1016 ***and Aroclor*** 1260, identification shall rely primarily on pattern recognition. However, retention times should be utilized as a guide.

14.8.2. Quantitation of a target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample extract and the calibration standards.

14.8.2.1. ***PCBs as Aroclor may be quantitated from the total area of the PCB pattern and on the basis of the Aroclor standard that is most similar to the sample (total area approach), or the area of 5 or more major characteristic peaks (subset peak approach).***

14.8.2.1.1. ***If total area approach is employed, any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area.***

14.8.2.1.2. ***Total area approach is recommended if weathering of PCBs in the environment and changes resulting from waste treatment processes alter the PCBs to the point that the pattern of a specific Aroclor is no longer***

recognizable, or if samples contain more than one Aroclor.

14.8.2.1.3. ***The reasons for applying total area approach on sample quantitation and the problems associated with sample matrix should be fully documented.***

14.8.2.2. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak(s) can be determined.

14.8.2.2.1. ***For multi-component analyte quantitation, a forced baseline or baseline-to-baseline integration across the entire target range is required to ensure the appropriate integration of analyte response.***

14.8.2.3. Determine the concentration based on the initial calibration curve.

14.8.2.3.1. Calculate the concentration of each target analyte in a sample extract using the average of the initial RFs and the total area of the ***five*** predetermined peaks. The formula for calculating concentration is listed in Section 15.7.

14.8.2.3.2. ***Refer to Appendix A for examples of the predetermined peaks of each multi-component analyte.***

14.8.2.3.3. ***The data system is programmed to perform the calculation of concentration.***

14.8.2.4. If the instrument response exceeds the calibration range, dilute the extract and reanalyze.

14.8.3. ***Tentative identification of a target analyte occurs when a peak from a sample extract falls within the analyte's retention time window. Confirmation is necessary when the composition of samples is not well characterized. Qualitative confirmation techniques are by second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors.***

14.8.4. ***Second column confirmation is made on a "confirmation" channel configured with a column of dissimilar stationery phase and a second detector. The principle is that the retention time of the target analyte will differ between the primary and confirmation column and, unless the detected compound is the particular target analyte, it will not be observed within both retention time windows.***

14.8.4.1. ***Report the higher result between the primary and confirmation column. The RPD between results must be ≤ 40%.***

14.8.4.1.1. ***If one result is significantly higher (e.g., > 40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are observed, examine the baseline parameters established by the instrument data system (or operator) during peak integration. A rising baseline may cause the mis-integration of the peak for the lower result.***

14.8.4.1.2. ***If no anomalies are observed, review the chromatographic conditions. If there is no evidence of chromatographic problems, then it may be appropriate to report the lower result.***

14.8.4.1.3. ***The data user must be advised of the disparity between the results on the two columns. Under some circumstances, including those involving in monitoring compliance with an action level or regulatory limit, further cleanup of the sample or additional analyses may be required when the two results in question span the action level or regulatory limit.***

14.8.4.2. ***In cases where a peak is not observed in the confirmation column's retention time window, the analyte is reported as "ND."***

14.8.4.3. ***A calibration curve and retention time window for each analyte/surrogate are also established and maintained for the confirmation channel. The calibration and quality control requirements for the confirmation channel are identical to those of the primary channel.***

14.8.5. ***GC/MS confirmation is more reliable than second column confirmation. In this case, where confirmation is required by project requirements, the sample is re-analyzed on GC/MS. When GC/MS results indicate that a target analyte is not present, the GC result is reported as "ND."***

14.8.6. ***Confirmation is required for all positive results unless the samples meet all of the following requirements:***

14.8.6.1. ***All samples (aqueous, solid, oil, or tissue) come from the same source (e.g., same monitoring well). However, samples of the same matrix from the same site but from differing sources (e.g., different monitoring wells) are not exempted.***

14.8.6.2. ***All chemical parameters have been previously analyzed, identified, and confirmed by a second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors. Documentation of such must be maintained.***

14.8.6.3. ***The resulting chromatograms are relatively simple and do not contain complex or overlapping peaks.***

14.8.6.4. ***Chromatograms are largely unchanged from those for which confirmation was carried out.***

14.8.7. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

14.8.7.1. ***When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.***

14.8.7.2. ***When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially integrating a peak, etc.), manual integrations performed by the analyst are necessary.***

14.8.7.3. ***Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.***

14.9. ***Recommended Instrument Maintenance***

14.9.1. ***Perform the following tasks to remedy the column adsorption problem.***

14.9.1.1. ***Inject an 800-ppb single-component pesticide standard solution to prime (or deactivate) the column.***

14.9.1.2. ***Run one or more solvent blanks consisting of hexane until no carryover is observed prior to analyzing any standards or samples.***

14.9.2. ***Perform the following tasks to eliminate the degradation problem.***

14.9.2.1. ***For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter.***

14.9.2.2. ***Break off the first few centimeters (up to 30 cm) of the injection port side of the column.***

14.9.2.3. ***Check the injector temperature and lower it to 205°C, if necessary.***

14.9.2.4. ***Remove the columns and solvent backflush according to the manufacturer's instructions.***

14.9.2.5. ***If all else fail, it may be necessary to deactivate the metal injector body and/or replace the columns.***

14.9.3. ***Perform the following tasks to rinse the analytical column.***

14.9.3.1. ***Depending on the nature of the residues expected, the first rinse might be reagent water, followed by methanol and acetone, with methylene chloride as the final rinse. In some cases, methylene chloride may be the only solvent necessary.***

14.9.3.2. ***After the final rinse, the analytical column should be filled with methylene chloride and remained flooded overnight to allow materials within the stationary phase to migrate into the solvent.***

14.9.3.3. ***The analytical column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen passing through the column.***

15. ►CALCULATIONS

15.1. The response factor is calculated as follows:

$$RF = \frac{A_x}{C_x}$$

where: RF = response factor for target analyte being measured.
A_x = area of the characteristic peaks for target analyte being measured.
C_x = concentration of target analyte being measured in µg/L.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RF_{ave} - RF_{daily}|}{RF_{ave}} \times 100$$

where: %D = percent difference.
RF_{daily} = daily RF for the target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.4. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x}{RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in µg/L.
A_x = area of the characteristic peaks for target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.

V_{ex} = volume of extract in mL.
V_A = volume of aqueous sample ***solvent*** extracted in mL.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration for a solid (***oil, or tissue***) sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S}$$

where: C_S = concentration of target analyte in solid (***oil, or tissue***) sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid (***oil, or tissue***) sample ***solvent*** extracted in g.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.10. ***The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:***

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: C_S = ***concentration of target analyte in solid sample in µg/kg.***
C_{ex} = ***concentration of target analyte in extract in µg/L.***
V_{ex} = ***volume of extract in mL.***
W_S = ***mass of solid sample solvent extracted in g.***
C_{ss} = ***solids content in %.***
D = ***dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.***

15.11. The target analyte concentration for a wipe (or filter) sample is calculated as follows:

$$C_W = C_{ex} \times V_{ex} \times D$$

where: C_W = concentration of target analyte in wipe (or filter) sample in µg/sample.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in L.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.12. ***The target analyte concentration for a mobility-procedure extract is calculated as follows:***

$$C_{MP} = \frac{C_{ex} \times V_{ex} \times D}{V_{MP}}$$

where: C_{MP} = ***concentration of target analyte in mobility-procedure extract in µg/L.***
C_{ex} = ***concentration of target analyte in extract in µg/L.***
V_{ex} = ***volume of extract in mL.***
V_{MP} = ***volume of mobility-procedure extract solvent extracted in mL. Unless specified otherwise, V_{MP} = 100.***
D = ***dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.***

15.13. ***Refer to the preparatory method(s) for additional calculations.***

15.14. All concentrations shall be reported in µg/L (ppb) for aqueous samples, µg/kg (ppb) for oil, soil and solid waste, ***or tissue*** samples, and µg/sample for wipe and filter samples.

15.14.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

15.15. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples ***re-processed*** and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 50% and 135%, respectively. The RPD is ≤ 25%. All LCS/LCSD compounds must be within acceptance limits (see Section ***12.5.3.*** for additional information).

18.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.3. The acceptance criteria for surrogate compound recoveries are predetermined. The lower and upper acceptance limits for %REC of each surrogate compound ***in an***

aqueous sample are 50% and 135%, respectively. ***The lower and upper acceptance limits for %REC of each surrogate compound in a non-aqueous sample are*** 50% and 130%, respectively.

18.3.1. ***For EPA Region 9 requirement, refer to Section 12.6.2.1.2. for acceptance criteria.***

18.3.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

18.3.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.4.1. Check the surrogate ***standard*** solutions for degradation and contamination.

18.3.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recoveries, the same extract should be re-analyzed.

18.3.4.3. If incorrect procedures or degraded/contaminated ***standard*** solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be ***re-processed*** and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.4.3.1. If, upon ***re-processing*** and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples ***re-processed*** and re-analyzed.

18.3.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD compounds are predetermined. The lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 25%.

18.4.1. ***For EPA Region 9 requirement, refer to Section 12.6.3.1.2. for acceptance criteria.***

18.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for aqueous samples, µg/kg (ppb) for oil, soil and solid waste, ***or tissue*** samples, and µg/sample for wipe and filter samples.

18.7.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a

result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained

are within acceptance criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. ►REFERENCES

22.1. *Polychlorinated Biphenyls (PCBs) by Gas Chromatography*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8082, USEPA, Revision 0, December 1996.

22.2. ***Determinative Chromatographic Separations, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000B, USEPA, Revision 2, December 1996.***

22.3. *Determinative Chromatographic Separations*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000C, USEPA, Revision 3, March 2003.

22.4. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.5. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, ***February 2007***.

22.6. *Organic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, ***February 2007***.

22.7. *Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs)*, SW-846 Method 8081 or 8080, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Quantitation Peaks for Multiple-Component Target Compounds.

23.2. Appendix B: Additional Quality Control Criteria for Navy Project.

24. ►MODIFICATIONS

24.1. ***The following modifications from EPA Method 8082 Revision 0 are noted.***

Calscience SOP M407 Section	Reference Document EPA Method 8082 Section	Summary of Modification
All	All	None.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
4.0	Section 2: Add tissue matrix. Section 3: Update terminology for RL, and add reference to the determinations of DL and RL. Section 4: Revise the scope to indicate routine analytes. Section 5: Update method summary and EPA method numbers. Section 6: Delete internal standard definition. Add LOD and LOQ definitions. Section 7: Update interferences. Section 8: Update safety information. Section 9: Update the list of equipment and supplies. Section 10: Revise reagent and standard preparations. Section 11: Revise the requirements on collection and preservation. Section 12: Revise quality control criteria. Section 13: Add calibration procedures. Section 14: Update procedures. Section 15: Add references to solvent extraction, mobility extraction, and tissue matrix. Section 18: Update section references, and add EPA Region 9 requirements. Section 22: Update references. Section 23: Update appendices. Section 24: Add modifications. Section 25: Add revision history. Appendix A: Update Aroclor patterns. Appendix B: Update DoD quality control requirements and criteria.	J. Kang / K. Chang	01/28/13

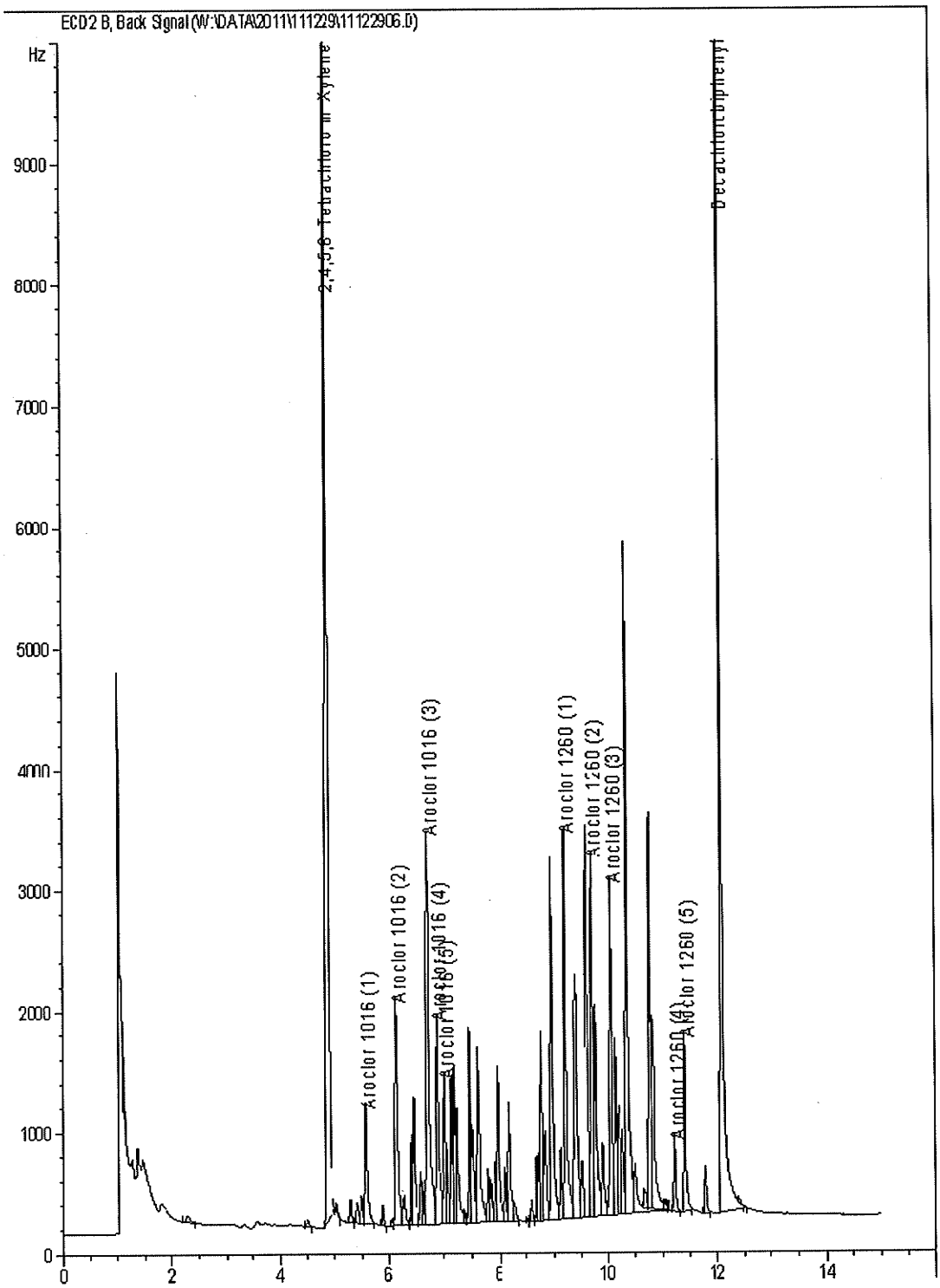
Appendix A

QUANTITATION PEAKS FOR MULTIPLE-COMPONENT TARGET COMPOUNDS

Calscience Environmental Laboratories, Inc.

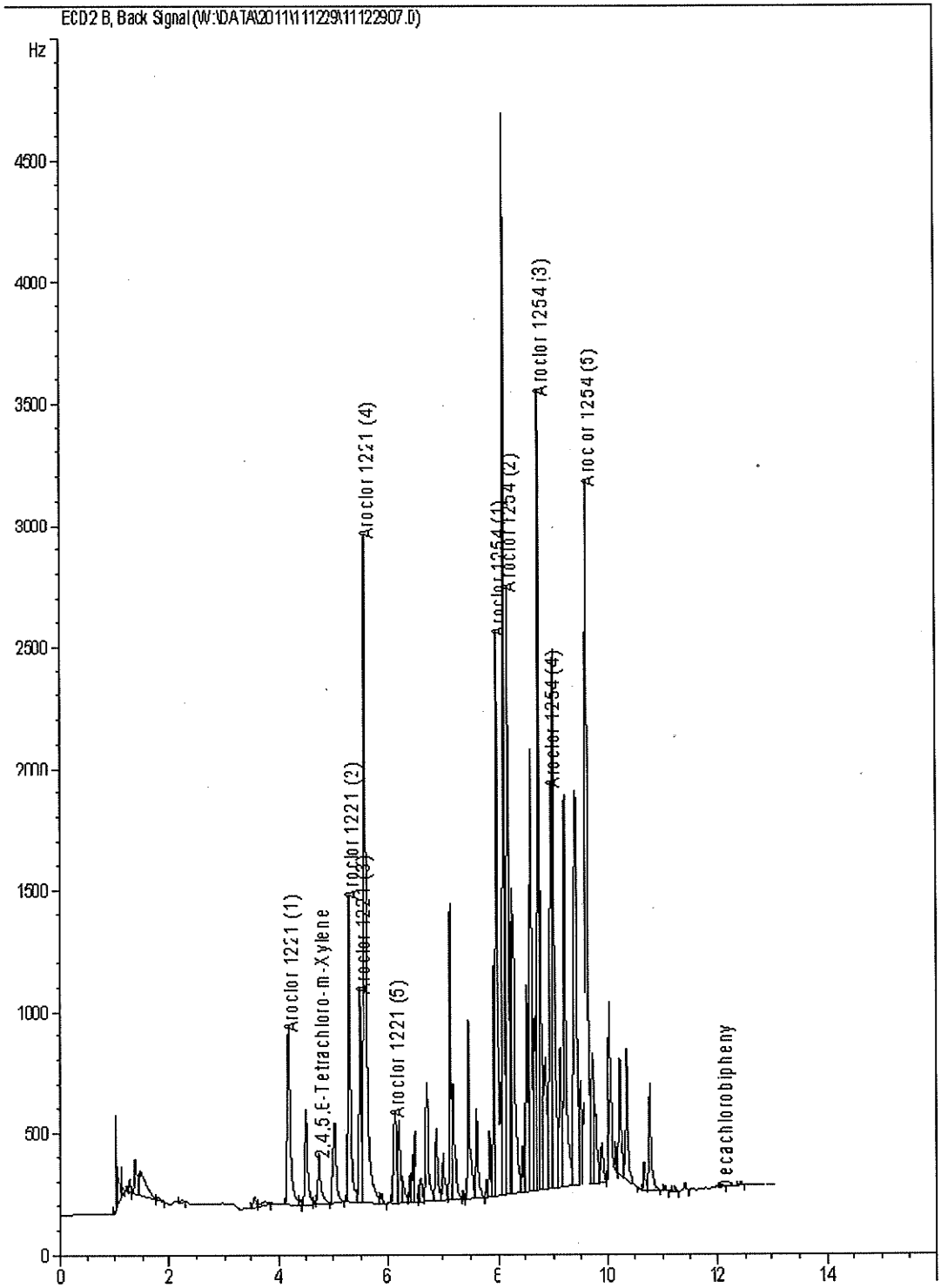
Appendix A

Quantitation Peaks for Aroclor 1016 and Aroclor 1260



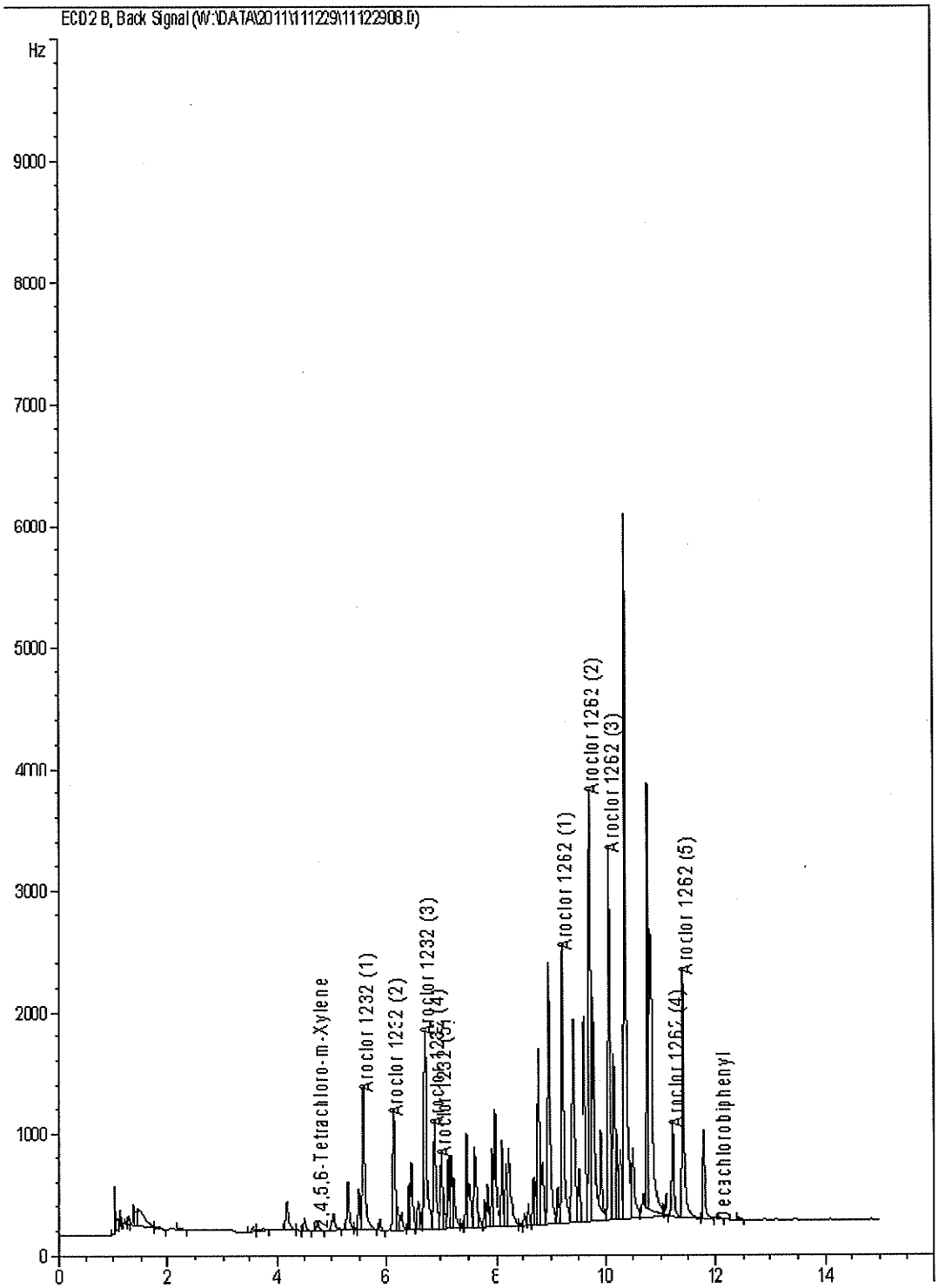
Appendix A

Quantitation Peaks for Aroclor 1221 and Aroclor 1254



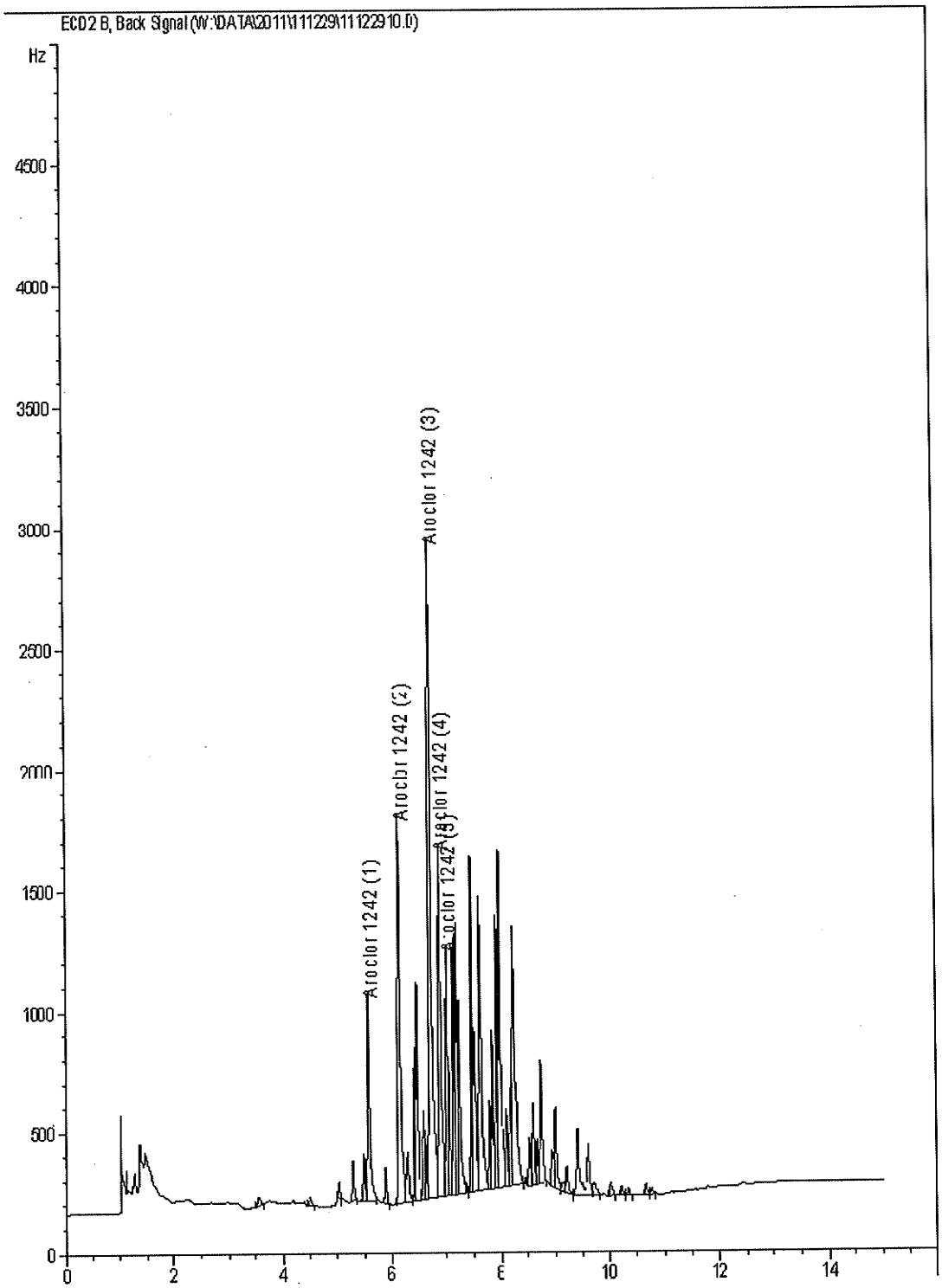
Appendix A

Quantitation Peaks for Aroclor 1232 and Aroclor 1262



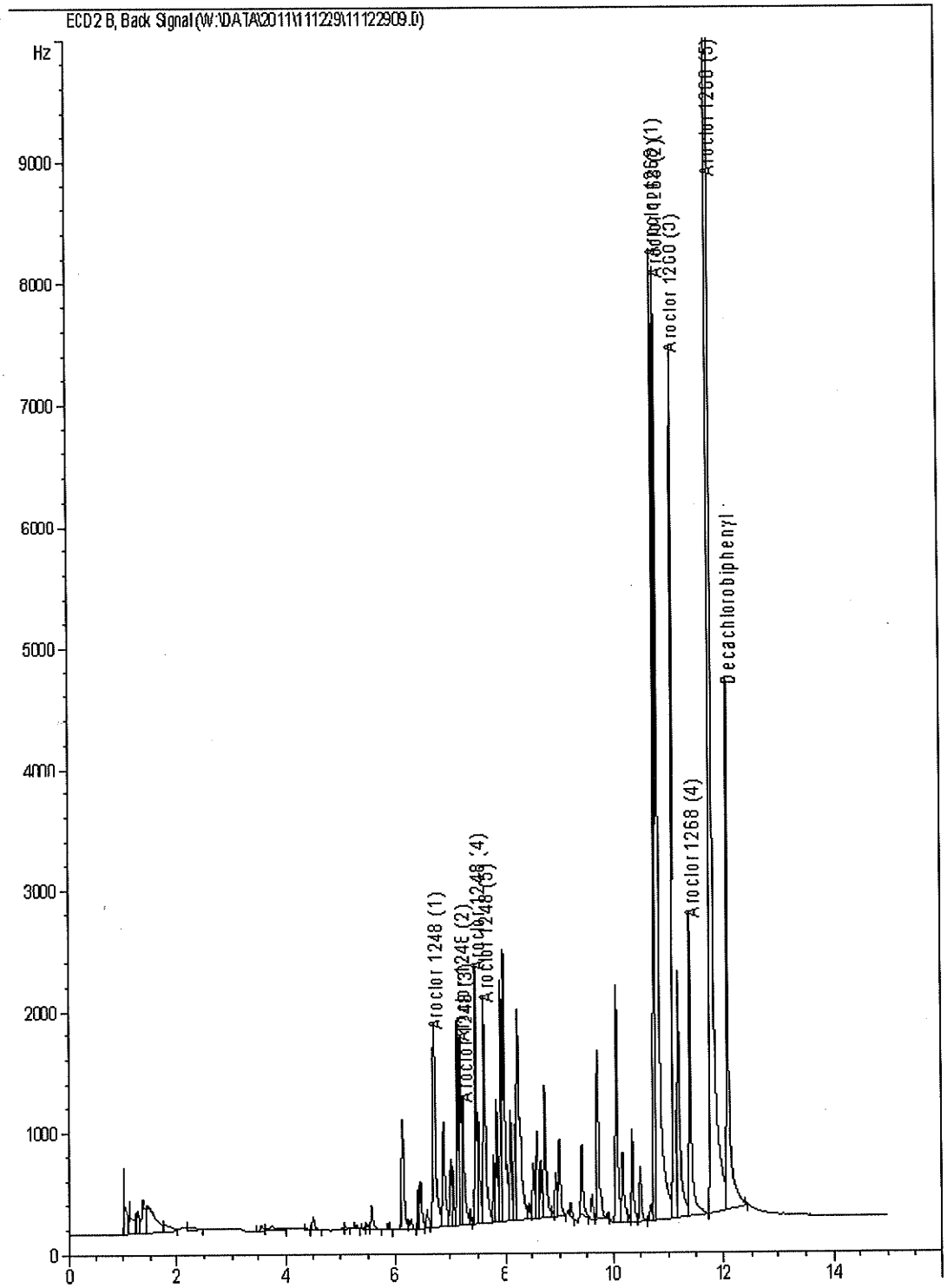
Appendix A

Quantitation Peaks for Aroclor 1242



Appendix A

Quantitation Peaks for Aroclor 1248 and Aroclor 1268



Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. ►EPA Method 8082, Polychlorinated Biphenyls (PCBs) as Aroclors by Gas Chromatography – Additional Quality Control Criteria for ***Department of Defense (DoD)*** Project.

2. ►DETECTION LIMITS

2.1. ***The quantitation limit must be set within the calibration range.***

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. ►STANDARDS

4.1. The spike standard solution shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. ►QUALITY CONTROL

5.1. ***Limit of Detection (LOD)***

5.1.1. ***LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.***

5.1.2. ***LOD*** verification must be performed immediately following ***an LOD determination and quarterly thereafter to verify method sensitivity***.

5.1.2.1. ***LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.***

5.1.2.2. ***LOD*** verification is deemed valid if ***the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.)***.

5.1.2.2.1. ***For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that***

is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, ***perform either one of the following tasks***.

5.1.2.3.1. ***Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.***

5.1.2.3.2. ***Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.***

5.1.3. No samples shall be analyzed without a valid ***LOD***.

5.2. ***Limit of Quantitation (LOQ)***

5.2.1. ***LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.***

5.2.1.1. ***The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.***

5.2.1.2. ***The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.***

5.2.2. ***LOQ verification must be performed quarterly to verify precision and bias at the LOQ.***

5.2.2.1. ***LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.***

5.2.2.2. ***LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.***

5.3. ***Initial Calibration (IC)***

5.3.1. ***The initial five-point calibration must be established for each Aroclor prior to the processing of sample extracts.***

5.3.1.1. ***Results may not be quantitated using a single point.***

5.4. Continuing Calibration Verification (CCV)

5.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 ***field*** samples or portion thereof within a 12-hour shift, and at the end of sequence.

5.4.2. ***The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.***

5.5. Retention Time Window

5.5.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a ***low-to-midpoint*** CCV standard at the beginning of an analytical sequence.

5.5.1.1. ***When initial calibration is performed, daily*** retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S.

5.5.1.2. ***When initial calibration is <u>not</u> performed***, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the ***low-to-midpoint*** CCV standard ± 3S.

5.6. Event Based Quality Control (MBs and LCS/LCSDs)

5.6.1. Method Blanks (MBs)

5.6.1.1. ***The MB is considered to be contaminated if one of the following conditions is met.***

5.6.1.1.1. The concentration of any target analyte in the MB ***exceeds 1/2 the RL***, <u>and</u> is greater than 1/10 the amount measured in any sample ***or 1/10 the regulatory limit (whichever is greater)***.

5.6.1.1.2. ***The concentration of any common laboratory contaminant in the MB exceeds RL, <u>and</u> is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).***

5.6.1.1.3. The ***MB result otherwise*** affects the sample results as per the test method requirements or the project specific data quality objectives ***(DQOs)***.

5.6.1.2. ***If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.***

5.6.1.2.1. If ***insufficient*** sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.6.2. Laboratory Control Samples (LCS/LCSDs)

5.6.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound in aqueous ***and solid matrices are listed below***.

Analyte	Aqueous Matrix Control Limit		Solid Matrix Control Limit	
	Lower	Upper	Lower	Upper
Aroclor 1016	25	145	40	140
Aroclor 1260	30	145	60	130

5.6.2.2. ***Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.***

5.6.2.2.1. ***Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.***

5.6.2.3. ***All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.***

5.7. Matrix Based Quality Control (Surrogates and MS/MSDs)

5.7.1. ***Surrogate***

5.7.1.1. ***The lower and upper acceptance limits for %REC of each surrogate compound in aqueous and solid matrices are listed below.***

Analyte	Aqueous Matrix Control Limit		Solid Matrix Control Limit	
	Lower	Upper	Lower	Upper
Decachlorobiphenyl	40	135	60	125

5.7.1.2. ***Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.***

5.7.2. Matrix Spikes (MS/MSDs) and Surrogate

5.7.2.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous ***and solid matrices are listed below. The RPD is ≤ 30%.***

Analyte	Aqueous Matrix Control Limit		Solid Matrix Control Limit	
	Lower	Upper	Lower	Upper
Aroclor 1016	25	145	40	140
Aroclor 1260	30	145	60	130

5.7.2.2. ***Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.***

5.7.2.2.1. ***Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.***

6. ►PROCEDURE

6.1. ***Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.***

6.2. ***Standard and sample vials are loaded in the following or other logical order:***

1) ***Instrument Blank (IB)***
2) ***Continuing Calibration Verification (CCV)***
3) ***Laboratory Control Sample (LCS)***
4) ***Laboratory Control Sample Duplicate (LCSD)***
5) ***Method Blank (MB)***
6) ***Samples (up to 10 per batch, excluding QC check samples and MBs)***
7) ***Matrix Spike (MS)***
8) ***Matrix Spike Duplicate (MSD)***
9) ***Ending CCV***

6.2.1. ***Items 2 and 9: A CCV is used to verify the acceptance of the initial five-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.***

6.2.2. ***Item 6: Up to 10 sample (excluding QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.***

6.2.3. ***Item 7: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.***

6.2.3.1. ***The sample selected for spiking must be one of the samples collected for the specific DoD project.***

6.2.4. ***Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the***

analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

6.3. Data Interpretation

6.3.1. The flagging criteria and data reporting procedure for second column confirmation are as follows:

6.3.1.1. If RPD is > 40%, apply the appropriate data qualifier (J-flag) and document in the case narrative.

6.3.1.2. ***Follow project-specific reporting requirements when reporting data.***

6.3.1.2.1. ***If project-specific reporting requirements are unavailable, apply method-specific reporting requirements.***

6.3.1.2.2. ***If method-specific reporting requirements are unavailable, report the results from the primary column or detector, unless there is a scientifically valid and documented reason for not doing so.***

6.3.2. ***Identify unconfirmed results with the appropriate data qualifiers and document in the case narrative.***

7. REFERENCES

7.1. ►Department of Defense Quality Systems Manuals for Environmental Laboratories, Version ***4.2, October 25, 2010***.

Title : **EPA METHOD 8151A, CHLORINATED HERBICIDES BY GAS CHROMATOGRAPHY VIA METHYLATION DERIVATIZATION**

Document No. : SOP-M402
Revision No. : 3.5
Supersedes : 3.4

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Revision 3.5 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 10/03/14
MANAGEMENT **DATE**

_____ 10-03-14
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 8151A, Chlorinated Herbicides by Gas Chromatography via Methylation Derivatization.

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous, soil, and waste matrices.

3. ►DETECTION / QUANTITATION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

	Water	Soil
Herbicides (Free Acid)	0.5~500 µg/L	10.0~10000 µg/kg (wet-weight)

3.2. The RLs will be proportionally higher for sample extracts which require dilution or cleanup.

3.3. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. EPA Method 8151A is used to determine the concentrations of certain chlorinated acid herbicides and related compounds in various matrices. Since these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), a hydrolysis step can be used to convert herbicide esters into the acid form prior to analysis.

4.2. The following compounds are routinely determined by this method:

Compound	Synonym
2,4-D	2,4-dichlorophenoxyacetic acid
2,4-DB	4-(2,4-dichlorophenoxy) butyric acid
dicamba	3,6-dichloro-2-methoxybenzoic acid
DNBP (dinoseb)	2-sec-butyl-4,6-dinitrophenol
2,4-DP (dichloroprop)	2-(2,4-dichlorophenoxy) propionic acid
2,2-DPA (dalapon)	2,2-dichloropropanoic acid
MCPA	2-methyl-4-chlorophenoxyacetic acid
MCPP (mecoprop)	2-(2-methyl-4-chlorophenoxy) propionic acid
2,4,5-T	2,4,5-trichlorophenoxyacetic acid
2,4,5-TP (silvex)	2-(2,4,5-trichlorophenoxy) propanoic acid

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography (GC) and skilled in the interpretation of gas chromatograms.

5. METHOD SUMMARY

5.1. EPA Method 8151A describes chromatographic procedures that will allow for the analysis of methyl ester derivatives in the extract and their qualitative and quantitative analysis by gas chromatography. Detection is achieved using an electron capture detector (ECD).

5.2. Prior to performing this procedure, the appropriate sample preparation technique (Appendix A) must be performed on each sample.

5.2.1. Aqueous samples are extracted with diethyl ether and esterified with diazomethane.

5.2.2. Soil, sediment, and other solid samples are extracted with acetone and diethyl ether, and esterified with diazomethane.

5.2.3. Solid samples for TCLP analysis are prepared using the appropriate mobility extraction method, and the resulting mobility-procedure extracts (leachates) are extracted with diethyl ether and esterified with diazomethane.

5.2.4. If herbicide esters are to be determined, hydrolysis conditions for the esters in water and soil extracts are described.

5.3. Acceptable preparatory methods include, but are not limited to, the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Hydrolysis/Extraction/Esterification	8151A	SOP-M402 (Appendix A)
TCLP	1311	SOP-M226
STLC (California Code of Regulations)	CCR T22.11.5.A-II	SOP-M228

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.3.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***.

6.3.2. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a

group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. Limit of Detection (LOD): ***The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.12. Limit of Quantitation (LOQ): ***The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed

simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly

prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.27. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

6.28. ***Refer to the current revision of the Eurofins Calscience Quality Systems Manual for additional terms and definitions.***

7. INTERFERENCES

7.1. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination. In addition, sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2. Interference can also occur when "dirty" samples leave residue in the analytical column. To minimize this effect, guard columns should be used and cut frequently or replaced. Also, the analytical column can be "baked" after such samples. Other maintenance procedures include cleaning the inlet or replacing injection liner/seal.

7.3. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.4. Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure.

7.5. Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

7.5.1. The presence of residual acetone during solid sample extract hydrolysis may result in the formation of aldol condensation products which will cause GC interference.

7.6. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences varies considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

7.7. ***►Refer to the specific SOPs of the preparatory methods and Appendix A for other potential interferences.***

8. ►SAFETY

8.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all

designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.2. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

8.3. ***Refer to the specific SOPs of the preparatory methods and Appendix A for additional safety issues.***

9. EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Agilent 6890N Gas Chromatograph or equivalent configured with the following components:

9.1.1. Splitless injection port.

9.1.2. Autoinjector, Agilent 7683B Series or equivalent.

9.2. Instrument Software

9.2.1. ►***Require a PC based data system or equivalent.***

9.2.2. Agilent GC ChemStation Version B.03.02 [341] or equivalent.

9.3. ►Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.3.2. ***Additional information can be found in the user manual or operating guide for the specific instrument.***

9.4. Primary Detection Channel

9.4.1. Detector: Electron capture detector (ECD).

9.4.2. Analytical Column: 30-m × 0.32-mm ID, 0.50-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides or equivalent.

9.5. Confirmation Detection Channel

9.5.1. Detector: Electron capture detector (ECD).

9.5.2. Analytical Column: 30-m × 0.32-mm ID, 0.25-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides2 or equivalent.

9.6. Guard Column: 5-m × 0.32-mm ID, intermediate-polarity deactivated, uncoated fused-silica, Restek IP Deactivated Guard Column or equivalent.

9.7. Carrier Gas: Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent.

9.8. Makeup Gas: Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent.

9.9. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.10. Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

9.11. Autoinjector vials, 12-mm × 32-mm (2-mL capacity), crimp top, clear glass, with aluminum crimp caps and Teflon-lined septa, disposable.

9.12. Refer to the specific SOPs of the preparatory methods and Appendix A for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Sodium thiosulfate, $Na_2S_2O_3$, anhydrous, white solid, reagent grade or equivalent.

10.1.4. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v).

10.1.4.1. Prepare the 10% $Na_2S_2O_3$ solution by dissolving 200 g of anhydrous $Na_2S_2O_3$ in reagent water and dilute to 2 L with additional reagent water.

10.1.5. Hexane, C_6H_{14}, clear colorless liquid, pesticide grade or equivalent.

10.1.6. Refer to the specific SOPs of the preparatory methods and Appendix A for additional reagents.

10.1.7. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. ►Standards

10.2.1. Pre-certified stock standard solutions, each in sealed glass ampules, ***contain*** various concentrations of ***herbicide*** target analytes in ***free acid*** form, are used to prepare calibration standards.

10.2.1.1. Prepare each ***herbicide*** working standard solution by diluting the appropriate volumes of the ***herbicide*** stock standard ***and the 100-ppm surrogate working standard*** to 10 mL with hexane.

10.2.1.2. The working standards are prepared as follows:

Analyte (free acid)	Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume (mL)
dalapon	250	0.8	20	10
dicamba	10		0.8	
MCPP	10000		800	
MCPA	10000		800	
dichlorprop	100		8.0	
2,4-D	100		8.0	
2,4,5-TP (silvex)	10		0.8	
2,4,5-T	10		0.8	
2,4-DB	100		8.0	
dinoseb	50		4.0	
surrogate (DCAA)	100	0.4	4.0	

10.2.2. ***Pre-certified stock standard solution, in sealed glass ampule, contains 1000 ppm of 2,4-dichlorophenylacetic acid (DCAA) in free acid form, is used to prepare surrogate working standards.***

10.2.2.1. ***Prepare the 100-ppm surrogate working standard solution by diluting 5.0 mL of the 1000-ppm surrogate stock standard to 50 mL with methanol.***

10.2.3. Calibration standard solutions ***contain*** various concentrations of target analytes in ***free acid*** form and surrogate in ***free acid*** form in hexane.

10.2.3.1. Dilute the appropriate volumes of the ***herbicide*** working standard to the specified volumes with hexane ***and derivatize each calibration standard*** for initial calibration.

10.2.3.1.1. ***Measure 2.00 mL of each calibration standard and derivatize via the procedure outlined in Appendix A Sections 10.15. through 10.20.***

10.2.3.1.2. ***Transfer each derivatized calibration standard to a crimp-top autoinjector vial or a screw-top storage vial and label appropriately. The derivatized calibration standards may now be analyzed.***

10.2.3.1.3. ***Thoroughly document all aspects of the derivatization in an extraction logbook.***

10.2.3.2. Use the following calibration levels as guidance to prepare the calibration standards.

Calibration Level	Initial		Final
	Concentration (ppm)	Volume (mL)	Volume (mL)
1	0.8~800	0.25	2.00
2	0.8~800	1.00	4.00
3	0.8~800	2.00	4.00
4	0.8~800	3.00	4.00
5	0.8~800	3.75	3.75

Analyte (free acid)	Calibration Level (ppm)				
	1	2	3	4	5
dalapon	2.5	5.0	10	15	20
dicamba	0.1	0.2	0.4	0.6	0.8
MCPP	100	200	400	600	800
MCPA	100	200	400	600	800
dichlorprop	1.0	2.0	4.0	6.0	8.0
2,4-D	1.0	2.0	4.0	6.0	8.0
2,4,5-TP (silvex)	0.1	0.2	0.4	0.6	0.8
2,4,5-T	0.1	0.2	0.4	0.6	0.8
2,4-DB	1.0	2.0	4.0	6.0	8.0
dinoseb	0.5	1.0	2.0	3.0	4.0
surrogate (DCAA)	0.5	1.0	2.0	3.0	4.0

10.2.3.3. The midpoint standard is also used as the continuing calibration verification solution.

10.2.4. Initial calibration verification (ICV) solution ***contains*** midpoint concentration of each target analyte in ***free acid*** form and 2.0 ppm of surrogate in ***free acid*** form in hexane. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.4.1. Dilute the appropriate volumes of the second source ***herbicide*** stock standard to 4.0 mL with hexane ***and derivatize the ICV solution*** for initial calibration verification.

10.2.4.1.1. ***Measure 2.00 mL of the ICV solution and derivatize via the procedure outlined in Appendix A Sections 10.15. through 10.20.***

10.2.4.1.2. ***Transfer the derivatized ICV solution to a crimp-top autoinjector vial or a screw-top storage vial and label appropriately. The derivatized ICV solution may now be analyzed.***

10.2.4.1.3. ***Thoroughly document all aspects of the derivatization in an extraction logbook.***

10.2.4.2. Use the following calibration level as guidance to prepare the ICV solution.

Analyte (free acid)	Calibration Level (ppm)	Initial Conc. (ppm)	Initial Volume (mL)	Final Volume (mL)
dalapon	10	250	0.16	4.0
dicamba	0.4	10		
MCPP	400	10000		
MCPA	400	10000		
dichlorprop	4.0	100		
2,4-D	4.0	100		
2,4,5-TP (silvex)	0.4	10		
2,4,5-T	0.4	10		
2,4-DB	4.0	100		
dinoseb	2.0	50		
surrogate (DCAA)	2.0	100	0.08	4.0

10.2.5. Continuing calibration verification (CCV) solution ***contains*** midpoint concentration of each target analyte in ***free acid*** form and 2.0 ppm of surrogate in ***free acid*** form in hexane. The CCV solution is of a source same as that used for the initial multi-point calibration.

10.2.5.1. Dilute the appropriate volumes of the working standard to 4.0 mL with hexane ***and derivatize the CCV solution*** for continuing calibration verification.

10.2.5.1.1. ***Measure 2.00 mL of the CCV solution and derivatize via the procedure outlined in Appendix A Sections 10.15. through 10.20.***

10.2.5.1.2. ***Transfer the derivatized CCV solution to a crimp-top autoinjector vial or a screw-top storage vial and label appropriately. The derivatized CCV solution may now be analyzed.***

10.2.5.1.3. ***Thoroughly document all aspects of the derivatization in an extraction logbook.***

10.2.5.2. Use the following calibration level as guidance to prepare the CCV solution.

Analyte (free acid)	Calibration Level (ppm)	Initial Conc. (ppm)	Initial Volume (mL)	Final Volume (mL)
dalapon	10	20	2.0	4.0
dicamba	0.4	0.8		
MCPP	400	800		
MCPA	400	800		
dichlorprop	4.0	8.0		
2,4-D	4.0	8.0		
2,4,5-TP (silvex)	0.4	0.8		
2,4,5-T	0.4	0.8		
2,4-DB	4.0	8.0		
dinoseb	2.0	4.0		
surrogate (DCAA)	2.0	4.0	2.0	4.0

10.2.6. Refer to the specific SOPs of the preparatory methods and Appendix A for additional standards.

10.2.7. All working standards must be replaced after six months (unless specified otherwise) or sooner if routine QC or comparison with check standards indicates a problem.

10.2.7.1. Store all working standards under dark and refrigerated condition.

10.2.8. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2.8.1. Check all opened stock standards frequently for signs of degradation or evaporation.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1-L pre-cleaned amber glass containers with Teflon-lined closures. Collect all samples in duplicate.

11.1.1. If the aqueous sample is known or suspected to contain residual chlorine, add 4 mL of the 10% $Na_2S_2O_3$ solution per 1 L of sample. The 10% $Na_2S_2O_3$ solution may be added to the sample container prior to sample collection.

11.1.2. If MS/MSD analyses are required, collect one sample in quadruplicate.

11.2. Solid samples should be collected in 4-oz or 8-oz pre-cleaned clear glass wide-mouth jars, or 6-in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.3. Mobility-procedure extracts should be collected in 500-mL pre-cleaned amber glass containers with Teflon-lined closures.

11.3.1. If the mobility-procedure extract is known or suspected to contain residual chlorine, add 2 mL of the 10% $Na_2S_2O_3$ solution per 500 mL of mobility-procedure extract.

11.3.2. Completely fill and hermetically seal the sample container with minimum headspace.

11.4. ►Samples shall be maintained in a chilled state, ***0–6°C, not frozen***, post sample collection until received at the laboratory.

11.5. Upon receipt, the samples are stored in a 0–6°C cooler.

11.5.1. Aqueous samples must be solvent extracted within 7 days of sample collection.

11.5.2. Non-aqueous samples must be solvent extracted within 14 days of sample collection.

11.5.3. Mobility-procedure extracts must be solvent extracted within 7 days post mobility extraction.

11.5.3.1. Mobility-procedure extracts shall be stored in a 0–6°C cooler post mobility extraction if solvent extraction is not to be performed within 24 hours.

11.5.4. All solvent extracts are then stored under dark and refrigerated (0–6°C) conditions and must be analyzed within 40 days post solvent extraction.

12. ►QUALITY CONTROL

12.1. Initial Calibration (IC)

12.1.1. The initial multi-point calibration must be established prior to the processing of sample extracts.

12.1.1.1. The calibration curve is established with a minimum of five calibration standards, but may contain six or seven calibration standards.

12.1.2. The IC is deemed valid if the %RSD for each analyte ***(including surrogate)*** is ≤ 20%.

12.1.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.1.3.1. If the RSD of any analyte is unacceptable, review the results (e.g., proper identification, area count, response factor, etc.) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards.

12.1.3.2. If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis to rule out problems due to random chance.

12.1.3.2.1. In some cases, replace the calibration standard may be necessary.

12.1.3.3. If a calibration standard is replaced and/or reanalyzed, recalculate the RSD, and document the rationale for re-analysis.

12.2. Initial Calibration Verification (ICV)

12.2.1. ***Immediately following the establishment of a valid initial calibration, an ICV standard must be analyzed prior to sample analysis.***

12.2.2. The initial calibration is deemed valid if the %D for each analyte ***(including surrogate)*** is ≤ 20%.

12.2.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result and ***perform one of the following tasks***.

12.2.3.1. Re-analyze the ICV ***once*** within 2 hours after the failed ICV.

12.2.3.2. ***Acquire a new ICV standard solution and analyze once within 2 hours after the failed ICV.***

12.2.3.3. ***Evaluate the instrument conditions and re-process the calibration curve data.***

12.2.4. If the ICV remains unacceptable, investigate, effect corrective action, which may include re-preparation of standard solutions or instrument maintenance, and recalibrate.

12.2.5. ***If the initial calibration has been verified by the ICV, sample analysis may proceed.***

12.3. Continuing Calibration Verification (CCV)

12.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.3.1.1. For EPA Region 9 requirement, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.3.2. The initial calibration is deemed valid if the %D for each analyte ***(including surrogate)*** is ≤ 20%.

12.3.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and ***perform the following tasks***.

12.3.3.1. Re-analyze the CCV ***once*** within 2 hours after the failed CCV.

12.3.3.2. ***Document the reason(s) for re-analyzing the CCV and the corrective action(s) taken.***

12.3.4. If the CCV remains unacceptable, effect corrective action and recalibrate.

12.3.4.1. ***If a failed CCV is the first of the day, effect corrective action and recalibrate prior to analyzing any samples.***

12.3.4.2. ***If a failed CCV is not the first of the day, effect corrective action, recalibrate, and re-analyze all samples since the last acceptable CCV.***

12.3.5. ***If the initial calibration has been verified by the CCV, sample analysis may proceed.***

12.4. Retention Time Window

12.4.1. Establishment of retention time window width ***for each analyte (including surrogate)*** is accomplished by making three injections of CCV standards throughout the course of a 72-hour period. Serial injections over a shorter period of time may result in narrow retention time window width that does not accurately account for variations over several days.

12.4.1.1. Retention time window width is ± 3S (where S is the standard deviation of the three retention times for that analyte ***or*** surrogate) or ± 0.030 minute, whichever is greater.

12.4.2. Establishment of retention time window position ***for each analyte (including surrogate)*** is accomplished by using the midpoint calibration standard once per initial calibration, and by using a CCV standard at the beginning of an analytical sequence.

12.4.2.1. When initial calibration is performed, daily retention time window for each analyte ***or*** surrogate is the retention time of the analyte ***or*** surrogate in the midpoint calibration standard ± 3S or ± 0.030 minute, whichever is greater.

12.4.2.2. When initial calibration is <u>not</u> performed, daily retention time window for each analyte ***or*** surrogate is the retention time of the analyte ***or*** surrogate in the CCV standard ± 3S or ± 0.030 minute, whichever is greater.

12.4.3. Retention time for each analyte ***(including surrogate)*** in the calibration verification standard is verified as follows:

12.4.3.1. When initial calibration is performed, the ICV standard and all CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the midpoint calibration standard.

12.4.3.2. When initial calibration is <u>not</u> performed, all succeeding CCV standards throughout the course of an analytical sequence

within a 12-hour shift must fall within the daily retention time window established by the first CCV standard.

12.4.3.3. If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and/or position, if necessary.

12.5. Event Based Quality Control (MBs and LCS/LCSDs)

12.5.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), a laboratory control sample ***(LCS)***, and ***a*** laboratory control sample duplicate ***(LCSD)***.

12.5.1.1. ***LCSD shall be prepared and processed if there is insufficient sample amount to perform matrix based QC (i.e., MS/MSD), or if it is mandatory per client request or project specific DQOs.***

12.5.2. The acceptance criteria for MBs are as follows:

12.5.2.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

12.5.2.2. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.5.2.3. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. ***Refer to the current revision of SOP-T020*** to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.5.3. The acceptance criteria for LCS/LCSD compounds are as follows:

12.5.3.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 30% and 130%, respectively. The RPD is ≤ 30% ***(between LCS and LCSD)***.

12.5.3.1.1. If historical data is available, the lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.5.3.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each LCS/LCSD compound (except dinoseb) are 80% and 120%, respectively.

12.5.3.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of LCS/LCSD dinoseb are 40% and 160%, respectively.

12.5.3.2. All LCS ***(including LCSD if required)*** compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, determine the cause of the problem and effect corrective action. ***Refer to the current revision of SOP-T020 to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.***

12.6. Matrix Based Quality Control (Surrogates and MS/MSDs)

12.6.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of surrogate added to each sample, a matrix spike ***(MS)***, and a matrix spike duplicate (***MSD***).

12.6.2. The acceptance criteria for surrogate compound are as follows:

12.6.2.1. The lower and upper acceptance limits for %REC of the surrogate compound in an aqueous sample are 30% and 123%, respectively. The lower and upper acceptance limits for %REC of the surrogate compound in a non-aqueous sample are 30% and 130%, respectively.

12.6.2.1.1. If historical data is available, the lower and upper acceptance limits for %REC of the surrogate compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.2.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of the surrogate compound in a water sample are 75% and 125%, respectively.

12.6.2.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of the surrogate compound in a soil sample are 65% and 135%, respectively.

12.6.2.2. If the surrogate compound recovery is acceptable, report the surrogate and sample data without qualification.

12.6.2.3. If the surrogate recovery is not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration or a problem may have occurred during extraction or cleanup. The data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.6.2.4. By itself, unacceptable surrogate recovery does not invalidate sample data. The following must be accomplished if surrogate recovery is not acceptable.

12.6.2.4.1. Check the surrogate standard solutions for degradation and contamination.

12.6.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recovery, the same ***sample should be re-processed or*** extract re-analyzed.

12.6.2.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recovery, the affected sample(s) must be re-processed and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recovery and the sample data reported with qualification.

12.6.2.4.3.1. If, upon re-processing and re-analysis, the surrogate remains unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recovery and the sample data reported with qualification.

12.6.2.4.3.2. If the MB surrogate is unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.6.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

12.6.3. The acceptance criteria for MS/MSD compounds are as follows:

12.6.3.1. The lower and upper acceptance limits for %REC of each MS/MSD compound are 30% and 130%, respectively. The RPD is ≤ 30% ***(between MS and MSD)***.

12.6.3.1.1. If historical data is available, the lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.3.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound (except dinoseb) are 65% and 135%, respectively.

12.6.3.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of MS/MSD dinoseb are 40% and 160%, respectively.

12.6.3.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.6.3.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.4. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.7. If the %REC or RPD of the LCS/LCSD and MS/MSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.8. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Chromatograph Initial Calibration

13.1.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.1.1.1. Because of the sensitivity of the electron capture detector, always clean the injection port and column prior to performing the initial calibration.

13.1.1.2. Recalibration is required for the following maintenance procedures.

13.1.1.2.1. Change, replace, or reverse the analytical column.

13.1.2. After obtaining an acceptable multi-point calibration curve and prior to processing field or QC sample extracts, an ICV standard must be analyzed

to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.2.

13.1.3. The initial multi-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

13.2. ►Retention Time Window

13.2.1. Retention time window width for each analyte ***(including surrogate)*** is generated by running three CCV standards over a 72-hour period. Retention time window width determination shall be performed at method set-up, following column changes, after major instrument maintenance or when a significant retention time shift is suspected.

13.2.2. Document the serial number of the analytical column associated with the retention time window study.

13.2.3. Record the retention time in minutes for each analyte ***or*** surrogate to three decimal places.

14. PROCEDURE

14.1. Instrument Setup

14.1.1. Use the following GC operating conditions as guidance to establish the GC temperature program and flow rate necessary to separate the analytes of interest.

Description	GC Operating Condition
Inlet mode	split
Inlet temperature	250°C
Inlet pressure	7.25 psi
Split ratio	10:1
Split flow rate	28.1 mL/min
Total flow rate	33.1 mL/min
Carrier gas flow rate	1.4 mL/min
Makeup gas flow rate	30.0 mL/min
Detector temperature	300°C
Initial temperature	70°C, hold 0.50 min
Temperature program	70°C to 190°C at 20.00°C/min 190°C, hold 1.00 min 190°C to 300°C at 11.00°C/min
Final temperature	300°C, hold 2.50 min

14.1.2. Autoinjector is set to inject 2 µL of field or QC sample extract.

14.1.3. Once established, the same operating conditions must be applied for all subsequent standard, sample, and blank analyses.

14.2. ►Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence. If the QC and retention

time criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.3. and Section 12.4.3.

14.2.1. For EPA Region 9 requirement, refer to Section 12.3.1.1. for CCV frequency.

14.2.2. If a failed CCV is the first of the day, effect corrective action ***and recalibrate*** prior to analyzing any samples.

14.2.3. If a failed CCV is <u>not</u> the first of the day, effect corrective action, ***recalibrate***, and re-analyze all samples since the last acceptable CCV.

14.3. Following extraction by one of the methods specified in Section 5.2., the extracts for the QC and actual environmental samples are received in autoinjector vials. The autoinjector vials are then loaded onto the GC sample tray.

14.4. ►***Blank***, standard, and sample vials are loaded in the following or other logical order:

1) Instrument Blank (IB)
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 20 per batch, excluding QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

14.4.1. Item 1: The IB is a vial of hexane used to determine whether the GC system is free of interferants. Additional instrument blanks may also be added elsewhere in the sequence, as necessary (i.e., after suspected high level samples). IB is optional.

14.4.2. Items 2 and 9: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

14.4.2.1. For EPA Region 9 requirement, refer to Section 12.3.1.1. for CCV frequency.

14.4.2.2. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample extract re-analyses that would be required in the event of an unacceptable CCV.

14.4.3. Item 3: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.3.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid samples, the LCS consists of the specified compounds spiked into washed sea sand. For mobility-procedure extracts, the LCS consists of the specified compounds spiked into the mobility-procedure extract designated as LCS.

14.4.3.2. One LCS is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.4. Item 4: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.4.5. Item 5: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (e.g., surrogates, etc.).

14.4.5.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of washed sea sand. For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB.

14.4.5.2. One MB is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.5.3. When samples that are processed together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of hexane must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.4.6. Item 6: Up to 20 sample (excluding QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

14.4.6.1. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.4.7. Item 7: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.7.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.5.

14.4.7.2. ►One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.4.8. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.4.9. Solvent blanks may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration sample extracts), to check for potential carryover or cross-contamination.

14.5. Ensure that a sufficient amount of hexane is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles at the beginning of the sequence.

14.6. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or on the sequence table printout.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. ►Establish the daily retention time window for each analyte ***and*** surrogate (see Section 12.4.2.1. and Section 12.4.2.2.).

14.8.1.1. Tentative identification of an analyte ***or*** surrogate occurs when a peak from a sample extract falls within the daily retention time window.

14.8.1.2. Use the succeeding CCV standards analyzed throughout the course of an analytical sequence within a 12-hour shift to evaluate retention time stability (see Section 12.4.3.). If any analyte(s) ***or*** surrogate in the CCV standard fall outside of their daily retention time window(s), determine the cause of the problem and effect appropriate corrective action.

14.8.1.2.1. If any analyte(s) ***or*** surrogate in the CCV standard fall outside of their daily retention time window(s),

then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.

14.8.2. Quantitation of a target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample extract and the calibration standards.

14.8.2.1. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak(s) can be determined.

14.8.2.2. Determine the concentration based on the initial calibration curve.

14.8.2.2.1. Calculate the concentration of each target analyte in a sample extract using the average of the initial RFs and the area of the characteristic peak. The formula for calculating concentration is listed in Section 15.7.

14.8.2.2.2. ►***The molecular weight correction for the methyl ester form versus the free acid form is not needed due to the derivatization of the calibration standards.***

14.8.2.2.3. The data system is programmed to perform the calculation of concentration.

14.8.2.3. If the instrument response exceeds the calibration range, dilute the extract and reanalyze.

14.8.3. Tentative identification of a target analyte occurs when a peak from a sample extract falls within the analyte's retention time window. Confirmation is necessary when the composition of samples is not well characterized. Qualitative confirmation techniques are by second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors.

14.8.4. Second column confirmation is made on a "confirmation" channel configured with a column of dissimilar stationery phase and a second detector. The principle is that the retention time of the target analyte will differ between the primary and confirmation column and, unless the detected compound is the particular target analyte, it will not be observed within both retention time windows.

14.8.4.1. Report the higher result between the primary and confirmation column. The RPD between results must be ≤ 40%.

14.8.4.1.1. If one result is significantly higher (e.g., > 40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high

result. If no overlapping peaks are observed, examine the baseline parameters established by the instrument data system (or operator) during peak integration. A rising baseline may cause the mis-integration of the peak for the lower result.

14.8.4.1.2. If no anomalies are observed, review the chromatographic conditions. If there is no evidence of chromatographic problems, then it may be appropriate to report the lower result.

14.8.4.1.3. The data user must be advised of the disparity between the results on the two columns. Under some circumstances, including those involving in monitoring compliance with an action level or regulatory limit, further cleanup of the sample or additional analyses may be required when the two results in question span the action level or regulatory limit.

14.8.4.2. In cases where a peak is not observed in the confirmation column's retention time window, the analyte is reported as "ND."

14.8.4.3. A calibration curve and retention time window for each analyte/surrogate are also established and maintained for the confirmation channel. The calibration and quality control requirements for the confirmation channel are identical to those of the primary channel.

14.8.5. GC/MS confirmation is more reliable than second column confirmation. In this case, where confirmation is required by project requirements, the sample is re-analyzed on GC/MS. When GC/MS results indicate that a target analyte is not present, the GC result is reported as "ND."

14.8.6. Confirmation is required for all positive results unless the samples meet all of the following requirements:

14.8.6.1. All samples (aqueous or solid) come from the same source (e.g., same monitoring well). However, samples of the same matrix from the same site but from differing sources (e.g., different monitoring wells) are not exempted.

14.8.6.2. All chemical parameters have been previously analyzed, identified, and confirmed by a second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors. Documentation of such must be maintained.

14.8.6.3. The resulting chromatograms are relatively simple and do not contain complex or overlapping peaks.

14.8.6.4. Chromatograms are largely unchanged from those for which confirmation was carried out.

14.8.7. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

14.8.7.1. When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.

14.8.7.2. When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially integrating a peak, etc.), manual integrations performed by the analyst are necessary.

14.8.7.3. Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.

15. ►CALCULATIONS

15.1. The response factor is calculated as follows:

$$RF = \frac{A_x}{C_x}$$

where: RF = response factor for target analyte being measured.
A_x = area of the characteristic peak(s) for target analyte being measured.
C_x = concentration of target analyte being measured in mg/L.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.
RF_{ave} = mean of the 5, 6, or 7 initial RFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RF_{ave} - RF_{daily}|}{RF_{ave}} \times 100$$

where: %D = percent difference.
RF_{daily} = daily RF for the target analyte.
RF_{ave} = mean of the 5, 6, or 7 initial RFs for the target analyte.

15.4. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x}{RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in mg/L.
A_x = area of the characteristic peak(s) for target analyte.
RF_{ave} = mean of the 5, 6 or 7 initial RFs for the target analyte.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A} \times F$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = volume of extract in mL.
V_A = volume of aqueous sample solvent extracted in L.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.
F = molecular weight correction factor.

15.9. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S} \times F$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid sample solvent extracted in kg.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.
F = molecular weight correction factor.

15.10. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S \times \left(\frac{C_{ss}}{100}\right)} \times F$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid sample solvent extracted in kg.
C_{ss} = solids content in %.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.
F = molecular weight correction factor.

15.11. The target analyte concentration for a mobility-procedure extract is calculated as follows:

$$C_{MP} = \frac{C_{ex} \times V_{ex} \times D}{V_{MP}} \times F$$

where: C_{MP} = concentration of target analyte in mobility-procedure extract in µg/L.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = volume of extract in mL.
V_{MP} = volume of mobility-procedure extract solvent extracted in L.

Unless specified otherwise, V_{MP} = 0.100.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.
F = molecular weight correction factor.

15.12. Refer to the preparatory method(s) and Appendix A for additional calculations.

15.13. All concentrations shall be reported in µg/L (ppb) for aqueous samples and µg/kg (ppb) for soil and solid waste samples.

15.13.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

15.14. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. ►Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. ***Refer to the current revision of SOP-T020*** to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 30% and 130%, respectively. The RPD is ≤ 30% ***(between LCS and LCSD)***. All LCS ***(including LCSD if required)*** compounds must be within acceptance limits (see Section 12.5.3. for additional information).

18.2.1. For EPA Region 9 requirement, refer to Section 12.5.3.1.2. and Section 12.5.3.1.3. for acceptance criteria.

18.2.2. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD ***(when applicable)*** is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2.1. ***If the LCS/LCSD is used in place of the MS/MSD due to insufficient sample amount, or if LCS/LCSD is required per***

client or project specific DQO, both the LCS and LCSD data must be reported.

18.3. The acceptance criteria for surrogate compound recovery are predetermined. The lower and upper acceptance limits for %REC of the surrogate compound in an aqueous sample are 30% and 123%, respectively. The lower and upper acceptance limits for %REC of the surrogate compound in a non-aqueous sample are 30% and 130%, respectively.

18.3.1. For EPA Region 9 requirement, refer to Section 12.6.2.1.2. and Section 12.6.2.1.3. for acceptance criteria.

18.3.2. If the surrogate compound recovery is acceptable, report the surrogate and sample data without qualification.

18.3.3. If the surrogate recovery is not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.4. By itself, unacceptable surrogate recovery does not invalidate sample data. The following must be accomplished if surrogate recovery is not acceptable.

18.3.4.1. Check the surrogate standard solutions for degradation and contamination.

18.3.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recovery, the same ***sample should be re-processed or*** extract re-analyzed.

18.3.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recovery, the affected sample(s) must be re-processed and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recovery and the sample data reported with qualification.

18.3.4.3.1. If, upon re-processing and re-analysis, the surrogate remains unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recovery and the sample data reported with qualification.

18.3.4.3.2. If the MB surrogate is unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

18.3.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected

occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD compounds are predetermined. The lower and upper acceptance limits for %REC of each MS/MSD compound are 30% and 130%, respectively. The RPD is ≤ 30% ***(between MS and MSD)***.

18.4.1. For EPA Region 9 requirement, refer to Section 12.6.3.1.2. and Section 12.6.3.1.3. for acceptance criteria.

18.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in ***the current revision of*** SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for aqueous samples and µg/kg (ppb) for soil and solid waste samples.

18.7.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. ►The Operations ***Director***, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. ►CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the ***Group Leader*** of the appropriate department. All samples associated with an unacceptable QC set are then subject to re-analysis, depending upon the QC type in question.

20.1.1. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the ***Group Leader*** confirms the unacceptable result.

20.1.1.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.1.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, ***refer to the current revision of SOP-T020 for procedures on data reporting and corrective action***.

20.1.1.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to re-analysis. No corrective action is required for that batch.

20.1.2. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Eurofins Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8151A, USEPA, Revision 1, December 1996.

22.2. *Determinative Chromatographic Separations*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000C, USEPA, Revision 3, March 2003.

22.3. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.4. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.5. *Organic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, February 2007.

22.6. *Chlorinated Herbicides*, SW-846 Method 8151, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. ►APPENDICES, TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Hydrolysis, Extraction, and Esterification Procedures.

23.2. Appendix B: Diazomethane Generator.

23.3. Appendix ***C***: Procedure for Lower Limit of Quantitation.

23.4. Appendix ***D***: Additional Quality Control Criteria for Department of Defense Project.

23.5. Appendix ***E***: Control Limits for Department of Defense Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8151A Revision 1 are noted.

ECI SOP M402 Section	Reference Document EPA Method 8151A Section	Summary of Modification
10.1.	5.0	Grade of diethyl ether for extraction and specifications of acid and base for hydrolysis are modified.
10.2.	5.0	Expiration dates of the stock and working standards are modified.
Appendix A	7.0	Use of isooctane and methanol, and adjustment of extract volume before and after esterification are modified.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
3.4	Section 3: Add reference to RL and DL. Section 4: Revise the scope to specify routine analytes. Section 5: Update preparatory methods. Section 6: Add LOD and LOQ definitions. Section 9: Update the list of equipment and supplies. Section 10: Revise standard preparation. Section 11: Revise the requirements on collection and preservation. Section 12: Revise quality control criteria. Section 13: Revise sub-section titles and calibration levels. Section 14: Update GC operating conditions, add reference to mobility-procedure extract, and revise manual integration procedure. Section 15: Revise formulas to apply additional calibration levels. Section 18: Rearrange paragraphs and update section references. Section 23: Revise Appendix D title and add appendices for Department of Defense (DoD) quality control criteria. Section 24: Revise modifications. Section 25: Add revision history. Appendix D: Revise the whole appendix for lower limit of quantitation. Appendix E: Specify DoD quality control requirements and criteria. Appendix F: Specify DoD QC sample control limits.	J. Kang / K. Chang	2013-01-28
3.5	All: Update company name. Sections 3, 6, 7, 8, 9, 11, 13, 14, 17, 18, 19, and 20: Update verbiages for consistency with the other SOPs. Section 10: Update standard preparation procedure. Section 12: Update quality control criteria to reflect current laboratory practices. Section 14: Revise quantitation procedure due to derivatization of standards. Section 15: Delete molecular weight correction formula.	K. Chang	2014-10-13

Revision	Description	Author(s)	Effective Date
3.5	Section 23: Delete Appendix C. Section 25: Add revision history. Appendix A Sections 5, 7, 8, 9, and 10: Correct section number references and update verbiages for consistency with the other SOPs. Appendix A Section 7: Update standard preparation procedure. Appendix C Section 3: Add reference to free acid. Appendix C Section 5: Update standard preparation procedure. Appendices D and E: Update DoD quality control requirements and criteria.	K. Chang	2014-10-13

Appendix A

HYDROLYSIS, EXTRACTION, AND ESTERIFICATION PROCEDURES

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8151A, Chlorinated Herbicides by Gas Chromatography via Methylation Derivatization – Hydrolysis, Extraction, and Esterification Procedures.

2. SCOPE AND APPLICATION

2.1. This method is restricted to use by or under the supervision of analysts/technicians experienced in the use of the equipment and apparatus required to execute the procedure, and experienced in handling diazomethane.

3. METHOD SUMMARY

3.1. EPA Method 8151A provides extraction, derivatization, and gas chromatographic conditions for the analysis of chlorinated acid herbicides. An option for the hydrolysis of esters is also described.

4. INTERFERENCES

4.1. The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid rinsed first, and followed by rinsing with organic-free reagent water to constant pH.

4.2. Hydrolysis may result in the loss of dinoseb and the formation of aldol condensation products if any residual acetone remains from the extraction of solids.

4.3. Sodium sulfate must be acidified with 1:1 sulfuric acid prior to use to avoid the loss of herbicides.

4.4. Sample extracts should be dry prior to methylation to prevent poor recoveries.

4.5. Diazomethane solutions decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling stones.

5. SAFETY

5.1. Diazomethane is a carcinogen and can explode under certain conditions. Due to the potential hazards associated with the use of diazomethane, the following precautions should be taken:

5.1.1. Use the diazomethane generator behind a safety shield in a well ventilated fume hood.

5.1.2. Use mechanical pipetting aides.

5.1.3. Do not heat diazomethane above 90°C. Exposure to heat or high-intensity light may result in explosion.

5.1.4. Avoid grinding surfaces, ground-glass joints, sleeve bearings, and glass stirrers. Explosion may occur upon shock or contact with rough surfaces.

5.1.5. Keep diazomethane away from alkali metals. Contact between diazomethane and alkali metals may cause explosion.

5.2. Diethyl ether is an extremely flammable liquid and vapor with a low flash point. It is also a peroxide-forming chemical prone to explosion. Extra precautions must be taken.

5.2.1. Visually inspect the diethyl ether container prior to use for peroxide formation which exists as crystalline solid or viscous liquid residues.

5.2.1.1. If peroxide formation is suspected, do not open the container. Peroxides deposited on the cap threads may detonate due to friction.

5.2.2. Tightly seal and store the diethyl ether container away from heat and light in a flammable storage cabinet or an explosion-proof refrigerator when diethyl ether is not in use.

5.2.3. Use peroxide test strip to screen diethyl ether for peroxide presence bimonthly or when the container was not opened for more than one week.

5.2.3.1. If peroxide presence is confirmed, do not use the solvent for standard preparation or sample extraction. Remove the solvent from lab and alert waste disposal personnel.

5.2.4. Discard diethyl ether one year after opening or on expiration date, whichever comes first.

5.2.5. Keep diethyl ether away from volatile solvents and metals (e.g. metal spatulas, magnetic stirring bars, etc.). Vaporized volatile solvents may increase peroxide concentration, and contamination with metals may induce explosive decomposition.

5.3. Extraction, hydrolysis, and esterification must be performed in a fume hood vented to the exterior of the laboratory.

5.4. For the safety of the analyst, cracked or broken glassware should be immediately discarded into a broken glassware receptacle. Broken glassware shall not be used in any step of the extraction, hydrolysis, and esterification.

5.5. To ensure the safety of the analyst during any possible emergency situation, it is recommended that chemists do not perform extractions, hydrolysis, and esterification alone. Another chemist should be present during any extraction, hydrolysis, and esterification process.

5.6. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

5.7. ►Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should

review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

6. EQUIPMENT AND SUPPLIES

6.1. Separatory funnels, 2-L, pear-shaped, borosilicate glass or transparent polytetrafluoroethylene (PTFE), with PTFE stopcock and PTFE stopper or screw cap, Kimax Squibb Separatory Funnel, Nalgene Squibb Transparent FEP Separatory Funnel, or equivalent.

6.2. VOA vials, 28-mm × 95-mm (40-mL capacity), screw top, clear or amber glass, with Teflon- or aluminum foil-lined open top or closed top screw caps and Teflon-lined septa, EPA VOA Vial or equivalent.

6.3. Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

6.4. Autoinjector vials, 12-mm × 32-mm (2-mL capacity), crimp top, clear glass, with aluminum crimp caps and Teflon-lined septa, disposable.

6.5. Vial inserts, 300−µL, clear glass, with conical bottom and spring.

6.6. Graduated cylinders, 100-mL, 1000-mL, 2000-mL, or other capacity, glass, Class A.

6.7. Erlenmeyer flasks, 250-mL, 500-mL, 2-L, or other capacity, glass.

6.8. Boiling flasks, 500-mL or other capacity, glass, with round bottom and short neck.

6.9. Beakers, 400-mL, 2-L, or other capacity, glass.

6.10. Pipets, Pasteur, glass, disposable.

6.11. Spatula, stainless steel.

6.12. Stirring rod, glass.

6.13. Aluminum foil.

6.14. Parafilm, thermoplastic, Parafilm M® Laboratory Film or equivalent.

6.15. pH indicator paper, wide range. pH range should include the desired extraction pH.

6.16. Peroxide test strips, 0.5−25-mg/L (ppm) with peroxide removal instruction, EM Quant® or equivalent.

6.17. Glass wool, borosilicate glass fiber without binder resin, Pyrex® or equivalent.

6.17.1. Acid wash glass wool with 1:1 H_2SO_4 solution prior to use.

6.18. Solids content determination apparatus:

6.18.1. Weighing dish, aluminum, disposable.

6.18.2. Drying oven, thermostatically controlled, forced draft, capable of maintaining 104 ± 1°C.

6.18.3. Desiccator, containing indicating-type desiccant.

6.18.4. Forceps, stainless steel.

6.19. Vacuum filtration apparatus:

6.19.1. Vacuum apparatus.

6.19.2. Buchner funnel, ceramic, capable of supporting a 90-mm diameter filter.

6.19.3. Filtration flask, 500-mL, glass, with tubulation.

6.19.4. Filter, 20-µm effective pore size, 90-mm diameter, cellulose, Whatman Ashless Grade 41 Quantitative Filter Paper or equivalent.

6.19.4.1. Acid wash cellulose filter with 1:1 H_2SO_4 solution prior to use.

6.20. Filtration apparatus:

6.20.1. Hirsch funnel, short-stemmed, glass.

6.20.2. Filter paper, silicone-treated, 150-mm or 185-mm diameter, Whatman 1PS Phase Separator or equivalent.

6.20.2.1. Acid wash filter paper with 1:1 H_2SO_4 solution prior to use.

6.21. Kuderna-Danish (K-D) apparatus:

6.21.1. Concentrator tube, 10-mL, 19/22 joint size, graduated, without hooks, borosilicate glass, Kimble Kontes 570051-1025 or equivalent.

6.21.2. Evaporation flask, 250-mL or 500-mL, 24/40 top joint size, 19/22 bottom joint size, borosilicate glass, Kimble Kontes 570011-0250, Kimble Kontes 570037-0500, or equivalent.

6.21.2.1. Attach evaporation flask to concentrator tube with clamps.

6.21.3. Snyder column, three-ball macro, 24/40 joint size, without hooks, borosilicate glass, Kimble Kontes 503000-0121 or equivalent.

6.21.4. Snyder column, two-ball micro, 19/22 joint size, without hooks, borosilicate glass, Kimble Kontes 569011-0219 or equivalent.

6.21.5. Clamps, fitting 19/22 joint size, polyacetal, Kimble Kontes 675300-0019 or equivalent.

6.22. Boiling stones, Teflon.

6.22.1. Rinse boiling stones with methylene chloride prior to use.

6.23. Water bath, heated, capable of temperature control within ± 5°C.

6.23.1. Place water bath in a fume hood.

6.24. Thermometer, calibrated.

6.25. Heating mantle, rheostat controlled.

6.26. Gloves, heat resistant.

6.27. Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or higher.

6.28. Diazomethane generator:

6.28.1. Test tubes, 25-mm × 150-mm, borosilicate glass, reusable.

6.28.2. Stoppers, size 5 (27-mm top diameter and 23-mm bottom diameter), two holes (5-mm hole size), Neoprene rubber or equivalent.

6.28.3. Tubing, amber latex rubber, thin wall.

6.28.4. Tubing, borosilicate glass, standard wall.

6.29. Weighing paper, 4-in × 4-in.

6.30. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

6.31. Centrifuge, 250–6000-rpm digital variable speed, 1–30-min continuous digital timer, VWR International Clinical 200 Large Capacity Centrifuge or equivalent.

6.32. Drying oven, thermostatically controlled, capable of maintaining 130°C.

6.33. Shaker, 40–400-rpm variable speed, 0–60-min mechanical timer, Thermo Scientific Lab-Line MaxQ 3000 Open-Air Shaker Model SHKA3000 or equivalent.

6.34. Dispensers, 1–10-mL, 2.5–25-mL, and 5–50-mL, calibrated, analog display, adjustable volume.

6.35. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

6.36. Equipment Software

6.36.1. None.

6.37. Equipment Maintenance and Troubleshooting

6.37.1. Refer to the user manual or equivalent document(s) of the specific equipment.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Reagent water, interferant free.

7.1.2. Sand, washed, sea or standard Ottawa.

7.1.3. Sodium chloride, NaCl, white crystals, reagent grade or equivalent.

7.1.4. Sodium hydroxide, NaOH, white pellets and granules, reagent grade or equivalent.

7.1.5. Sodium hydroxide, NaOH, 10-N.

7.1.5.1. Prepare the 10-N NaOH solution by dissolving 400 g of NaOH in reagent water, cool and dilute to 1000 mL with additional reagent water.

7.1.6. Sulfuric acid, H_2SO_4, 90–98% (v/v), concentrated, colorless liquid, reagent grade or equivalent.

7.1.7. Sulfuric acid, H_2SO_4, 1:1 (v/v).

7.1.7.1. Prepare the 1:1 H_2SO_4 solution by slowly adding 500 mL of concentrated H_2SO_4 to 500 mL of reagent water.

7.1.7.2. Chill the 1:1 H_2SO_4 solution to 4°C prior to use.

7.1.8. Hydrochloric acid, HCl, 36.5–38.0% (v/v), concentrated, colorless to pale yellow liquid, reagent grade or equivalent.

7.1.9. Methylene chloride, CH_2Cl_2, clear colorless liquid, boiling point 39.8°C, pesticide grade or equivalent.

7.1.10. Acetone, CH_3COCH_3, clear colorless liquid, boiling point 56.2°C, pesticide grade or equivalent.

7.1.11. Diethyl ether (or ethyl ether), $C_4H_{10}O$, clear colorless liquid, boiling point 34.6°C, butylhydroxytoluene (BHT) stabilized, certified, reagent grade or equivalent.

7.1.11.1. Diethyl ether is a peroxide-forming chemical prone to explosion. Refer to Section 5.2. of this appendix for safety precautions on the use and handling of diethyl ether.

7.1.12. Sodium sulfate, Na_2SO_4, anhydrous, white powder, reagent grade or equivalent.

7.1.12.1. Purify sodium sulfate by heating at 400°C for 4 hours in a shallow tray, or by pre-cleaning with methylene chloride. If sodium sulfate is pre-cleaned with methylene chloride, use method blank to demonstrate that the drying agent is free of interferences.

7.1.12.2. Slurry sufficient amount of sodium sulfate with enough diethyl ether to just cover the solid, add 0.1 mL of concentrated sulfuric acid per 100 g of sodium sulfate, and mix thoroughly.

7.1.12.3. Assemble a vacuum filtration apparatus with a clean cellulose filter. Decant the mixture into the Buchner funnel and apply vacuum to remove diethyl ether.

7.1.12.4. Mix 1 g of the acidified sodium sulfate with 5 mL of reagent water, and check the pH of the mixture with pH paper.

7.1.12.4.1. If the pH is less than 4, transfer the remaining acidified sodium sulfate into a beaker covered with aluminum foil, and store at 130°C.

7.1.12.4.2. ►If the pH is greater than or equal to 4, repeat Sections ***7.1.12.2.*** through ***7.1.12.4.*** of this appendix.

7.1.13. Methanol, CH_3OH, clear colorless liquid, pesticide grade or equivalent.

7.1.14. Isooctane (or 2,2,4-trimethylpentane), C_8H_{18}, clear colorless liquid, pesticide grade or equivalent.

7.1.15. Potassium hydroxide, KOH, white pellets, reagent grade or equivalent.

7.1.16. Potassium hydroxide, KOH, 37% (w/v).

7.1.16.1. Prepare the 37% KOH solution by dissolving 370 g of KOH in reagent water and dilute to 1 L with additional reagent water.

7.1.17. Diazald® (or N-methyl-N-nitroso-p-toluenesulfonamide) $C_8H_{10}N_2O_3S$, 99% (w/w), yellow powder, reagent grade or equivalent.

7.1.17.1. Diazald has the risk of explosion by shock, friction, fire, or other sources of ignition.

7.1.17.2. Diazald is a diazomethane precursor. Refer to Section 5.1. of this appendix for safety precautions on diazomethane generation.

7.1.17.3. Store Diazald under dark and refrigerated conditions.

7.1.18. Carbitol® (or 2-(2-ethoxyethoxy) ethanol), $C_6H_{14}O_3$, clear colorless liquid, reagent grade or equivalent.

7.1.19. Silicic acid, H_2O_3Si, white powder, reagent grade or equivalent.

7.1.19.1. Store silicic acid at 130°C.

7.1.20. Hexane, C_6H_{14}, clear colorless liquid, pesticide grade or equivalent.

7.1.21. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

7.2. ►Standards

7.2.1. Pre-certified stock standard solutions, each in sealed glass ampules, ***contain*** various concentrations of ***herbicide*** target analytes in free acid form, are used ***as*** check standards.

7.2.2. ***Pre-certified stock standard solution, in sealed glass ampule, contains 1000 ppm of 2,4-dichlorophenylacetic acid (DCAA) in free acid form, is used to prepare surrogate working standards.***

7.2.2.1. Prepare the 100-ppm surrogate working standard solution by diluting 5.0 mL of the 1000-ppm surrogate stock standard solution to 50 mL with methanol.

7.2.3. Surrogate ***working*** standard solution ***contains 100*** ppm of 2,4-dichlorophenylacetic acid (DCAA) in free acid form in methanol.

7.2.3.1. Add 100 µL of the 100-ppm surrogate working standard to each sample including each quality control (QC) check sample and method blank prior to solvent extraction.

7.2.3.2. Add 100 µL of the 100-ppm surrogate working standard to each mobility-procedure extract including each mobility-procedure extract designated as QC check sample and method blank prior to solvent extraction.

7.2.4. Spike stock standard solution containing various concentrations of target analytes in free acid form in methanol.

7.2.4.1. ***Use the second source herbicide stock standard solution as the spike stock standard solution.*** The spike stock standard solution is as follows:

Analyte (free acid)	Initial Conc. (ppm)
dalapon	250
dicamba	10
MCPP	10000
MCPA	10000
dichlorprop	100
2,4-D	100
2,4,5-TP (silvex)	10
2,4,5-T	10
2,4-DB	100
dinoseb	50

7.2.4.2. The spike stock standard is used to prepare QC check samples such as laboratory control samples (LCS/LCSDs) and matrix spikes (MS/MSDs).

7.2.4.3. Add 200 µL of the spike stock standard to each LCS/LCSD and MS/MSD sample prior to solvent extraction.

7.2.4.4. Add 200 µL of the spike stock standard to each mobility-procedure extract designated as LCS/LCSD and MS/MSD prior to solvent extraction.

7.2.5. All working standards must be replaced after six months (unless specified otherwise) or sooner if ***routine QC or*** comparison with check standards indicates a problem.

7.2.5.1. ***Store all working standards under dark and refrigerated condition.***

7.2.6. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

7.2.6.1. ***Check all opened stock standards frequently for signs of degradation or evaporation.***

8. ►QUALITY CONTROL

8.1. Event Based Quality Control (MBs and LCS/LCSDs)

8.1.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), a laboratory control sample ***(LCS)***, and ***a*** laboratory control sample duplicate ***(LCSD)***.

8.1.1.1. ***LCSD shall be prepared and processed if there is insufficient sample amount to perform matrix based QC (i.e., MS/MSD), or if it is mandatory per client request or project specific DQOs.***

8.1.2. One MB consisting of clean reagent water or washed sea sand is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

8.1.3. One LCS consisting of the specified compounds spiked into clean reagent water or washed sea sand is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. The LCSD is handled identically to the LCS.

8.1.4. The MB/LCS/LCSD is processed concurrently with the associated samples. In the processing of the MB/LCS/LCSD, reagents and procedures identical to those for actual samples are used (e.g., surrogates, etc.).

8.2. Matrix Based Quality Control (Surrogates and MS/MSDs)

8.2.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of surrogate added to each sample, a matrix spike ***(MS)***, and ***a*** matrix spike duplicate (***MSD***).

8.2.2. One MS consisting of the actual sample matrix spiked with known concentrations of specific target analytes is required for every batch of 20 samples per matrix or portion thereof processed concurrently. The MSD is handled identically to the MS.

8.2.3. The sample which is spiked for the MS/MSD is processed concurrently with the associated samples. In the processing of the MS/MSD, reagents and procedures identical to those for actual samples are used (e.g., surrogates, etc.).

8.3. A variety of problems can occur during the course of the extraction process and can drastically affect the integrity of the data produced.

8.3.1. If the extract is inadvertently concentrated to dryness, the sample can be irrevocably altered. A portion of the analyte content can be lost to the atmosphere. In this case, if there is sufficient sample, the best solution is to re-extract the sample. If there is insufficient sample, first let the extractor cool and allow the vapor to condense to see how much solvent can be recovered. Then add fresh solvent to the desired final volume (see Appendix A). If the latter is the only option, a notation must be made of the error. In addition, the analyst and the client must be made aware of the error. Low surrogate recoveries are indicative of the possible loss of target analytes. To avoid this problem, extraction should never be left unattended during concentration.

8.3.2. If the Snyder column floods, special care must be taken to correct the problem without losing any of the sample. In case of flooding, gently remove the Snyder column from the concentrator. Once it has cooled sufficiently, and the vapors have condensed, gently shake the column and allow the solvent to drain back into the concentrator. If the column is shaken while it is still hot and attached to the concentrator, the pressure build-up can force vapor out of the column and into the atmosphere, irrevocably altering the sample.

9. CALIBRATION AND STANDARDIZATION

9.1. Top Loading Balance

9.1.1. Calibrate one top loading balance at 100 g, 1000 g, and 2000 g using Class 2 weights as outlined in the current revision of SOP-T043.

9.1.2. Calibrate another top loading balance at 0.1 g, 1 g, 100 g, and 500 g using Class 2 weights as outlined in the current revision of SOP-T043.

9.1.3. If control limits are not specified, calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

9.2. Thermometer

9.2.1. ►Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T043.

9.3. Dispenser

9.3.1. Calibrate the dispenser according to the procedure outlined in the current revision of SOP-T043.

10. PROCEDURE

10.1. Aqueous Sample Preparation

10.1.1. The amount of sample required for analytical determination is established by the determinative method or the project's Quality Assurance Project Plan (QAPP).

10.1.1.1. The amount of sample generally required is 1000 mL nominal.

10.1.2. Mark the level of an aqueous sample on the outside of the sample bottle with a sharpie.

10.1.2.1. Alternatively, zero a top loading balance, and weigh the aqueous sample including the sample bottle. Record the mass to the nearest 1 g.

10.1.3. Quantitatively transfer the whole aqueous sample from the sample bottle into a clean separatory funnel.

10.1.3.1. For MB/LCS/LCSD, measure exactly 1000 mL of clean reagent water.

10.1.3.2. For MS/MSD, measure exactly 1000 mL of aqueous sample in each analytical batch selected for spiking.

10.1.4. Add 100 µL of the 100-ppm surrogate working standard solution to all samples, matrix spikes, laboratory control samples, and method blanks.

10.1.5. Add 200 µL of the spike stock standard solution to all matrix spikes and laboratory control samples.

10.1.6. If emulsion is known to be a problem, add 250 g of sodium chloride to the aqueous sample. Seal and shake the separatory funnel briefly to dissolve the salt.

10.1.7. Determine whether hydrolysis is required.

10.1.7.1. If both herbicide esters and herbicide acids are to be determined, proceed to Section 10.3. of this appendix for aqueous sample hydrolysis procedure.

10.1.7.2. If only herbicide acids are to be determined, proceed to Section 10.4. of this appendix for aqueous sample extraction procedure.

10.1.8. At the completion of the extraction step, measure the volume of the aqueous sample used by filling the sample bottle to the marked line with tap water, and then transfer the tap water into a 1000-mL or 2000-mL graduated cylinder. Record the volume to the nearest 10 mL or the smallest graduation of the graduated cylinder.

10.1.8.1. Alternatively, zero the same top loading balance, and weigh the sample bottle. Record the mass to the nearest 1 g.

10.1.8.2. Calculate the volume of the aqueous sample used. The formula for calculating volume is listed in Section 11.1. of this appendix. Record the volume to the nearest 10 mL.

10.2. Mobility-Procedure Extract Preparation

10.2.1. Measure exactly 100 mL of the mobility-procedure extract into a clean separatory funnel. Record the volume to the nearest 1 mL.

10.2.1.1. For MB/LCS/LCSD, measure exactly 100 mL of mobility-procedure extract designated as MB/LCS/LCSD. Refer to the mobility extraction method for information.

10.2.1.2. For MS/MSD, measure exactly 100 mL of mobility-procedure extract designated as MS/MSD. Refer to the mobility extraction method for information.

10.2.2. Add 100 µL of the 100-ppm surrogate working standard solution to all sample, matrix spike, laboratory control sample, and method blank mobility-procedure extracts.

10.2.3. Add 200 µL of the spike stock standard solution to all matrix spike and laboratory control sample mobility-procedure extracts.

10.2.4. Add exactly 900 mL of reagent water to the mobility-procedure extract.

10.2.5. If emulsion is known to be a problem, add 250 g of sodium chloride to the mobility-procedure extract. Seal and shake the separatory funnel briefly to dissolve the salt.

10.2.6. Determine whether hydrolysis is required.

10.2.6.1. If both herbicide esters and herbicide acids are to be determined, proceed to Section 10.3. of this appendix for aqueous sample hydrolysis procedure.

10.2.6.2. If only herbicide acids are to be determined, proceed to Section 10.4. of this appendix for aqueous sample extraction procedure.

10.3. Aqueous Sample Hydrolysis (Optional)

10.3.1. Add 17 mL of 10-N NaOH solution to the aqueous sample. Seal and shake the separatory funnel briefly.

10.3.2. Check the pH by transferring a few drops of the aqueous sample onto a wide-range pH paper. If the pH is < 12, add more 10-N NaOH solution to adjust the pH to ≥ 12.

10.3.3. Seal the separatory funnel and allow the hydrolysis of the aqueous sample to complete at ambient temperature for 1–2 hours. Shake the separatory funnel periodically.

10.3.4. Add 60 mL of methylene chloride to the sample bottle. Seal and shake the sample bottle vigorously with periodic venting to rinse the sample bottle. Transfer this rinse solvent to the separatory funnel.

10.3.5. Seal and shake the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure.

10.3.6. Allow the organic solvent layer to separate from the aqueous phase for a minimum of 10 minutes.

10.3.6.1. If the emulsion interface between layers is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the phase separation.

10.3.6.2. Break the emulsion or separate the phases of the emulsion by stirring, filtering the emulsion through acid washed glass wool, or centrifuging.

10.3.7. Discard the methylene chloride phase (lower layer).

10.3.8. Repeat the extraction two more times using 60 mL of fresh methylene chloride each time (Sections 10.3.4. through 10.3.7. of this appendix).

10.3.8.1. Methylene chloride may be added directly to the separatory funnel without using the sample bottle.

10.3.9. Proceed to Section 10.4. of this appendix for aqueous sample extraction procedure.

10.3.9.1. The aqueous phase remained in the separatory funnel is the hydrolyzed aqueous sample.

10.4. Aqueous Sample Extraction

10.4.1. Add 17 mL of cold 1:1 H_2SO_4 solution to the aqueous sample or the hydrolyzed aqueous sample. Seal and shake the separatory funnel briefly.

10.4.2. Check the pH by transferring a few drops of the aqueous sample or the hydrolyzed aqueous sample onto a wide-range pH paper. If the pH is > 2, add more 1:1 H_2SO_4 solution to adjust the pH to ≤ 2.

10.4.3. Add 120 mL of diethyl ether to the sample bottle. Seal and shake the sample bottle vigorously with periodic venting to rinse the sample bottle. Transfer this rinse solvent to the separatory funnel.

10.4.3.1. For hydrolyzed aqueous sample extraction, diethyl ether may be added directly to the separatory funnel without using the sample bottle.

10.4.4. Seal and shake the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure.

10.4.5. Allow the organic solvent layer to separate from the aqueous phase for a minimum of 10 minutes.

10.4.5.1. If the emulsion interface between layers is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the phase separation.

10.4.5.2. Break the emulsion or separate the phases of the emulsion by stirring, filtering the emulsion through acid washed glass wool, or centrifuging.

10.4.6. Temporarily transfer the aqueous phase (lower layer) to a 2-L Erlenmeyer flask.

10.4.7. Collect the diethyl ether extract (upper layer) in a 500-mL Erlenmeyer flask containing 10 g of acidified sodium sulfate. Swirl the flask periodically to mix the extract and the drying agent.

10.4.8. Transfer the aqueous phase back to the separatory funnel.

10.4.9. Repeat the extraction two more times using 60 mL of fresh diethyl ether each time (Sections 10.4.3. through 10.4.8. of this appendix).

10.4.9.1. Diethyl ether may be added directly to the separatory funnel without using the sample bottle.

10.4.10. Collect and combine the three diethyl ether extracts in the same Erlenmeyer flask. Label the combined extract appropriately.

10.4.11. Swirl the Erlenmeyer flask and determine whether the amount of drying agent in the extract is sufficient.

10.4.11.1. If some free flowing crystals are visible, the amount of sodium sulfate is adequate.

10.4.11.2. If all of the sodium sulfate solidifies in a cake, add 2 g of acidified sodium sulfate and swirl the flask. Repeat the procedure until some free flowing crystals are visible.

10.4.12. Seal the Erlenmeyer flask with aluminum foil followed by Parafilm. Allow the extract to dry in an operational fume hood for a minimum of 2 hours.

10.4.12.1. The fume hood shall remain energized continuously in order to minimize ether buildup.

10.4.12.2. The extract shall be kept away from heat and light.

10.4.12.3. The extract may be stored in a flammable material refrigerator overnight.

10.4.13. Filter the dried extract through a glass funnel containing acid washed silicone-treated filter paper (or acid washed glass wool). Collect the filtered extract in a 250-mL Erlenmeyer flask. Use a glass stirring rod to crush any caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask thoroughly with 20–30 mL of diethyl ether, and add it to the funnel to complete the quantitative transfer.

10.4.14. Proceed to Section 10.9. of this appendix for concentration procedure.

10.5. Solid Sample Preparation

10.5.1. Homogenize sample as outlined in the current revision of SOP-M230.

10.5.2. The amount of sample required for analytical determination is established by the determinative method or the project's Quality Assurance Project Plan (QAPP).

10.5.2.1. The amount of sample generally required is 50 g nominal.

10.5.3. Solids Content Determination

10.5.3.1. When sample results are to be reported on a dry weight basis, a second portion of sample should be weighed at the same time as the portion used for analytical determination.

10.5.3.2. ►Immediately after weighing the sample for extraction, weigh 5–10 g of the sample into a tared weighing dish. Dry this aliquot overnight at 105°C. Allow the dried sample to cool in a desiccator before weighing. The formula for calculating solids content is listed in Section ***11.3.*** of this appendix.

10.5.3.3. Additional information regarding determination of solids content is provided in SOP-M700.

10.5.4. Measure 50.0 ± 2.5 g of a homogenized solid sample into a clean 500-mL Erlenmeyer flask. Record the mass to the nearest 0.1 g.

10.5.4.1. For MB/LCS/LCSD, measure exactly 50.0 g of washed sea sand. Record the washed sea sand identification number.

10.5.4.2. For MS/MSD, measure exactly 50.0 g of solid sample in each analytical batch selected for spiking.

10.5.5. Check the pH of the solid sample with wide-range pH paper. Adjust the pH to 2 with concentrated HCl and monitor the pH for 15 minutes with occasionally stirring.

10.5.5.1. Add more concentrated HCl, if necessary, until the pH remains at 2.

10.5.6. Add 100 µL of the 100-ppm surrogate working standard solution to all samples, matrix spikes, laboratory control samples, and method blanks.

10.5.7. Add 200 µL of the spike stock standard solution to all matrix spikes and laboratory control samples.

10.5.8. Proceed to Section 10.6. of this appendix for solid sample extraction procedure.

10.6. Solid Sample Extraction

10.6.1. Add 20 mL of acetone to the solid sample. Seal the Erlenmeyer flask with aluminum foil, hold the flask in place with the clamps on the open-air shaker, and agitate the solid sample at 200 rpm for 20 minutes.

10.6.2. Add 80 mL of diethyl ether to the solid sample. Seal the Erlenmeyer flask with aluminum foil, hold the flask in place with the clamps on the open-air shaker, and agitate the solid sample at 200 rpm for 20 minutes.

10.6.3. Decant the acetone-ether extract into a graduated cylinder and measure the volume.

10.6.4. Transfer the acetone-ether extract to a separatory funnel containing 250 mL of reagent water.

10.6.4.1. If an emulsion forms, slowly add 5 g of acidified sodium sulfate until the extract and water layers separate.

10.6.4.2. A quantity of acidified sodium sulfate equal to the mass of the solid sample may be added, if necessary.

10.6.5. Repeat the extraction two more times using 20 mL of fresh acetone followed by 80 mL of fresh diethyl ether, and agitate the solid sample at 200 rpm for 10 minutes each time (Sections 10.6.1. through 10.6.4. of this appendix).

10.6.6. Measure the volume of each extract and combine the three extracts in the same separatory funnel. Label the combined extract appropriately.

10.6.7. Calculate the total volume of the acetone-ether extract recovered. If the total volume of the acetone-ether extract recovered is less than 75% (i.e., 225 mL) of the total volume of the extraction solvents, repeat the extraction as follows:

10.6.7.1. Extract the solid sample using 20 mL of fresh acetone followed by 80 mL of fresh diethyl ether, and agitate the solid sample at

200 rpm for 10 minutes (Sections 10.6.1. through 10.6.4. of this appendix).

10.6.7.2. Measure the volume of the extract and combine all extracts in the same separatory funnel. Calculate the total volume of the acetone-ether extract recovered.

10.6.7.3. Repeat the extraction a few more times, if necessary, until the total volume of the acetone-ether extract recovered is at least 225 mL.

10.6.8. Check the pH by transferring a few drops of the mixture in the separatory funnel onto a wide-range pH paper. If the pH is > 2, add concentrated HCl to adjust the pH to ≤ 2.

10.6.9. Seal and shake the separatory funnel gently for 1 minute with periodic venting to release excess pressure.

10.6.10. Allow the organic solvent layer to separate from the aqueous phase.

10.6.11. Temporarily transfer the aqueous phase (lower layer) to a 500-mL Erlenmeyer flask.

10.6.12. Collect the diethyl ether extract (upper layer) in a 500-mL round-bottom boiling flask.

10.6.13. Transfer the aqueous phase back to the separatory funnel.

10.6.14. Add 25 mL of diethyl ether to the separatory funnel.

10.6.15. Seal and shake the separatory funnel gently for 1 minute with periodic venting to release excess pressure.

10.6.16. Allow the organic solvent layer to separate from the aqueous phase.

10.6.17. Discard the aqueous phase (lower layer).

10.6.18. Collect and combine the two diethyl ether extracts in the same round-bottom boiling flask. Label the combined extract appropriately.

10.6.19. Determine whether hydrolysis is required.

10.6.19.1. If both herbicide esters and herbicide acids are to be determined, proceed to Section 10.7. of this appendix for solid sample extract hydrolysis procedure.

10.6.19.2. If only herbicide acids are to be determined, proceed to Section 10.8. of this appendix for solid sample extract cleanup procedure.

10.7. Solid Sample Extract Hydrolysis (Optional)

10.7.1. Add 5 mL of 10-N NaOH solution and 30 mL of reagent water to the solid sample extract.

10.7.2. Add one or two clean boiling stones to the round-bottom boiling flask. Place the round-bottom boiling flask on a hot water bath, and allow the

hydrolysis of the solid sample extract to complete at 60–65°C for 1–2 hours.

10.7.3. Remove the round-bottom boiling flask from the hot water bath and cool to ambient temperature.

10.7.4. Quantitatively transfer the whole hydrolyzed solid sample extract (excluding the boiling stones) from the round-bottom boiling flask into a clean separatory funnel.

10.7.5. Add 100 mL of methylene chloride to the separatory funnel. Seal and shake the separatory funnel vigorously with periodic venting to release excess pressure.

10.7.6. Allow the organic solvent layer to separate from the aqueous phase.

10.7.7. Discard the methylene chloride phase (lower layer).

10.7.8. Repeat the extraction two more times using 100 mL of fresh methylene chloride each time (Sections 10.7.5. through 10.7.7. of this appendix).

10.7.9. Add cold 1:1 H_2SO_4 solution to the aqueous phase to adjust the pH to < 2.

10.7.10. Add 40 mL of diethyl ether to the separatory funnel. Seal and shake the separatory funnel vigorously with periodic venting to release excess pressure.

10.7.11. Allow the organic solvent layer to separate from the aqueous phase.

10.7.12. Temporarily transfer the aqueous phase (lower layer) to a 500-mL Erlenmeyer flask.

10.7.13. Collect the diethyl ether extract (upper layer) in a 500-mL round-bottom boiling flask containing 10 g of acidified sodium sulfate. Swirl the flask periodically to mix the extract and the drying agent.

10.7.14. Transfer the aqueous phase back to the separatory funnel.

10.7.15. Repeat the extraction two more times using 20 mL of fresh diethyl ether each time (Sections 10.7.10. through 10.7.14. of this appendix).

10.7.16. Collect and combine the three diethyl ether extracts in the same round-bottom boiling flask. Label the combined extract appropriately.

10.7.17. Swirl the round-bottom boiling flask and determine whether the amount of drying agent in the extract is sufficient.

10.7.17.1. If some free flowing crystals are visible, the amount of sodium sulfate is adequate.

10.7.17.2. If all of the sodium sulfate solidifies in a cake, add 2 g of acidified sodium sulfate and swirl the flask. Repeat the procedure until some free flowing crystals are visible.

10.7.18. Seal the round-bottom boiling flask with aluminum foil followed by Parafilm. Allow the extract to dry in an operational fume hood for a minimum of 2 hours.

10.7.18.1. The fume hood shall remain energized continuously in order to minimize ether buildup.

10.7.18.2. The extract shall be kept away from heat and light.

10.7.18.3. The extract may be stored in a flammable material refrigerator overnight.

10.7.19. Filter the dried extract through a glass funnel containing acid washed silicone-treated filter paper (or acid washed glass wool). Collect the filtered extract in a 250-mL Erlenmeyer flask. Use a glass stirring rod to crush any caked sodium sulfate during the transfer. Rinse the round-bottom boiling flask thoroughly with 20–30 mL of diethyl ether, and add it to the funnel to complete the quantitative transfer.

10.7.19.1. The extract is the hydrolyzed solid sample extract.

10.7.20. Determine whether additional cleanup of the non-hydrolyzed herbicides is required.

10.7.20.1. If additional cleanup is required, proceed to Section 10.8. of this appendix for solid sample extract cleanup procedure.

10.7.20.2. If no additional cleanup is required, proceed to Section 10.9. of this appendix for concentration procedure.

10.8. Solid Sample Extract Cleanup

10.8.1. Prepare the 12.3% KOH solution by carefully mixing 15 mL of 37% KOH solution with 30 mL of reagent water.

10.8.2. Quantitatively transfer the whole solid sample extract from the round-bottom boiling flask or the whole hydrolyzed solid sample extract from the Erlenmeyer flask into a clean separatory funnel.

10.8.3. Add 15 mL of 12.3% KOH solution to the separatory funnel. Seal and shake the separatory funnel vigorously with periodic venting to release excess pressure.

10.8.4. Allow the organic solvent layer to separate from the aqueous phase.

10.8.4.1. The aqueous phase contains the herbicide salts.

10.8.5. Discard the diethyl ether phase (upper layer).

10.8.6. Repeat the extraction two more times using 15 mL of fresh 12.3% KOH solution each time (Sections 10.8.3. through 10.8.5. of this appendix).

10.8.7. Add cold 1:1 H_2SO_4 solution to the aqueous phase to adjust the pH to < 2.

10.8.8. Add 40 mL of diethyl ether to the separatory funnel. Seal and shake the separatory funnel vigorously with periodic venting to release excess pressure.

10.8.9. Allow the organic solvent layer to separate from the aqueous phase.

10.8.10. Temporarily transfer the aqueous phase (lower layer) to a 500-mL Erlenmeyer flask.

10.8.11. Collect the diethyl ether extract (upper layer) in a 500-mL round-bottom boiling flask containing 10 g of acidified sodium sulfate. Swirl the flask periodically to mix the extract and the drying agent.

10.8.12. Transfer the aqueous phase back to the separatory funnel.

10.8.13. Repeat the extraction two more times using 20 mL of fresh diethyl ether each time (Sections 10.8.8. through 10.8.12. of this appendix).

10.8.14. Collect and combine the three diethyl ether extracts in the same round-bottom boiling flask. Label the combined extract appropriately.

10.8.15. Swirl the round-bottom boiling flask and determine whether the amount of drying agent in the extract is sufficient.

10.8.15.1. If some free flowing crystals are visible, the amount of sodium sulfate is adequate.

10.8.15.2. If all of the sodium sulfate solidifies in a cake, add 2 g of acidified sodium sulfate and swirl the flask. Repeat the procedure until some free flowing crystals are visible.

10.8.16. Seal the round-bottom boiling flask with aluminum foil followed by Parafilm. Allow the extract to dry in an operational fume hood for a minimum of 2 hours.

10.8.16.1. The fume hood shall remain energized continuously in order to minimize ether buildup.

10.8.16.2. The extract shall be kept away from heat and light.

10.8.16.3. The extract may be stored in a flammable material refrigerator overnight.

10.8.17. Filter the dried extract through a glass funnel containing acid washed silicone-treated filter paper (or acid washed glass wool). Collect the filtered extract in a 250-mL Erlenmeyer flask. Use a glass stirring rod to crush any caked sodium sulfate during the transfer. Rinse the round-bottom boiling flask thoroughly with 20–30 mL of diethyl ether, and add it to the funnel to complete the quantitative transfer.

10.8.18. Proceed to Section 10.9. of this appendix for concentration procedure.

10.9. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 250-mL or 500-mL evaporation flask.

10.10. Pour the dried extract into a K-D concentrator. Rinse the Erlenmeyer flask thoroughly with diethyl ether, and add it to the funnel to complete the quantitative transfer.

10.11. Add one or two clean boiling stones to the evaporation flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top of the column. Place the K-D apparatus on a hot water bath (49.6–54.6°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the

concentration in 10–20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

10.12. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1–2 mL of diethyl ether. The extract may be further concentrated by using the technique outlined in Section 10.13. of this appendix.

10.13. If further concentration is needed, either the micro Snyder column technique or nitrogen blowdown technique can be used to adjust the extract to the final volume required.

10.13.1. If micro Snyder column technique is used, add another clean boiling stone to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding 0.5 mL of diethyl ether to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5–10 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of diethyl ether.

10.13.2. If nitrogen blowdown technique is used, place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to the desired final volume by blowing a gentle stream of high-purity nitrogen above the extract. The internal wall of the concentrator tube must be rinsed several times with diethyl ether during the operation. Position the concentrator tube to avoid water condensation (i.e. the solvent level should be below the level of the water bath). Do not allow the extract to become dry.

10.13.2.1. If a water bath is not to be utilized, transfer the extract to a VOA vial, and apply the nitrogen blowdown technique to adjust the extract volume.

10.14. Transfer the extract obtained from either Section 10.12. or 10.13. to a VOA vial and label appropriately.

10.14.1. Add 0.5 mL of isooctane (optional) and 0.25 mL of methanol to the extract.

10.14.1.1. Isooctane and methanol serve as stabilizing agents in the concentrated extract prior to esterification.

10.14.2. Adjust the extract volume to 2.0 mL with diethyl ether. The extract is now ready for esterification (methylation) with diazomethane.

10.15. Assemble a diazomethane generator (see Appendix B).

10.15.1. Add 5 mL of diethyl ether to the first test tube (Tube 1).

10.15.2. Add 1 mL of diethyl ether, 1 mL of Carbitol, 1.5 mL of 37% KOH solution, and 0.1–0.2 g of Diazald to the second test tube (Tube 2).

10.15.2.1. The amount of Diazald is sufficient for esterification of 2–3 extracts.

10.15.2.2. After the initial Diazald is consumed, add 0.1–0.2 g of Diazald to the second test tube (Tube 2) to continue the esterification of the next 2–3 extracts.

10.15.2.3. The amount of KOH present in the solution is sufficient to perform a maximum of 20 minutes of esterification.

10.15.3. Connect one end of the glass tubing from the first test tube (Tube 1) and the PTFE tubing to the nitrogen gas cylinder flow controller.

10.15.4. Set the nitrogen gas flow to 10 mL/min.

10.15.5. Open the valve when the extract is ready for esterification.

10.16. Place one end of the glass tubing from the second test tube (Tube 2) into the VOA vial containing the extract.

10.17. Apply the nitrogen gas flow (10 mL/min) to bubble diazomethane through the extract for 10 minutes or until a permanent bright yellow color is obtained.

10.17.1. If the extract color is yellowish prior to esterification, bubble diazomethane through the extract for 10 minutes.

10.18. Cap the VOA vial and store the VOA in an operational fume hood for 20 minutes.

10.18.1. The fume hood shall remain energized continuously in order to minimize ether buildup.

10.19. Add 0.1–0.2 g of silicic acid to the derivatized extract to destroy any un-reacted diazomethane.

10.20. Allow the derivatized extract to stand until the evolution of nitrogen gas has stopped.

10.21. Adjust the derivatized extract volume to 5.0 mL with hexane.

10.22. Transfer the derivatized extract obtained from Section 10.21. to a crimp-top autoinjector vial or a screw-top storage vial and label appropriately. The derivatized extract may now be analyzed.

10.22.1. If the analysis will not be performed immediately, store the derivatized sample extracts under dark and refrigerated (0–6°C) conditions.

10.23. Thoroughly document all aspects of the extraction in an extraction logbook. This logbook includes, but is not limited to:

10.23.1. Extraction date, start time, and end time.

10.23.2. pH adjustment date and time.

10.23.3. Sample matrix, initial amount, and final volume.

10.23.4. Reagent lot (or identification) number and amount.

10.23.5. Solvent lot (or identification) number and volume.

10.23.6. Standard lot (or identification) number, concentration, and volume added.

10.23.7. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

11. CALCULATIONS

11.1. The volume of an aqueous sample used for solvent extraction is calculated as follows:

11.1.1. If the whole aqueous sample is used for solvent extraction, the volume is calculated as follows:

$$V_A = (M_2 - M_0) \times \rho$$

where: V_A = volume of aqueous sample used for solvent extraction in mL.
M_2 = mass of sample bottle with the whole aqueous sample in g.
M_0 = mass of sample bottle in g.
ρ = density of aqueous sample in mL/g. Assume $\rho = 1$.

11.1.2. If only a portion of the aqueous sample is used for solvent extraction, the volume is calculated as follows:

$$V_A = (M_2 - M_1) \times \rho$$

where: V_A = volume of aqueous sample used for solvent extraction in mL.
M_2 = mass of sample bottle with the whole aqueous sample in g.
M_1 = mass of sample bottle with the remaining aqueous sample in g.
ρ = density of aqueous sample in mL/g. Assume $\rho = 1$.

11.2. The dilution factor is calculated as follows:

$$D = \frac{V_f}{V_i}$$

where: D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.
V_f = volume of extract after dilution in mL.
V_i = volume of extract before dilution in mL.

11.3. The solids content for a sample is calculated as follows:

$$C_{ss} = \frac{M_2 - M_0}{M_1 - M_0} \times 100$$

where: C_{ss} = solids content in %.
M_2 = mass of weighing dish and oven-dried sample in g.
M_0 = mass of weighing dish in g.
M_1 = mass of weighing dish and as-received sample in g.

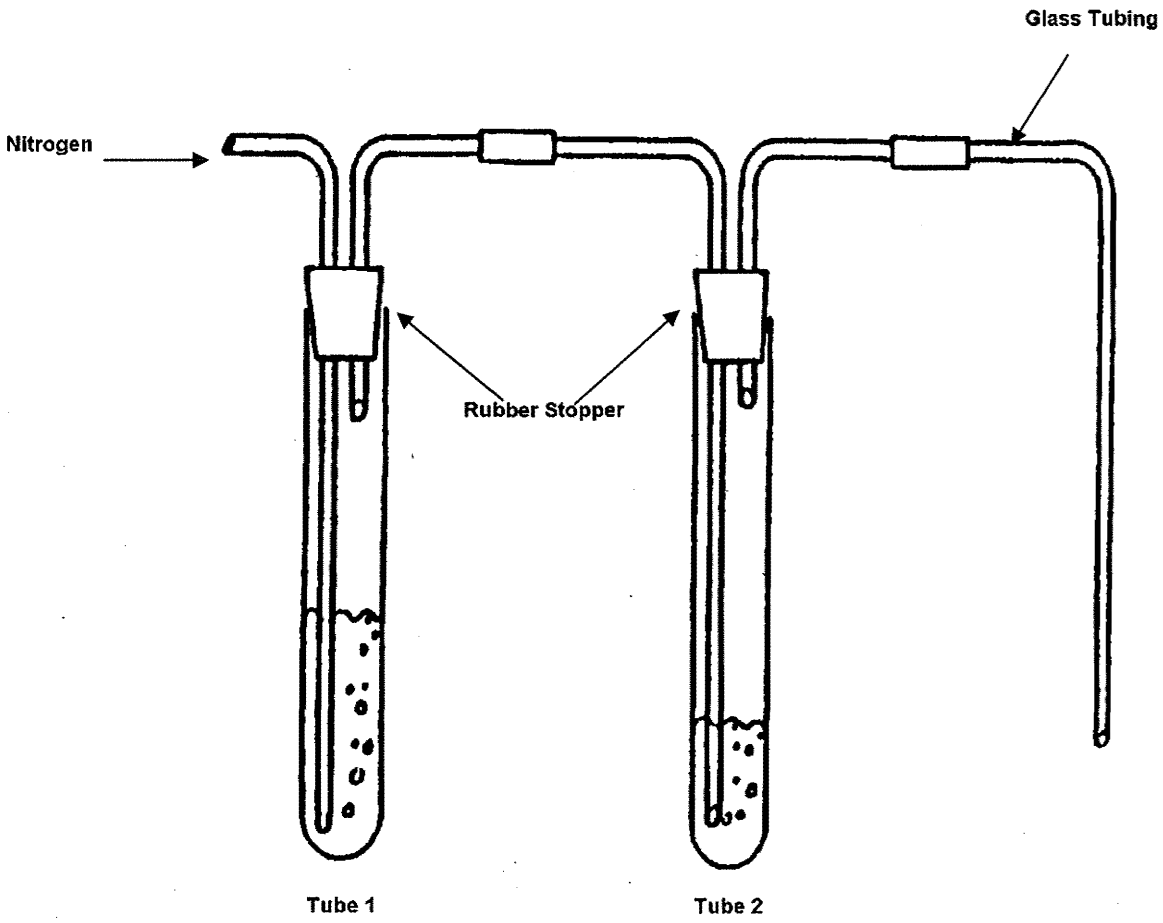
Appendix B

DIAZOMETHANE GENERATOR

Eurofins Calscience, Inc.

Appendix B

Diazomethane Generator



Appendix C

PROCEDURE FOR LOWER LIMIT OF QUANTITATION

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8151A, Chlorinated Herbicides by Gas Chromatography via Methylation Derivatization – Procedure for Lower Limit of Quantitation.

2. APPLICABLE MATRICES

2.1. This method is applicable to soil and solid wastes.

3. DETECTION LIMITS

3.1. ►The reporting limits (RLs) for this method are as follows:

	Soil
Herbicides ***(Free Acid)***	0.5~200 µg/kg (wet-weight)

4. SCOPE AND APPLICATION

4.1. The procedure described herein either supersedes or is in addition to the standard procedure.

5. ►STANDARDS

5.1. Calibration standard solutions ***contain*** various concentrations of target analytes in ***free acid*** form and surrogate in ***free acid*** form in hexane.

5.1.1. Dilute the appropriate volumes of the ***herbicide*** working standard to the specified volumes with hexane ***and derivatize each calibration standard*** for initial calibration.

5.1.1.1. ***Measure 2.00 mL of each calibration standard and derivatize via the procedure outlined in Appendix A Sections 10.15. through 10.20.***

5.1.1.2. ***Transfer each derivatized calibration standard to a crimp-top autoinjector vial or a screw-top storage vial and label appropriately. The derivatized calibration standards may now be analyzed.***

5.1.1.3. ***Thoroughly document all aspects of the derivatization in an extraction logbook.***

5.1.2. Use the following calibration levels as guidance to prepare the calibration standards.

Calibration Level	Initial		Final
	Concentration (ppm)	Volume (mL)	Volume (mL)
1	0.8~800	0.005	2.00
2	0.8~800	0.025	2.00
3	0.8~800	0.250	2.00
4	0.8~800	0.500	2.00
5	0.8~800	2.000	4.00
6	0.8~800	1.500	2.00
7	0.8~800	5.720	5.72

Analyte (free acid)	Calibration Level (ppm)						
	1	2	3	4	5	6	7
dalapon	0.05	0.25	2.5	5.0	10	15	20
dicamba		0.01	0.1	0.2	0.4	0.6	0.8
MCPP		10	100	200	400	600	800
MCPA		10	100	200	400	600	800
dichlorprop		0.10	1.0	2.0	4.0	6.0	8.0
2,4-D		0.10	1.0	2.0	4.0	6.0	8.0
2,4,5-TP (silvex)		0.01	0.1	0.2	0.4	0.6	0.8
2,4,5-T		0.01	0.1	0.2	0.4	0.6	0.8
2,4-DB		0.10	1.0	2.0	4.0	6.0	8.0
dinoseb		0.05	0.5	1.0	2.0	3.0	4.0
surrogate (DCAA)		0.05	0.5	1.0	2.0	3.0	4.0

5.1.3. The midpoint standard is also used as the continuing calibration verification solution.

5.2. Initial calibration verification (ICV) solution ***contains*** midpoint concentration of each target analyte in ***free acid*** form and 2.0 ppm of surrogate in ***free acid*** form in hexane. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

5.2.1. Dilute the appropriate volumes of the second source ***herbicide*** stock standard to 4.0 mL with hexane ***and derivatize the ICV solution*** for initial calibration verification.

5.2.1.1. ***Measure 2.00 mL of the ICV solution and derivatize via the procedure outlined in Appendix A Sections 10.15. through 10.20.***

5.2.1.2. ***Transfer the derivatized ICV solution to a crimp-top autoinjector vial or a screw-top storage vial and label appropriately. The derivatized ICV solution may now be analyzed.***

5.2.1.3. ***Thoroughly document all aspects of the derivatization in an extraction logbook.***

5.2.2. Use the following calibration level as guidance to prepare the ICV solution.

Analyte (free acid)	Calibration Level (ppm)	Initial Conc. (ppm)	Initial Volume (mL)	Final Volume (mL)
dalapon	10	250	0.16	4.0
dicamba	0.4	10		
MCPP	400	10000		
MCPA	400	10000		
dichlorprop	4.0	100		
2,4-D	4.0	100		
2,4,5-TP (silvex)	0.4	10		
2,4,5-T	0.4	10		
2,4-DB	4.0	100		
dinoseb	2.0	50		
surrogate (DCAA)	2.0	100	0.08	4.0

5.3. Continuing calibration verification (CCV) solution ***contains*** midpoint concentration of each target analyte in ***free acid*** form and 2.0 ppm of surrogate in ***free acid*** form in hexane. The CCV solution is of a source same as that used for the initial multi-point calibration.

5.3.1. Dilute the appropriate volumes of the working standard to 4.0 mL with hexane ***and derivatize the CCV solution*** for continuing calibration verification.

5.3.1.1. ***Measure 2.00 mL of the CCV solution and derivatize via the procedure outlined in Appendix A Sections 10.15. through 10.20.***

5.3.1.2. ***Transfer the derivatized CCV solution to a crimp-top autoinjector vial or a screw-top storage vial and label appropriately. The derivatized CCV solution may now be analyzed.***

5.3.1.3. ***Thoroughly document all aspects of the derivatization in an extraction logbook.***

5.3.2. Use the following calibration level as guidance to prepare the CCV solution.

Analyte (free acid)	Calibration Level (ppm)	Initial Conc. (ppm)	Initial Volume (mL)	Final Volume (mL)
dalapon	10	20	2.0	4.0
dicamba	0.4	0.8		
MCPP	400	800		
MCPA	400	800		
dichlorprop	4.0	8.0		
2,4-D	4.0	8.0		
2,4,5-TP (silvex)	0.4	0.8		
2,4,5-T	0.4	0.8		
2,4-DB	4.0	8.0		
dinoseb	2.0	4.0		
surrogate (DCAA)	2.0	4.0	2.0	4.0

5.4. Surrogate ***working*** standard solution ***contains 100*** ppm of 2,4-dichlorophenylacetic acid (DCAA) in free acid form in methanol.

5.4.1. Add 100 µL of the 100-ppm surrogate working standard to each sample including each quality control (QC) check sample and method blank prior to solvent extraction.

5.4.2. Add 100 µL of the 100-ppm surrogate working standard to each mobility-procedure extract including each mobility-procedure extract designated as QC check sample and method blank prior to solvent extraction.

5.5. Spike stock standard solution containing various concentrations of target analytes in free acid form in methanol.

5.5.1. Add 200 µL of the spike stock standard to each LCS/LCSD and MS/MSD sample prior to solvent extraction.

6. PROCEDURE

6.1. Solid Sample Preparation and Extraction via Appendix A

6.1.1. Prepare and extract a solid sample as outlined in Appendix A with the following modifications on sample mass and final extract volume.

6.1.1.1. Measure 100 ± 5 g of a homogenized solid sample into a clean 500-mL Erlenmeyer flask. Record the mass to the nearest 1 g.

6.1.1.1.1. For MB/LCS/LCSD, measure exactly 100 g of washed sea sand. Record the washed sea sand identification number.

6.1.1.1.2. For MS/MSD, measure exactly 100 g of solid sample in each analytical batch selected for spiking.

6.1.1.2. Adjust the derivatized extract volume to 2.0 mL with hexane.

Appendix D

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8151A, Chlorinated Herbicides by Gas Chromatography via Methylation Derivatization – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. ►QUANTITATION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. ►STANDARDS

4.1. ***Initial Calibration Verification (ICV)***

4.1.1. ***The concentration of the ICV standard shall be at or near the midpoint of the calibration range.***

4.2. ***Continuing Calibration Verification (CCV)***

4.2.1. ***The concentration of the CCV standard shall be greater than the low calibration standard and less than or equal to the midpoint of the calibration range.***

4.3. The use of a standard from a second lot ***obtained from the same manufacturer (independently prepared from different source materials)*** is acceptable ***for use as a second source standard***.

5. ►QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. ***Detection limit (DL)*** determination shall be performed ***for each analyte (including surrogate)*** at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. LOD verification must be performed immediately following ***each DL*** determination and quarterly thereafter.

5.1.2.1. LOD verification sample shall be prepared by spiking ***a quality system*** matrix at ***a concentration of at least 2 times but no greater than*** 4 times the ***DL for each analyte***.

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ***(S/N)*** ratio of each analyte is at least 3 and the results must

meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

5.1.2.2.1. For ***a*** data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations. ***This is initially estimated based on a minimum of 4 method blank analyses and later established with a minimum of 20 method blank results.***

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the ***DL*** determination and ***LOD*** verification.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.2.4. ***In situation where the test method is set up and used on an infrequent basis, LOD verification may be performed on a one per batch basis.***

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the ***calibration*** range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ ***for each analyte (including surrogate)***.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking ***a quality system*** matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.2.2.3. ***In situation where the test method is set up and used on an infrequent basis, LOQ verification may be performed on a one per batch basis.***

5.3. ***Initial Calibration (IC)***

5.3.1. ***The LOQ and the highest calibration standard establish the quantitation range.***

5.3.1.1. ***When sample results exceed the quantitation range, dilute and re-analyze the sample (when sufficient sample volume and holding time permit) to bring results within the quantitation range. Results outside the quantitation range shall be reported as estimated values and qualified using appropriate data qualifiers that are explained in the case narrative.***

5.4. Continuing Calibration Verification (CCV)

5.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

5.4.2. The initial calibration is deemed valid if the %D for each analyte ***(including surrogate)*** is ≤ 20%.

5.4.3. ***If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and re-analyze two consecutive CCVs within 1 hour after the failed CCV.***

5.4.3.1. ***If these two CCVs pass, report both CCVs and the sample data without re-analysis.***

5.4.3.2. ***If either of these two CCVs fails, or if the two CCVs cannot be analyzed within 1 hour, effective corrective action, recalibrate, and re-analyze all samples since the last acceptable CCV.***

5.5. Retention Time Window

5.5.1. Establishment of retention time window position ***for each analyte (including surrogate)*** is accomplished by using the midpoint calibration standard once per initial calibration, and by using a CCV standard at the beginning of an analytical sequence.

5.5.1.1. When initial calibration is performed, daily retention time window for each analyte ***or*** surrogate is the retention time of the analyte ***or*** surrogate in the midpoint calibration standard ± 3S.

5.5.1.2. When initial calibration is <u>not</u> performed, daily retention time window for each analyte ***or*** surrogate is the retention time of the analyte ***or*** surrogate in the CCV standard ± 3S.

5.6. Event Based Quality Control (MBs and LCS/LCSDs)

5.6.1. Method Blanks (MBs)

5.6.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.6.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the ***LOQ***, and is greater than 1/10 the amount measured in any ***associated*** sample or 1/10 the regulatory limit (whichever is greater).

5.6.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds ***LOQ***.

5.6.1.2. If the MB is contaminated, re-process the ***affected*** samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

5.6.1.2.1. If insufficient sample volume remains for re-processing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.6.2. Laboratory Control Samples (LCS/LCSDs)

5.6.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound in aqueous and solid matrices are listed in Appendix ***E***.

5.6.2.2. ***All reported analytes must be spiked. The concentration of each spike compound shall be at or below the midpoint of the calibration if project specific concentration is not specified.***

5.6.2.3. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.2.3.1. The laboratory's in-house control limits may not be greater than ± 3S of the average recovery ***if the control limits are statistically-derived based on historical data with at least 30 data points generated under the same analytical process***.

5.6.2.4. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.7. Matrix Based Quality Control (Surrogates and MS/MSDs)

5.7.1. Surrogates

5.7.1.1. ***The lower and upper acceptance limits for %REC of the surrogate compound in aqueous and solid matrices are listed in Appendix E.***

5.7.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall

be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.7.1.2.1. ***The laboratory's in-house control limits may not be greater than ± 3S of the average recovery if the control limits are statistically-derived based on historical data with at least 30 data points generated under the same analytical process.***

5.7.2. Matrix Spikes (MS/MSDs)

5.7.2.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous and solid matrices are listed in Appendix ***E***. The RPD is ≤ 30% ***(between MS and MSD)***.

5.7.2.2. ***All reported analytes must be spiked. The sample selected for spiking must be one of the samples collected for the specific DoD project.***

5.7.2.3. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.7.2.3.1. The laboratory's in-house control limits may not be greater than ± 3S of the average recovery ***if the control limits are statistically-derived based on historical data with at least 30 data points generated under the same analytical process***.

6. ►PROCEDURE

6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence. ***If the QC and retention time window criteria are met, the initial calibration is assumed to be valid and sample analysis may resume.***

6.1.1. ***If CCV fails, refer to Section 5.4.3. of this appendix for corrective action.***

6.2. ***Blank***, standard, and sample vials are loaded in the following or other logical order:

1) Instrument Blank (IB)
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 10 per batch, excluding QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

6.2.1. Items 2 and 9: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2.2. Item 6: Up to 10 sample (excluding QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

6.3. Data Interpretation

6.3.1. The flagging criteria and data reporting procedure for second column confirmation are as follows:

6.3.1.1. If RPD is > 40%, apply the appropriate data qualifier (J-flag) and ***discuss*** in the case narrative.

6.3.1.2. ***Apply*** project-specific reporting requirements when reporting data.

6.3.1.2.1. If project-specific reporting requirements are unavailable, apply method-specific reporting requirements.

6.3.1.2.2. If method-specific reporting requirements are unavailable, report the results from the primary column or detector, unless there is a scientifically valid and documented reason for not doing so ***and is concurred with by the client***.

6.3.2. ***Notify the client of any results that are unconfirmed (e.g., confirmation was not performed or confirmation was obscured by interference)***, identify the unconfirmed result ***in the report using*** the appropriate data qualifiers, and ***explain*** in the case narrative.

7. REFERENCES

7.1. ►Department of Defense Quality Systems Manual for Environmental Laboratories, Version ***5.0, July 2013***.

Appendix E

CONTROL LIMITS FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

Appendix E

DoD Control Limits of LCS/LCSD/MS/MSD and Surrogate Compounds in Aqueous Matrix

Analyte	Control Limit	
	Lower	Upper
2,4,5-T	42	147
2,4,5-TP (Silvex)	51	134
2,4-D	45	152
2,4-DB	35	153
Dalapon	19	139
Dicamba	50	141
2,4-DP (Dichloroprop)	46	159
MCPA	35	144
MCPP	33	157

Surrogate	Control Limit	
	Lower	Upper
DCAA	32	138

Appendix E

DoD Control Limits of LCS/LCSD/MS/MSD and Surrogate Compounds in Solid Matrix

Analyte	Control Limit	
	Lower	Upper
2,4,5-T	31	138
2,4,5-TP (Silvex)	43	129
2,4-D	28	144
2,4-DB	34	142
Dicamba	38	132
2,4-DP (Dichloroprop)	28	155
MCPA	28	135
MCPP	35	143

Surrogate	Control Limit	
	Lower	Upper
DCAA	27	122

Title : **EPA METHOD 8260B, VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY / MASS SPECTROMETRY (GC/MS)**

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APPROVED FOR RELEASE BY: _____ 08/05/13
MANAGEMENT **DATE**

_____ 08-05-13
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS).

2. APPLICABLE MATRICES

2.1. This method is applicable for ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

3. DETECTION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

	Water	Soil	Oil
VOCs	0.5~100 µg/L	5.0~250 µg/kg (wet-weight)	500~25000 µg/kg
Lower-QL VOCs	0.5~50.0 µg/L		

3.2. The RLs will be proportionally higher for samples which require dilution or reduced sample size.

3.3. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. EPA Method 8260B is used to determine the concentrations of most volatile organic compounds (VOCs) that have boiling points below 200°C and are insoluble or slightly soluble in water.

4.2. The following compounds are routinely determined by this method. Compounds with poor chromatographic behavior, poor purging efficiency, or other difficulties are indicated with the "*" symbol.

acetone*	chlorobenzene	1,2-dichloroethane
t-amyl methyl ether (TAME)	chloroethane	1,1-dichloroethene
benzene	chloroform	c-1,2-dichloroethene
bromobenzene	chloromethane*	t-1,2-dichloroethene
bromochloromethane	2-chlorotoluene	1,2-dichloropropane
bromodichloromethane	4-chlorotoluene	1,3-dichloropropane
bromoform	dibromochloromethane	2,2-dichloropropane
bromomethane*	1,2-dibromo-3-chloropropane*	1,1-dichloropropene
2-butanone*	1,2-dibromoethane (EDB)	c-1,3-dichloropropene
t-butyl alcohol (TBA)*	dibromomethane	t-1,3-dichloropropene
n-butylbenzene	1,2-dichlorobenzene	diisopropyl ether (DIPE)
s-butylbenzene	1,3-dichlorobenzene	ethanol*
t-butylbenzene	1,4-dichlorobenzene	ethylbenzene
carbon disulfide*	dichlorodifluoromethane*	ethyl t-butyl ether (ETBE)
carbon tetrachloride	1,1-dichloroethane	hexachloro-1,3-butadiene

2-hexanone*
isopropylbenzene
p-isopropyltoluene
methyl t-butyl ether (MTBE)
methylene chloride
4-methyl-2-pentanone (MIBK)*
naphthalene
n-propylbenzene
styrene
1,1,1,2-tetrachloroethane
1,1,2,2-tetrachloroethane
tetrachloroethene
tetrahydrofuran
toluene
1,2,3-trichlorobenzene
1,2,4-trichlorobenzene
1,1,1-trichloroethane
1,1,2-trichloroethane
trichloroethene
trichlorofluoromethane
1,2,3-trichloropropane
1,2,4-trimethylbenzene
1,3,5-trimethylbenzene
vinyl acetate
vinyl chloride
o-xylene
p/m-xylenes

4.3. The following compounds may also be determined by this method. Compounds with poor chromatographic behavior, poor purging efficiency, or other difficulties are indicated with the "*" symbol. Compounds requiring an unpreserved aqueous sample aliquot for analysis are denoted with the "**" symbol.

acetonitrile*
acrolein*
acrylonitrile*
allyl chloride
1,3-butadiene
2-chloroethyl vinyl ether**
chloroprene
1-chloropropane
2-chloropropane
cyclohexane
cyclohexanone
t-1,4-dichloro-2-butene*
diethyl ether
1,4-dioxane*
ethyl methacrylate
hexane
iodomethane
isobutyl alcohol*
isopropanol*
methacrylonitrile*
methyl acetate
methyl methacrylate
2-methyl-2-butanone (TAA)
methylcyclohexane
propanedinitrile
propionitrile
thiophene
1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)
2,2,4-trimethyl pentane

4.4. Upon client request, additional target analytes may be added to this analysis. However, it needs to be demonstrated that any added compounds lend themselves to EPA Method 8260B determination, either by regulatory reference or validation studies.

4.5. Most volatile organic compounds may be introduced into the GC/MS system via purge-and-trap method (EPA Method 5030) and closed system purge-and-trap method (EPA Method 5035).

4.6. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph / mass spectrometer (GC/MS) and skilled in the interpretation of mass spectra.

5. METHOD SUMMARY

5.1. EPA Method 8260B describes chromatographic procedures that will allow for the separation of volatile organic compounds and their qualitative and quantitative analysis by gas chromatography and mass spectrometry. Detection is achieved using a mass selective detector (MSD).

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample.

5.2.1. Volatile organic compounds in a sample are introduced into the gas chromatograph via the appropriate purge-and-trap method. The analytes are introduced directly to a wide-bore capillary column. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

5.3. Acceptable preparatory methods include, but are not limited to, the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Purge-and-Trap for Samples	5030	SOP-M212
Closed System Purge-and-Trap for Soil/Waste Samples	5035	SOP-M213
TCLP	1311	SOP-M226
SPLP	1312	SOP-M227
STLC (California Code of Regulations)	CCR T22.11.5.A-II	SOP-M228

5.4. Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator. Identification of target analytes is accomplished by comparing their mass spectra with the mass spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using an appropriate calibration curve for the intended application.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. ►Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero

baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.

6.13. Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.

6.14. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.15. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.16. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of

the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.17. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.18. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.19. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.20. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.21. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.22. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.23. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.24. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.26. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.27. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly

prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.28. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

6.29. Term Specific to GC/MS Analysis

6.29.1. Mass-to-Charge Ratio (m/z): The dimensionless quantity formed by dividing the mass of an ion in unified atomic mass units by its charge number (regardless of sign).

7. INTERFERENCES

7.1. Samples can become contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage.

7.1.1. Trip blanks prepared from both reagent water (when associated with aqueous samples) and methanol (when associated with soil/sediment samples) should be carried through sampling and subsequent storage and handling to serve as a check on such contamination. Refer to the current revision of SOP-T011, "Field QA/QC Samples" for guidance.

7.2. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

7.2.1. The use of high purity solvents, reagents and pre-conditioning of disposables that come in contact with the sample help to minimize interference problems.

7.3. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The laboratory where the analysis is to be performed should be free of solvents other than water and methanol.

7.3.1. Many common solvents, most notably acetone and methylene chloride, are frequently found in the laboratory air at low levels. The sample receiving chamber should be loaded in an environment that is clean enough to eliminate the potential for contamination from ambient sources.

7.4. The use of non-polytetrafluoroethylene (non-PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation.

7.4.1. Analyses of reagent blanks provide information about the presence of contaminants. However, subtracting blank values from sample results is not permitted.

7.5. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially.

7.5.1. Sample syringe and/or purging device should be thoroughly rinsed with organic-free reagent water between samples.

7.5.2. Analysis of a suspected high level sample should be followed by an analysis of organic-free reagent water to check for cross-contamination.

7.5.3. For volatile samples containing high concentrations of water-soluble materials, suspended solids, or high boiling-point compounds, it may be necessary to clean purging device, rinse it with organic-free reagent water, and then dry in an oven at 105°C between analyses.

7.6. If elevated baselines are observed during the analysis of blanks and standards, the chromatographic system should be considered contaminated. This contamination may be the result of impure carrier gas, inadequate gas conditioning, septum bleed, column oxidation, and/or pyrolysis products in the injector or column. Such contamination is unacceptable and should be addressed through a program of preventive maintenance and corrective action.

7.7. Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing.

7.8. Use of sensitive mass spectrometers to achieve lower quantitation levels will increase the potential to detect laboratory contaminants as interferences.

7.9. Co-elution of the p- and m-xylene isomers may occur.

7.10. Refer to the preparatory method for other potential interferences.

8. SAFETY

8.1. The following compounds covered by this method have been tentatively classified as known or suspected human carcinogens: benzene, bromodichloromethane, bromoform, carbon tetrachloride, chloroform, dibromochloromethane, 1,4-dichlorobenzene, 1,1-dichloroethane, 1,2-dichloroethane, methylene chloride, 1,1,2,2-tetrachloroethane, and vinyl chloride. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when analysts handle high concentrations of these compounds.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

8.4. Refer to the preparatory methods for additional safety issues.

9. EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Agilent 6890 Series Gas Chromatograph, Agilent 6890N Gas Chromatograph, Agilent 7890A Gas Chromatograph, or equivalent configured with the following components:

9.1.1. Purge-and-trap system (see the appropriate preparatory method).

9.2. Mass Spectrometer: Agilent 5973Network Mass Selective Detector (MSD), Agilent 5975B MSD, Agilent 5975C MSD, or equivalent capable of scanning from 35 to 270 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron-impact ionization (EI) mode, and configured with the following components:

9.2.1. Electron-ionization ion source.

9.2.2. Hyperbolic quadrupole mass filter.

9.2.3. High energy dynode (HED) electron multiplier (EM) detector.

9.3. ►Instrument Software

9.3.1. Requires a PC-based data system or equivalent.

9.3.2. Agilent MSD ChemStation Version E.02.00.493, Agilent MSD ChemStation Version E.02.01.1177, or equivalent equipped with NIST mass spectral library.

9.4. ►Instrument Maintenance and Troubleshooting

9.4.1. Refer to the current revision of SOP-T066 and instrument manuals for maintenance and troubleshooting.

9.4.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.5. Analytical Column: 25-m × 0.2-mm ID, 1.12-µm film thickness, mid-polar, low bleed, narrow-bore, capillary, fused silica, J&W Scientific DB-624 or equivalent.

9.6. Purge Gas: Helium, He, or nitrogen, N_2, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.7. Carrier Gas: Helium, He, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.8. VOA vials, 28-mm × 95-mm (40-mL capacity) and 28-mm × 57-mm (20-mL capacity), screw top, clear or amber glass, with Teflon-lined open top or closed top screw caps and Teflon-lined septa, EPA VOA Vial or equivalent.

9.8.1. Bake VOA vials in an oven at 90°C for 24 hours prior to use.

9.9. Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

9.10. Volumetric flasks, 25-mL, 50-mL, or other capacity, glass, Class A.

9.11. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.12. Syringes, 1-mL, 5-mL, and 25-mL, gastight, Removable Needle (RN), Teflon Luer Lock (TLL), or SampleLock (SL) termination, Hamilton 1000 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.13. Refer to the specific SOPs of the preparatory methods for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, nano-pure.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Sodium thiosulfate, $Na_2S_2O_3$, anhydrous, white solid, reagent grade or equivalent.

10.1.4. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v).

10.1.4.1. Prepare the 10% $Na_2S_2O_3$ solution by dissolving 100 g of anhydrous $Na_2S_2O_3$ in reagent water and dilute to 1 L with additional reagent water.

10.1.5. Hydrochloric acid, HCl, 36.5–38.0% (v/v), concentrated, colorless to pale yellow liquid, reagent grade or equivalent.

10.1.6. Hydrochloric acid, HCl, 1:1 (v/v).

10.1.6.1. Prepare the 1:1 HCl solution by slowly adding concentrated HCl to equal volume of reagent water.

10.1.7. Sodium bisulfate, $NaHSO_4$, monohydrate, colorless crystals, reagent grade or equivalent.

10.1.8. Methanol, CH_3OH, clear colorless liquid, purge and trap grade or equivalent.

10.1.9. Refer to the specific SOPs of the preparatory methods for additional reagents.

10.1.10. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. ►Standards

10.2.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000 ppm of each gaseous volatile organic target analyte are used to prepare calibration and check standards.

10.2.1.1. The gaseous target analytes are dichlorodifluoromethane (CFC-12), chloromethane (methyl chloride), vinyl chloride, bromomethane (methyl bromide), chloroethane (ethyl chloride), and trichlorofluoromethane (CFC-11).

10.2.1.2. Prepare each 50-ppm gaseous volatile organic working standard solution by diluting 1.25 mL of the 2000-ppm gaseous volatile organic stock standard to 50.0 mL with methanol.

10.2.1.3. The 50-ppm gaseous volatile organic working standard solutions must be stored under dark and refrigerated conditions, and replaced after two weeks or sooner if comparison with check standards indicates a problem.

10.2.1.4. Prepare the 0.5-ppm gaseous volatile organic working standard solution by diluting 10 µL of the 50-ppm gaseous volatile organic working standard to 1.00 mL with methanol.

10.2.1.5. The 0.5-ppm gaseous volatile organic working standard solution must be prepared fresh on the day of calibration.

10.2.2. ►Pre-certified stock standard solutions, each in sealed glass ampules, containing 50 ppm of each non-gaseous volatile organic target analyte (except acrolein, ***iodomethane, acetonitrile, isobutyl alcohol***, t-butyl alcohol, 1,4-dioxane, ethanol, and isopropanol), 100 ppm of acrolein, ***iodomethane, acetonitrile, isobutyl alcohol***, 250 ppm of t-butyl alcohol, 500 ppm of 1,4-dioxane, 500 ppm of ethanol, and 250 ppm of isopropanol are used to prepare calibration and check standards.

10.2.2.1. Prepare the 0.5-ppm non-gaseous volatile organic working standard solution by diluting the appropriate volume of the non-gaseous volatile organic stock standard to 1.00 mL with methanol.

10.2.2.2. ►The 0.5-ppm non-gaseous volatile organic working standard is prepared as follows:

Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
volatile organics	50	10	0.5	1.00
acrolein, ***iodomethane, acetonitrile, isobutyl alcohol***	100		1.0	
t-butyl alcohol	250		2.5	
1,4-dioxane	500		5.0	
ethanol	500		5.0	
isopropanol	250		2.5	

10.2.2.3. The 0.5-ppm non-gaseous volatile organic working standard solution must be prepared fresh on the day of calibration.

10.2.3. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2500/12500 ppm of each surrogate, 2500/12500 ppm of each internal standard (except TBA-d_9), and 12500/62500 ppm of TBA-d_9 are used to prepare surrogate and internal standard working standards.

10.2.3.1. The surrogates are 1,4-bromofluorobenzene (BFB), dibromofluoromethane, 1,2-dichloroethane-d_4, and toluene-d_8.

10.2.3.2. The internal standards are t-butyl alcohol-d_9 (TBA-d_9), chlorobenzene-d_5, 1,4-dichlorobenzene-d_4, 1,4-difluorobenzene, and pentafluorobenzene.

10.2.3.2.1. The internal standards selected should permit most analytes of interest in a chromatogram to have relative retention times of 0.80−1.20.

10.2.3.3. Prepare the 50-ppm and 250-ppm surrogate and internal standard working standard solutions by diluting the appropriate volumes of the surrogate and internal standard stock standards to 50 mL with methanol.

10.2.3.4. The 50-ppm surrogate and internal standard working standard is prepared as follows:

Surrogate and Internal Standard	Initial		Final	
	Conc. (ppm)	Volume (mL)	Conc. (ppm)	Volume (mL)
1,4-bromofluorobenzene	2500	1.0	50	50
dibromofluoromethane	2500		50	
1,2-dichloroethane-d_4	2500		50	
toluene-d_8	2500		50	
TBA-d_9	12500	1.0	250	
chlorobenzene-d_5	2500		50	
1,4-dichlorobenzene-d_4	2500		50	
1,4-difluorobenzene	2500		50	
pentafluorobenzene	2500		50	

10.2.3.5. The 250-ppm surrogate and internal standard working standard is prepared as follows:

Surrogate and Internal Standard	Initial		Final	
	Conc. (ppm)	Volume (mL)	Conc. (ppm)	Volume (mL)
1,4-bromofluorobenzene	12500	1.0	250	50
dibromofluoromethane	12500		250	
1,2-dichloroethane-d_4	12500		250	
toluene-d_8	12500		250	
TBA-d_9	62500	1.0	1250	
chlorobenzene-d_5	12500		250	
1,4-dichlorobenzene-d_4	12500		250	
1,4-difluorobenzene	12500		250	
pentafluorobenzene	12500		250	

10.2.4. Tuning standard solution contains 50 ppb of 1,4-bromofluorobenzene (BFB) in reagent water.

10.2.4.1. Prepare the first calibration standard or CCV solution, and purge and trap for hardware turning.

10.2.5. Calibration standard solutions contain various concentrations of target analytes, surrogates, and internal standards in methanol.

10.2.5.1. Add the appropriate volumes of the working and stock standards and the appropriate volume of the 250-ppm surrogate and internal standard working standard to 5.0 mL of reagent water, and purge and trap for initial calibration.

10.2.5.1.1. For lower limit of quantitation, add the appropriate volumes of the working and stock standards and the appropriate volume of the 50-ppm surrogate and internal standard working standard to 20 mL of reagent water.

10.2.5.1.2. If samples are preserved with sodium bisulfate, and the presence of the preservative affects the purging efficiencies of the analytes, it is recommended that the same amount (~1.00 g) of sodium bisulfate be added to the reagent water after adding the standards.

10.2.5.2. ►Use the following calibration levels as guidance to prepare the calibration standards.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
0.5	1.0	2.5	5.0	50	0.5~5.0	250	5.0	1.0
1.0	2.0	5.0	10	50	0.5~5.0	250	10.0	1.0
10	20	50	100	50	50~500	250	1.0	1.0
20	40	100	200	50	50~500	250	2.0	1.0
50	100	250	500	50	50~500	250	5.0	1.0
100	200	500	1000	50	50~500	250	10.0	1.0
200	400	1000	2000	50	50~500	250	20.0	1.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein, *Acetonitrile, Iodomethane or Isobutyl alcohol;* A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate; IS = Internal Standard; A = A1 + A2 + A3 + A4; Calibration Level of TBA-d_9 = 250 ppb; Initial Concentration of TBA-d_9 = 1250 ppm

10.2.5.3. ►Use the following calibration levels as guidance to prepare the calibration standards for lower limit of quantitation.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
0.5	1.0	2.5	5.0	10	0.5~5.0	50	20.0	4.0
2.0	4.0	10	20	10	0.5~5.0	50	80.0	4.0
5.0	10	25	50	10	50~500	50	2.0	4.0
10	20	50	100	10	50~500	50	4.0	4.0
20	40	100	200	10	50~500	50	8.0	4.0
30	60	150	300	10	50~500	50	12.0	4.0
40	80	200	400	10	50~500	50	16.0	4.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein, *Acetonitrile, Iodomethane, or Isobutyl alcohol;* A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate; IS = Internal Standard; A = A1 + A2 + A3 + A4; Calibration Level of TBA-d_9 = 50 ppb; Initial Concentration of TBA-d_9 = 250 ppm

10.2.5.4. The midpoint standards are also used as the continuing calibration verification solutions.

10.2.5.5. The calibration levels for the initial calibration of a non-routine target analyte may be established differently per client request or project specific DQOs.

10.2.6. Initial calibration verification (ICV) solutions contain the appropriate concentrations of each target analyte, surrogate, and internal standard in reagent water. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.6.1. Add the appropriate volumes of the second source working and stock standards and the appropriate volume of the 250-ppm

surrogate and internal standard working standard to 5.0 mL of reagent water, and purge and trap for initial calibration verification.

10.2.6.1.1. For lower limit of quantitation, add the appropriate volumes of the second source working and stock standards and the appropriate volume of the 50-ppm surrogate and internal standard working standard to 20 mL of reagent water.

10.2.6.1.2. If samples are preserved with sodium bisulfate, and the presence of the preservative affects the purging efficiencies of the analytes, it is recommended that the same amount (~1.00 g) of sodium bisulfate be added to the reagent water after adding the standards.

10.2.6.2. ►Use the following calibration level as guidance to prepare the ICV solution.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
50	100	250	500	50	50~500	250	5.0	1.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein, *Acetonitrile, Iodomethane, or Isobutyl alcohol;* A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate; IS = Internal Standard; A = A1 + A2 + A3 + A4; Calibration Level of TBA-d_9 = 250 ppb; Initial Concentration of TBA-d_9 = 1250 ppm

10.2.6.3. ►Use the following calibration level as guidance to prepare the ICV solution for lower limit of quantitation.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
10	20	50	100	10	50~500	50	4.0	4.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein, *Acetonitrile, Iodomethane, or Isobutyl alcohol;* A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate; IS = Internal Standard; A = A1 + A2 + A3 + A4; Calibration Level of TBA-d_9 = 50 ppb; Initial Concentration of TBA-d_9 = 250 ppm

10.2.6.4. The calibration level for the initial calibration verification of a non-routine target analyte may be established differently per client request or project specific DQOs.

10.2.7. Continuing calibration verification (CCV) solutions contain the appropriate concentrations of each target analyte, surrogate, and internal standard in reagent water. The CCV solution is of a source same as that used for the initial multi-point calibration.

10.2.7.1. Add the appropriate volumes of the working and stock standards and the appropriate volume of the 250-ppm surrogate and internal standard working standard to 5.0 mL of reagent water, and purge and trap for continuing calibration verification.

10.2.7.1.1. For lower limit of quantitation, add the appropriate volumes of the working and stock standards and the appropriate volume of the 50-ppm surrogate and internal standard working standard to 20 mL of reagent water.

10.2.7.1.2. If samples are preserved with sodium bisulfate, and the presence of the preservative affects the purging efficiencies of the analytes, it is recommended that the same amount (~1.00 g) of sodium bisulfate be added to the reagent water after adding the standards.

10.2.7.2. ►Use the following calibration level as guidance to prepare the CCV solution.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
50	100	250	500	50	50~500	250	5.0	1.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein, *Acetonitrile, Iodomethane, or Isobutyl alcohol*; A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate; IS = Internal Standard; A = A1 + A2 + A3 + A4; Calibration Level of TBA-d_9 = 250 ppb; Initial Concentration of TBA-d_9 = 1250 ppm

10.2.7.3. ►Use the following calibration level as guidance to prepare the CCV solution for lower limit of quantitation.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
10	20	50	100	10	50~500	50	4.0	4.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein, *Acetonitrile, Iodomethane, or Isobutyl alcohol;* A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate; IS = Internal Standard; A = A1 + A2 + A3 + A4; Calibration Level of TBA-d_9 = 50 ppb; Initial Concentration of TBA-d_9 = 250 ppm

10.2.7.4. The calibration level for the continuing calibration verification of a non-routine target analyte may be established differently per client request or project specific DQOs.

10.2.8. Surrogate and internal standard working standard solutions contain 50/250 ppm of each surrogate, 50/250 ppm of each internal standard (except TBA-d_9), and 250/1250 ppm of TBA-d_9 in methanol.

10.2.8.1. If autosampler is not capable of injecting standard solution automatically, manually add 5.0 µL of the 50-ppm surrogate and internal standard working standard to each sample including each calibration standard, calibration verification standard, quality control (QC) check sample, and method blank prior to purge-and-trap extraction via 5.0-mL purge volume.

10.2.8.1.1. For lower limit of quantitation, manually add 4.0 µL of the 50-ppm surrogate and internal standard working standard to each sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction via 20-mL purge volume.

10.2.8.1.2. For samples processed via mobility or methanol extraction, manually add 5.0 µL of the 50-ppm surrogate and internal standard working standard to each mobility-procedure or methanol extract including each mobility-procedure or methanol extract designated as QC check sample and method blank prior to purge-and-trap extraction via 5.0-mL purge volume.

10.2.8.2. If autosampler is capable of injecting standard solution automatically, configure the autosampler to inject 1.0 µL of the 250-ppm surrogate and internal standard working standard into each sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction via 5.0-mL purge volume.

10.2.8.2.1. For lower limit of quantitation, configure the autosampler to inject 4.0 µL of the 50-ppm surrogate and internal standard working standard into each sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction via 20-mL purge volume.

10.2.8.2.2. For samples processed via mobility or methanol extraction, configure the autosampler to inject 1.0 µL of the 250-ppm surrogate and internal standard working standard into each mobility-procedure or methanol extract including each mobility-procedure or methanol extract designated as QC check sample and method blank prior to purge-and-trap extraction via 5.0-mL purge volume.

10.2.9. Spike working standard solutions contain various concentrations of target analytes in methanol. The spike standard solution must be of a source

differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.9.1. Use the second source 50-ppm gaseous volatile organic working standard solution as the gaseous spike working standard solution. Use the second source non-gaseous volatile organic stock standard solution as the non-gaseous spike working standard solution.

10.2.9.2. The spike standards are used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

10.2.9.3. Add 5.0 µL of the gaseous spike working standard and 5.0 µL of the non-gaseous spike working standard to each MS/MSD and LCS/LCSD sample prior to purge-and-trap extraction via 5.0-mL purge volume.

10.2.9.3.1. For lower limit of quantitation, add 4.0 µL of the gaseous spike working standard and 4.0 µL of the non-gaseous spike working standard to each MS/MSD and LCS/LCSD sample prior to purge-and-trap extraction via 20-mL purge volume.

10.2.9.4. Add 5.0 µL of the gaseous spike working standard and 5.0 µL of the non-gaseous spike working standard to each mobility-procedure or methanol extract designated as MS/MSD and LCS/LCSD prior to purge-and-trap extraction via 5.0-mL purge volume.

10.2.10. All working standards must be replaced after three months (unless specified otherwise) or sooner if routine QC or comparison with check standards indicates a problem.

10.2.10.1. Store all working standards with minimal headspace under dark and refrigerated condition.

10.2.10.2. Return the working standards to the refrigerator or freezer as soon as possible after use to prevent the loss of volatile organic compounds.

10.2.10.3. Check all working standards frequently for signs of degradation or evaporation.

10.2.11. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2.11.1. Return the stock standards to the refrigerator or freezer as soon as possible after use to prevent the loss of volatile organic compounds.

10.2.11.2. Check all opened stock standards frequently for signs of degradation or evaporation.

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 40-mL pre-cleaned amber glass or clear glass VOA vials with Teflon-lined closures. Collect all samples in triplicate.

11.1.1. If the aqueous sample is known or suspected to contain residual chlorine, collect the sample in a 125-mL amber glass container containing 4 drops of the 10% $Na_2S_2O_3$ solution. Gently swirl to mix the sample, and transfer to pre-cleaned amber glass or clear glass VOA vials.

11.1.1.1. Aqueous sample containing greater than 5 mg/L of residual chlorine may require additional amount of the dechlorinating agent.

11.1.2. Adjust the pH of the aqueous sample to < 2 by adding 1:1 HCl solution while stirring.

11.1.2.1. If a dechlorinating agent and acid are both added as preservatives, the aqueous sample must be dechlorinated first and then acidified.

11.1.2.2. Reactive compounds (e.g., acrolein, acrylonitrile, 2-chloroethyl vinyl ether, styrene, and vinyl chloride) are unstable at low pH. It is recommended that a second set of the aqueous sample without acid preservative be collected.

11.1.2.3. If fuel oxygenated compounds are the only analytes of interest, and the aqueous sample will be purged at an elevated temperature of 80°C, no acid preservation is required.

11.1.2.4. If carbonaceous materials are present, the aqueous sample should not be acid preserved due to possible effervescence and loss of volatile organic compounds.

11.1.2.5. If aromatic and biologically active compounds are the analytes of interest, acid preservation is necessary.

11.1.3. Completely fill and hermetically seal the sample vial such that when the vial is inverted, no headspace is visible.

11.1.3.1. It is possible for the sample to generate some headspace in the form of micro bubbles during storage. The bubbles should not exceed ¼ in or 6 mm in diameter. In the event that the headspace greater than 6 mm is evident, and the vial is used for analysis, the data should be qualified.

11.1.4. A reagent water trip blank, preserved in the same manner as the field samples, should accompany each batch of aqueous samples.

11.2. Solid samples for EPA Method 5030 purge-and-trap extraction should be collected in 4-oz or 8-oz pre-cleaned clear glass wide-mouth jars, or 6-in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.2.1. A reagent water trip blank should accompany each batch of solid samples.

11.3. Solid samples for EPA Method 5035 closed system purge-and-trap extraction should be collected in Terra Core Samplers, En Core® Samplers, or equivalent. Collect all samples in triplicate.

11.3.1. Solid samples collected using the Terra Core or equivalent coring device shall be immediately extruded into a pre-weighed 40-mL amber glass or clear glass VOA vial containing 5 mL of sodium bisulfate solution and a magnetic stirring bar, or 10 mL of methanol, and sealed with a Teflon-lined septum and screw cap by client field personnel.

11.3.2. If sample result is to be reported on a dry weight basis, one additional solid sample should be collected in a 4-oz pre-cleaned clear glass wide-mouth jar with a Teflon-lined closure, and labeled specifically for solids content determination.

11.3.3. If MS/MSD analyses are required, collect one sample in quintuplicate.

11.3.4. A reagent water trip blank should accompany each batch of solid samples.

11.4. Oil samples should be collected in 40-mL pre-cleaned clear glass VOA vials with Teflon-lined closures.

11.4.1. A reagent water trip blank should accompany each batch of oil samples.

11.5. Mobility-procedure extracts should be collected in 20-mL pre-cleaned clear glass VOA vials with Teflon-lined closures.

11.5.1. If the mobility-procedure extract will not be analyzed within 24 hours, collect the mobility-procedure extract in a 40-mL pre-cleaned amber glass or clear glass VOA vial, and adjust the pH to < 2 by adding 1:1 HCl solution while stirring.

11.5.1.1. If effervescence (bubbling, hissing, or foaming of liquid as gas escapes) is observed upon adding 1:1 HCl solution, do not acid preserve the mobility-procedure extract.

11.5.2. Completely fill and hermetically seal the sample vial such that when the vial is inverted, no headspace is visible.

11.5.2.1. It is possible for the sample to generate some headspace in the form of micro bubbles during storage. The bubbles should not exceed ¼ in or 6 mm in diameter. In the event that the headspace greater than 6 mm is evident, and the vial is used for analysis, the data should be qualified.

11.6. ►***Aqueous and oil*** samples should be maintained in a chilled state ***(0-6°C), not frozen,*** post sample collection until received at the laboratory. ***If shipped on same day as collection, sediment samples should be maintained in a chilled state, 0-6°C, post sample collection. Otherwise freeze sediment samples as soon as possible after collection and maintain them at ≤ -10°C until shipment.*** Solid samples may be frozen if solids content determination is not required. Freezing of solid samples may require contract approval.

11.6.1. Freezing solid samples within 48 hours of sample collection can minimize biodegradation of aromatic hydrocarbons (e.g., benzene, toluene, ethylbenzene, and xylenes).

11.7. ►Upon receipt, the ***aqueous, oil, and unfrozen solid*** samples are stored in a 0-6°C cooler. ***Sediment samples are stored in a ≤ -10°C freezer.*** Solid samples may be stored in a ***≤ -10°C*** freezer if solids content determination is not required.

11.7.1. Aqueous samples with acid preservation (pH < 2) must be analyzed within 14 days of sample collection.

11.7.2. Aqueous samples without acid preservation (pH ≥ 2) must be analyzed within 7 days of sample collection.

11.7.2.1. Aqueous samples containing highly reactive compounds (e.g., acrolein, acrylonitrile, 2-chloroethyl vinyl ether, styrene, vinyl chloride, etc.) as target analytes should be analyzed as soon as possible.

11.7.3. Solid samples collected in jars or sleeves must be analyzed within 14 days of sample collection.

11.7.4. High concentration (> 200 µg/kg) solid samples collected in jars or sleeves must be preserved with methanol and analyzed within 14 days of sample collection.

11.7.4.1. Methanol extracts shall be stored in a 0-6°C cooler. Per client request or project specific data quality objectives (DQOs), apply the specified minimum contact time between the solid sample and methanol prior to analysis.

11.7.5. Solid samples collected in Terra Core Samplers, En Core® Samplers, or equivalent must be preserved with sodium bisulfate solution and analyzed within 14 days of sample collection.

11.7.5.1. Solid samples collected using the En Core® or equivalent coring/transport device shall be preserved within 48 hours of sample collection. Refer to the current revision of SOP-M213 for preservation procedure.

11.7.5.2. Solid samples may also be analyzed within 48 hours of sample collection without sodium bisulfate preservation.

11.7.6. High concentration (> 200 µg/kg) solid samples collected in Terra Core Samplers, En Core® Samplers, or equivalent must be preserved with methanol and analyzed within 14 days of sample collection.

11.7.6.1. High concentration solid samples collected using the En Core® or equivalent coring/transport device shall be preserved within 48 hours of sample collection. Refer to the current revision of SOP-M213 for preservation procedure.

11.7.6.2. Methanol extracts shall be stored in a 0-6°C cooler. Per client request or project specific DQOs, apply the specified minimum

contact time between the solid sample and methanol prior to analysis.

11.7.7. Oil samples must be preserved with methanol and analyzed within 14 days of sample collection.

11.7.7.1. Methanol extracts shall be stored in a 0-6°C cooler. Per client request or project specific DQOs, apply the specified minimum contact time between the solid sample and methanol prior to analysis.

11.7.8. Mobility-procedure extracts with acid preservation (pH < 2) must be analyzed within 14 days post mobility extraction for aqueous samples, or within 7 days post mobility extraction for solid samples.

11.7.8.1. Mobility-procedure extracts shall be stored in a 0-6°C cooler post mobility extraction if analysis is not to be performed within 24 hours.

11.7.9. Mobility-procedure extracts without acid preservation (pH ≥ 2) must be analyzed within 24 hours post mobility extraction.

11.7.10. Storage blanks consisting of clean reagent water should be used to monitor potential cross-contamination of samples due to improper storage conditions.

12. ►QUALITY CONTROL

12.1. Hardware Tuning

12.1.1. Prior to running the calibration standards, the tuning standard solution must be analyzed and meet the defined acceptance criteria.

12.1.2. The following criteria must be demonstrated every 12 hours.

m/z	Relative Abundance Criteria
50	15 – 40% of m/z 95
75	30 – 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 – 9% of m/z 95
173	< 2% of m/z 174
174	> 50% of m/z 95
175	5 – 9% of m/z 174
176	> 95% but < 101% of m/z 174
177	5 – 9% of m/z 176

12.1.3. If these criteria are not met, then the analytical system is deemed unacceptable for sample analysis to begin. Effect corrective action and re-tune the system.

12.2. Initial Calibration (IC)

12.2.1. The initial multi-point calibration must be established prior to the processing of samples.

12.2.1.1. The calibration curve is established with a minimum of five calibration standards, but may contain six or seven calibration standards.

12.2.2. The IC is deemed valid if the %RSD for each analyte (except CCC) is ≤ 15%, the %RSD for each CCC is ≤ 30%, and the average relative response factor (RRF) for each SPCC is as follows:

SPCC	Average RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

12.2.2.1. The calibration check compounds (CCCs) are chloroform, ethylbenzene, 1,1-dichloroethene, 1,2-dichloropropane, toluene, and vinyl chloride.

12.2.2.2. The system performance check compounds (SPCCs) are bromoform, chlorobenzene, chloromethane, 1,1-dichloroethane, and 1,1,2,2-tetrachloroethane.

12.2.3. If the %RSD for an analyte is ≤ 15%, the RRF is assumed to be constant over the calibration range, and the average RRF may be used for quantitation.

12.2.4. ►In those instances where the %RSD for one or more target analytes exceeds 15%, the initial calibration remains acceptable if the mean of the %RSD values for all analytes in the calibration is ≤ 15%. This approach (i.e., the average of all %RSD values ≤ 15%) is referred to as the grand mean approach. ***The grand mean approach cannot be used for Department of Defense projects***.

12.2.4.1. The mean %RSD is calculated by summing the %RSD value for each analyte and dividing by the total number of analytes.

12.2.4.1.1. The mean %RSD criterion applies to all analytes in the calibration standards, regardless of whether or not they are of interest for a specific project. In other words, if the analyte is part of the calibration standard, its %RSD value is included in the evaluation.

12.2.4.2. If the grand mean approach is utilized, the average RRF with %RSD > 15% may be used for quantitation.

12.2.4.2.1. Per client request or project specific data quality objectives (DQOs), a summary of the initial calibration data or a specific list of the target analytes for which the %RSD exceeded 15%, and the results of the mean %RSD calculation must be included in the data package.

12.2.4.3. The use of the grand mean approach will lead to greater uncertainty for those analytes for which the %RSD is > 15%. Review the associated quality control results carefully, with particular attention to the matrix spike and laboratory control sample results, to determine if the calibration linearity poses a significant concern.

12.2.4.3.1. ►If the grand mean approach is not acceptable due to client or project specific requirements ***(such as Department of Defense project criteria)***, employ one of the other calibration options (see Section 12.2.5.), or adjust instrument operating conditions and/or the calibration range until the %RSD is ≤ 15%.

12.2.5. Other calibration options are as follows:

12.2.5.1. The first calibration option is linear least squares regression with equal weighting factor. The IC is deemed valid if the correlation coefficient, r, is ≥ 0.99.

12.2.5.2. The section calibration option is quadratic least squares regression with equal weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.99.

12.2.5.2.1. This option requires at least six calibration levels.

12.2.6. The relative retention time (RRT) of each analyte in each calibration standard should agree to within ± 0.06 RRT units.

12.2.7. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.7.1. If the RSD or correlation of any analyte is unacceptable, review the results (e.g., proper identification, area count, response factor, etc.) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards.

12.2.7.2. If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis to rule out problems due to random chance.

12.2.7.2.1. In some cases, replace the calibration standard may be necessary.

12.2.7.3. If a calibration standard is replaced and/or reanalyzed, recalculate the RSD or correlation, and document the rationale for re-analysis.

12.3. Initial Calibration Verification (ICV)

12.3.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%, and the daily RRF for each SPCC is as follows:

SPCC	Daily RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

12.3.1.1. If the calibration option is average relative response, the %D is the percent difference.

12.3.1.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

12.3.2. The %D of each non-CCC is evaluated only per client request or project specific DQOs.

12.3.2.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, the initial calibration is deemed valid if the %D for each non-CCC is ≤ 25%.

12.3.3. The internal standard response and retention time for the ICV must be evaluated during or immediately after data acquisition.

12.3.3.1. If the extracted ion current profile (EICP) area of any internal standard in an ICV standard changes by a factor of two (−50% to +100%) from that in the midpoint calibration standard for the most recent initial calibration, the mass spectrometer must be inspected for malfunctions and corrective action effected.

12.3.3.2. If the retention time of any internal standard in an ICV standard changes by more than 30 seconds from that in the midpoint calibration standard for the most recent initial calibration, the gas chromatograph must be inspected for malfunctions and corrective action effected.

12.3.4. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result, re-prepare, and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective actions, which may include replacement of standard solutions or instrument maintenance, and recalibrate.

12.4. Continuing Calibration Verification (CCV)

12.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch.

12.4.2. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%, and the daily RRF for each SPCC is as follows:

SPCC	Daily RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

12.4.2.1. If the calibration option is average relative response, the %D is the percent difference.

12.4.2.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

12.4.2.3. For EPA Region 9 requirement, the initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.4.3. The %D of each non-CCC is evaluated only per client request or project specific DQOs.

12.4.3.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, the initial calibration is deemed valid if the %D for each non-CCC is ≤ 25%.

12.4.4. The internal standard response and retention time for the CCV must be evaluated during or immediately after data acquisition.

12.4.4.1. If the EICP area of any internal standard in a CCV standard changes by a factor of two (−50% to +100%) from that in the midpoint calibration standard for the most recent initial calibration, the mass spectrometer must be inspected for malfunctions and corrective action effected.

12.4.4.2. If the retention time of any internal standard in a CCV standard changes by more than 30 seconds from that in the midpoint calibration standard for the most recent initial calibration, the gas chromatograph must be inspected for malfunctions and corrective action effected.

12.4.4.3. Following corrective action, reanalysis of samples analyzed while the system was malfunctioning is required.

12.4.5. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result, re-prepare, and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.5. Event Based Quality Control (MBs and LCS/LCSDs)

12.5.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB) and a laboratory control sample and laboratory control sample duplicate (LCS/LCSD).

12.5.1.1. ►An LCS/LCSD shall be prepared whenever there is insufficient sample volume to perform the needed matrix

QC (duplicate or MS/MSD) or as required by project QAPP. In all other instances a single LCS shall be prepared.

12.5.2. The acceptance criteria for MBs are as follows:

12.5.2.1. Ideally, the concentration of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

12.5.2.2. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

12.5.2.3. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and re-analyzed.

12.5.3. The acceptance criteria for LCS/LCSD compounds are as follows:

12.5.3.1. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.5.3.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively. The RPD is ≤ 20%.

12.5.3.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each LCS/LCSD compound in a water sample are 70% and 130%, respectively. The RPD is ≤ 30%.

12.5.3.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each LCS/LCSD compound in a soil sample are 65% and 135%, respectively. The RPD is ≤ 50%.

12.5.3.2. All LCS/LCSD compounds must be within acceptance limits. However, if a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside of control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Lower and upper marginal exceedance (ME) limits can be established to determine when corrective action is necessary.

12.5.3.3. ME is defined as being beyond the LCS control limit (3 standard deviations), but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean.

12.5.3.4. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than 11 analytes.

12.5.3.5. The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number of Analytes Allowed in ME of the LCS Control Limit
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

12.5.3.6. Marginal exceedances must be random. If the same analyte exceeds the LCS control limit 2 out of 3 consecutive LCS, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

12.6. Matrix Based Quality Control (Surrogates, Internal Standards, and MS/MSDs)

12.6.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD), and surrogates and internal standards added to each sample.

12.6.2. The acceptance criteria for surrogate compounds are as follows:

12.6.2.1. The lower and upper acceptance limits for %REC of each surrogate compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.2.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each surrogate compound are 70% and 130%, respectively.

12.6.2.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each surrogate compound in a water sample are 85% and 115%, respectively.

12.6.2.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each surrogate compound in a soil sample are 70% and 125%, respectively.

12.6.2.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

12.6.2.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration or a problem may have occurred during extraction. The data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.6.2.4. Unacceptable surrogate recoveries do not automatically invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.6.2.4.1. Check the surrogate and internal standard solutions for degradation and contamination.

12.6.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recoveries, the same sample should be re-processed and re-analyzed.

12.6.2.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-processed and re-analyzed. If insufficient sample remains, reference the associated MB surrogate recoveries and report the sample data with qualification.

12.6.2.4.3.1. If, upon re-processing and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.2. If the MB surrogates are unacceptable, all associated sample data must invalidated and all associated samples re-processed and re-analyzed.

12.6.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

12.6.3. The acceptance criteria for internal standard compounds are as follows:

12.6.3.1. It is recommended that the internal standard responses (area counts) and retention times for each standard, sample, and blank be monitored for method performance, injection execution, system/instrument maintenance, analytical errors, or interferences.

12.6.3.2. The area count of each internal standard peak in a standard, sample, or blank should be within 50% to 200% of that in the midpoint calibration standard for the most recent initial calibration.

12.6.3.3. The retention time of each internal standard peak in a standard, sample, or blank should be within ± 30 seconds of that in the midpoint calibration standard for the most recent initial calibration.

12.6.4. The acceptance criteria for MS/MSD compounds are as follows:

12.6.4.1. The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.4.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each MS/MSD compound are 70% and 130%, respectively. The RPD is ≤ 30%.

12.6.4.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound in a water sample are 65% and 135%, respectively. The RPD is ≤ 30%.

12.6.4.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound in a soil sample are 50% and 150%, respectively. The RPD is ≤ 50%.

12.6.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.6.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.5. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the

analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.7. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.8. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Mass Spectrometer Tuning

13.1.1. Prior to initial calibration and the analysis of field or QC samples, the GC/MS system must be hardware tuned such that the analysis of 5–50 ng of BFB meets the tuning criteria. The acceptance criteria for the tune are listed in Section 12.1.

13.1.2. Obtain the mass spectrum of BFB as follows:

13.1.2.1. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required and must be accomplished using a single scan acquired within 20 scans of the elution of BFB.

13.1.2.1.1. The background subtraction should be designed only to eliminate column bleed or instrument background ions.

13.1.2.1.2. Do not subtract part of the BFB peak or any other discrete peak that does not coelute with BFB.

13.1.3. All subsequent standards, samples, and blanks associated with a specific tune must use identical mass spectrometer operating conditions.

13.1.4. Whenever invasive maintenance of the hardware is performed, the system must be re-tuned.

13.2. Mass Spectrometer Initial Calibration

13.2.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.2.

13.2.1.1. Recalibration is required for the following maintenance procedures.

13.2.1.1.1. Change, replace, or reverse the analytical column.

13.2.1.1.2. Replace the trap on a purge-and-trap system.

13.2.1.1.3. Change the entrance lens, draw-out lens, or repeller.

13.2.1.1.4. Change the electron multiplier and/or ion source chamber.

13.2.1.1.5. Clean the ion source and/or quadrupole rods.

13.2.2. After obtaining an acceptable multi-point calibration curve and prior to processing field or QC samples, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.3.

13.2.3. The initial multi-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

14. PROCEDURE

14.1. Instrument Setup

14.1.1. Refer to the current revision of SOP-M212 or SOP-M213 for purge-and-trap system setup.

14.1.2. Use the following GC/MS operating conditions as guidance to establish the GC/MS temperature program and flow rate necessary to separate the analytes of interest.

Description	GC/MS Operating Condition
Mode	split
Split ratio	100 : 1
Split flow rate	48.9 mL/min
Inlet pressure	7.41 psi
Total flow rate	52.5 mL/min
Initial temperature	40°C, hold 4.00 min
Temperature program	40°C to 190°C at 12.00°C/min 190°C, hold 0.50 min 190°C to 230°C at 45.00°C/min
Final temperature	230°C, hold 3.11 min
Transfer line temperature	260°C
Scan range	35~270 amu
Detector threshold	150

14.1.3. The sampling rate shall result in at least five full mass spectra across the chromatographic peak, and within 1 second or less per mass spectrum.

14.1.4. Once established, the same operating conditions must be applied to all subsequent standard, sample, and blank analyses.

14.2. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.4.

14.2.1. If a CCV fails, effect corrective action prior to analyzing any samples.

14.3. Following purge-and-trap preparation by the method specified in Section 5.2., the QC and actual environmental samples are received in purge vessels. The purge vessels are then loaded onto the purge-and-trap system.

14.4. Standard and sample purge vessels are loaded in the following or other logical order:

1) Tuning Standard / Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicate (LCSD)
4) Method Blank (MB)
5) Samples (up to 20 per batch, excluding QC check samples and MBs)
6) Matrix Spike (MS)
7) Matrix Spike Duplicate (MSD)

14.4.1. Item 1: An acceptable tune demonstrates satisfactory hardware performance, and a CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. A tune meeting the acceptance criteria and an acceptable CCV are required daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch.

14.4.1.1. The tuning standard is also the CCV solution.

14.4.2. Item 2: The LCS is a known matrix that has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.2.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid samples, the LCS consists of the specified compounds spiked into washed sea sand. For mobility-procedure extracts, the LCS consists of the specified compounds spiked into the mobility-procedure extract designated as LCS. For methanol extracts, the LCS consists of the specified compounds spiked into the methanol extract designated as LCS.

14.4.2.2. One LCS is required every day preparatory methods (i.e., methanol extractions, purge-and-trap extractions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.3. ►Item 3: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.8. ***The LCSD is required if MS/MSD are not prepared and analyzed along with field samples.***

14.4.4. Item 4: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (e.g., surrogates, internal standards, etc.).

14.4.4.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of washed sea sand. For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB. For methanol extracts, the MB consists of the methanol extract designated as MB.

14.4.4.2. One MB is required every day preparatory methods (i.e., methanol extractions, purge-and-trap extractions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.5. Item 5: Up to 20 samples (excluding QC check samples and method blanks) per batch. High concentration samples should be sufficiently diluted to ensure that instrument is not contaminated. Dilution of samples will result in increased reporting limits.

14.4.5.1. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.4.6. Item 6: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.6.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.7.

14.4.6.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently. This approach is considered "closed batch" as opposed to "open batch."

14.4.7. Item 7: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.8.

14.4.8. Solvent blanks consisting of reagent water may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration samples), to check for potential carryover or cross-contamination.

14.5. Ensure that a sufficient amount of the appropriate surrogate and internal standard working standard solution is present in the autosampler standard vial(s) if the autosampler is configured to inject standard solution automatically, and that a sufficient unused volume exists in the autosampler waste containers at the beginning of the sequence.

14.6. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or on the sequence table printout.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. Evaluate the response (area count) and retention time of each internal standard compound in each standard, sample, and blank (see Section 12.6.3.).

14.8.2. Qualitative identification of each analyte/surrogate is based on retention time of the sample component, and on comparison of the sample mass spectrum, after background correction, with the characteristic ions in a reference mass spectrum.

14.8.2.1. The reference mass spectrum must be generated using the same conditions of this method.

14.8.2.2. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum.

14.8.2.3. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte.

14.8.2.3.1. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

14.8.3. Target analytes are identified as present when the following criteria are met.

14.8.3.1. The intensities of the characteristic ions of an analyte maximize in the same scan or within one scan of each other.

14.8.3.1.1. Selection of a peak by a data system target analyte search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target analyte at an analyte-specific retention time will be accepted as meeting this criterion.

14.8.3.2. The RRT of the sample analyte is within ± 0.06 RRT units of the RRT of the standard analyte.

14.8.3.3. The relative intensities of the characteristic ions in the sample spectrum agree within ± 30% of the relative intensities of these ions in the reference spectrum.

14.8.3.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.

14.8.3.4.1. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.8.3.5. Examination of extracted ion current profiles (EICPs) of appropriate ions can aid in the selection of spectra and in qualitative identification of analytes.

14.8.3.5.1. When analytes coelute, the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting analyte.

14.8.4. Tentative identification of a non-target analyte can be accomplished by using the data system library search. Refer to SOP-T025 for procedure.

14.8.4.1. The search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

14.8.4.2. The guidelines for making tentative identifications are as follows:

14.8.4.2.1. Relative intensities of major ions (ions greater than 10% of the most abundant ion) in the reference spectrum should be present in the sample spectrum.

14.8.4.2.2. Relative intensities of major ions in the sample spectrum should agree within ± 20% of those in the reference spectrum.

14.8.4.2.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

14.8.4.2.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting analytes.

14.8.4.2.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from sample spectrum due to

background contamination or coeluting analytes. Data system library reduction program can sometimes create these discrepancies.

14.8.5. Quantitation of a target analyte is based on the integrated abundance from the EICP of the primary characteristic ion.

14.8.5.1. Proper quantitation requires the appropriate selection of a baseline and integration from which the area of the characteristic ion peak can be determined.

14.8.5.2. Determine the concentration based on the initial calibration curve.

14.8.5.2.1. Calculate the concentration of each target analyte in a sample extract using the average of the initial RRFs, the area of the characteristic ion peak, and the internal standard concentration and ion peak area. The formula for calculating concentration is listed in Section 15.9.

14.8.5.2.2. The data system is programmed to perform the calculation of concentration.

14.8.5.3. If the instrument response exceeds the calibration range, dilute the sample and reanalyze.

14.8.5.4. For any non-target analyte identified in a sample extract, estimate the concentration as follows:

14.8.5.4.1. Obtain the area of the characteristic ion peak for the non-target analyte and the internal standard ion peak area from the total ion chromatogram.

14.8.5.4.2. Assume the average of the initial RRFs for the non-target analyte to be 1.

14.8.5.4.3. Calculate and report the concentration as an estimated value.

14.8.6. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

14.8.6.1. When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.

14.8.6.2. When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially integrating a peak, etc.), manual integrations performed by the analyst are necessary.

14.8.6.3. Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.

15. CALCULATIONS

15.1. The relative response factor is calculated as follows:

$$RRF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where: RRF = relative response factor for target analyte being measured.
A_x = area of the characteristic ion for target analyte being measured.
C_{is} = concentration of internal standard in µg/L.
A_{is} = area of the characteristic ion for internal standard.
C_x = concentration of target analyte being measured in µg/L.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RRF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RRFs for the target analyte.
RRF_{ave} = mean of the 5, 6, or 7 initial RRFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RRF_{ave} - RRF_{daily}|}{RRF_{ave}} \times 100$$

where: %D = percent difference.
RRF_{daily} = daily RRF for the target analyte.
RRF_{ave} = mean of the 5, 6, or 7 initial RRFs for the target analyte.

15.4. The percent drift of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent drift.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.
Note: Concentrations must be in equivalent units.

15.5. The relative retention time of each target analyte is calculated as follows:

$$RRT = \frac{RT_x}{RT_{is}}$$

where: RRT = relative retention time of target analyte.
RT_x = retention time of target analyte.
RT_{is} = retention time of internal standard.
Note: Retention times are in minutes to three decimal places.

15.6. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.
Note: Concentrations must be in equivalent units.

15.7. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.
Note: Concentrations must be in equivalent units.

15.8. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.
Note: Concentrations must be in equivalent units.

15.9. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x \times C_{is}}{A_{is} \times RRF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in µg/L.
A_x = area of the characteristic ion for target analyte.

C_{is} = concentration of internal standard in µg/L.
A_{is} = area of the characteristic ion for internal standard.
RRF_{ave} = mean of the 5, 6, or 7 initial RRFs for the target analyte.

15.10. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_p \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
For lower limit of quantitation, $V_p = 20$.
V_A = volume of aqueous sample purge-and-trap extracted in mL.
D = dilution factor, if the aqueous sample was serially diluted prior to purge-and-trap extraction. If no dilution was made, D = 1.

15.11. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p}{W_S}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
W_S = mass of solid sample purge-and-trap extracted in g.

15.12. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
W_S = mass of solid sample purge-and-trap extracted in g.
C_{ss} = solids content in %.

15.13. The target analyte concentration for a methanol extracted solid (or oil) sample without moisture correction is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p \times P_1}{V_S}$$

where: C_S = concentration of target analyte in solid (or oil) sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
V_S = volume of methanol extract purge-and-trap extracted in mL.
P_1 = preparation factor without moisture correction for methanol extracted solid (or oil) sample in mL/g.

15.14. The target analyte concentration for a methanol extracted solid sample <u>without</u> methanol/water dilution factor correction is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p \times P_2}{V_S}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
V_S = volume of methanol extract purge-and-trap extracted in mL.
P_2 = preparation factor without methanol/water dilution factor correction for methanol extracted solid sample in mL/g.

15.15. The target analyte concentration for a methanol extracted solid sample <u>with</u> methanol/water dilution factor correction is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p \times P_3}{V_S}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
V_S = volume of methanol extract purge-and-trap extracted in mL.
P_3 = preparation factor with methanol/water dilution factor correction for methanol extracted solid sample in mL/g.

15.16. The target analyte concentration for a mobility-procedure extract is calculated as follows:

$$C_{MP} = \frac{C_{ex} \times V_p \times D}{V_{MP}}$$

where: C_{MP} = concentration of target analyte in mobility-procedure extract in mg/L.
C_{ex} = concentration of target analyte in extract in mg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
V_{MP} = volume of mobility-procedure extract purge-and-trap extracted in mL.
D = dilution factor, if the mobility-procedure extract was serially diluted

prior to purge-and-trap extraction.
If no dilution was made, D = 1.

15.17. Refer to the preparatory method(s) for additional calculations.

15.18. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and µg/kg (ppb) for oil, soil and solid waste samples.

15.18.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

15.19. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

18.1.1. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and re-analyzed.

18.2. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually. All LCS/LCSD compounds must be within acceptance limits (see Section 12.5.3. for additional information).

18.2.1. For EPA Region 9 requirement, refer to Section 12.5.3.1.2. and Section 12.5.3.1.3. for acceptance criteria.

18.2.2. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.3. ►The LCSD is only ***analyzed when required by project QAPP*** or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.3. The acceptance criteria for surrogate compound recoveries vary depending upon historical data. The lower and upper acceptance limits for %REC of each surrogate compound are based upon the historical average recovery ± 3S that is updated at least annually.

18.3.1. For EPA Region 9 requirement, refer to Section 12.6.2.1.2. and Section 12.6.2.1.3. for acceptance criteria.

18.3.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

18.3.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.4. Unacceptable surrogate recoveries do not necessarily invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.4.1. Check the surrogate and internal standard solutions for degradation and contamination.

18.3.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recoveries, the same sample should be re-processed and re-analyzed.

18.3.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-processed and re-analyzed. If insufficient sample remains, reference the associated MB surrogate recoveries and report the sample data with qualification.

18.3.4.3.1. If upon re-processing and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

18.3.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

18.4.1. For EPA Region 9 requirement, refer to Section 12.6.4.1.2. and Section 12.6.4.1.3. for acceptance criteria.

18.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and µg/kg (ppb) for oil, soil and solid waste samples.

18.7.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly

documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical

batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS)*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8260B, USEPA, Revision 2, December 1996.

22.2. *Determinative Chromatographic Separations*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000B, USEPA, Revision 2, December 1996.

22.3. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.4. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.5. *Organic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, February 2007.

22.6. *Volatile Organic Compounds (VOCs)*, SW-846 Method 8260, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. ►Appendix A: List of Primary and Secondary Ions of Target Analytes, Surrogates, and Internal Standards.

23.2. Appendix B: Additional Quality Control Criteria for Department of Defense Project.

23.3. Appendix C: Control Limits for Department of Defense Project.

23.4. Appendix D: Additional Quality Control Criteria for BP Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8260B Revision 2 are noted.

Calscience SOP M311 Section	Reference Document EPA Method 8260B Section	Summary of Modification
12.2.	7.3	The requirement of providing the data user a summary of the initial calibration data or a specific list of the target analytes for which the %RSD exceeded the specified limit is modified.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
0.1	Section 3: Update terminology for RL and add reference to the determinations of DL and RL. Section 4: Revise the scope to include additional analytes, and update EPA method numbers. Section 5: Update EPA method numbers. Section 6: Add LOD and LOQ definitions. Section 7: Update interferences.	K. Chang	08/17/12

Revision	Description	Author(s)	Effective Date
0.1	Section 9: Update the list of equipment and supplies. Section 10: Revise standard preparation. Section 11: Revise the requirements on preservation, headspace, and container. Section 12: Revise quality control criteria. Section 13: Revise subtitles. Section 14: Revise tuning and data reporting procedures. Section 18: Update section references, and add EPA Region 9 requirements. Section 24: Revise modifications. Section 25: Add revision history. Appendix A: Update the ion list for additional analytes. Appendix B: Update DoD quality control requirements and criteria.	K. Chang	08/17/12
0.2	Correct minor typos/grammar throughout. Section 4: Delete unused prep methods. Section 6: Update "batch" definition. Section 9: Revise equipment. Section:10: Update calibration tables Section 11: Revise sample preservation and storage. Section 12: Revise quality control criteria. Section 14: Revise LCSD requirement. Section 18: Revise LCSD requirement. Section 25: Update Revision History Appendix A: Update the ion table	I. Kwak / L. Hunt	08/12/13

Appendix A

LIST OF PRIMARY AND SECONDARY IONS OF TARGET ANALYTES, SURROGATES, AND INTERNAL STANDARDS

Calscience Environmental Laboratories, Inc.

►Appendix A

Primary and Secondary Ions

Compound Name	Characteristic Ion(s)	
	Primary	Secondary
acetone	58	43
acetonitrile	41	40
acrolein	56	55
acrylonitrile	53	52 , 51
allyl chloride	76	41 , ***40*** , 78
tert-amyl methyl ether (TAME)	73	87 , 55
benzene	78	***51***
bromobenzene	156	77 , 158
bromochloromethane	128	49 , 130
bromodichloromethane	83	85 , 127
1,4-bromofluorobenzene (surrogate)	95	174
bromoform	173	175 , 254
bromomethane	94	96
1,3-butadiene	54	53 , 39
2-butanone	72	43
tert-butyl alcohol (TBA)	59	57 , 41
tert-butyl alcohol-d_9 (internal standard)	65	66
n-butylbenzene	91	92 , 134
sec-butylbenzene	105	134
tert-butylbenzene	***134***	***119*** , 91
carbon disulfide	76	78
carbon tetrachloride	117	119
chlorobenzene	112	77 , 114
chlorobenzene-d_5 (internal standard)	117	***82***
chloroethane	64	66
2-chloroethyl vinyl ether	63	65 , 106
chloroform	83	85
chloromethane	50	52
chloroprene	53	88 , 90 , 51
1-chloropropane	42	41 , 39
2-chloropropane	43	41 , 39 , 63
2-chlorotoluene	91	126
4-chlorotoluene	91	126
cyclohexane	84	56 , 41 , 55
cyclohexanone	55	69 , 98 , 42
dibromochloromethane	129	***127***

Appendix A

Primary and Secondary Ions (Cont.)

Compound Name	Characteristic Ion(s)			
	Primary	Secondary		
1,2-dibromo-3-chloropropane	75	155		
1,2-dibromoethane	107	109 ,	188	
dibromofluoromethane (surrogate)	113	***111***		
dibromomethane	93	95 ,	174	
1,2-dichlorobenzene	146	111 ,	148	
1,3-dichlorobenzene	146	111 ,	148	
1,4-dichlorobenzene	146	111 ,	148	
1,4-dichlorobenzene-d_4 (internal standard)	152	150		
trans-1,4-dichloro-2-butene	53	88 ,	75	
dichlorodifluoromethane	85	87		
1,1-dichloroethane	63	65 ,	83	
1,2-dichloroethane	62	98 ,	64 ,	49
1,2-dichloroethane-d_4 (surrogate)	65	102 ,	67	
1,1-dichloroethene	96	61 ,	63	
cis-1,2-dichloroethene	96	61 ,	98	
trans-1,2-dichloroethene	96	61 ,	98	
1,2-dichloropropane	63	112		
1,3-dichloropropane	76	78		
2,2-dichloropropane	77	97		
1,1-dichloropropene	75	110 ,	77	
cis-1,3-dichloropropene	75	77 ,	39	
trans-1,3-dichloropropene	75	77 ,	39	
diethyl ether	74	45 ,	59	
1,4-difluorobenzene (internal standard)	114	***88***		
diisopropyl ether (DIPE)	45	87		
1,4-dioxane	88	58 ,	43 ,	57
ethanol	45	46 ,	43	
ethylbenzene	91	106		
ethyl tert-butyl ether (ETBE)	59	87		
ethyl methacrylate	69	41 ,	99	
hexachloro-1,3-butadiene	225	223 ,	227	
hexane	57	56 ,	43 ,	41
2-hexanone	43	58 ,	57 ,	100
iodomethane	142	127	141	
isobutyl alcohol (iso-butanol)	43	41 ,	42 ,	74
isopropanol (2-propanol)	45	59		

Appendix A

Primary and Secondary Ions (Cont.)

Compound Name	Characteristic Ion(s)	
	Primary	Secondary
isopropylbenzene	105	120
p-isopropyltoluene	119	91 , 134
methacrylonitrile	41	67
methyl acetate	43	74 , 59
methyl tert-butyl ether (MTBE)	73	57
methyl methacrylate	69	41 , 100 , 39
2-methyl-2-butanone (TAA)	59	55 , 73
methylcyclohexane	83	55 , 98 , 41
methylene chloride	84	86
4-methyl-2-pentanone (MIBK)	100	43 , 58 , 85
naphthalene	128	***127***
pentafluorobenzene (internal standard)	168	***137***
propanedinitrile	66	38 , 39 , 65
propionitrile	54	52 , 55 , 40
n-propylbenzene	91	120
styrene	104	78
1,1,1,2-tetrachloroethane	131	133 , 119
1,1,2,2-tetrachloroethane	83	131 , 85
tetrachloroethene	164	129 , 131 , 166
tetrahydrofuran	42	41 , 71 , 72
thiophene	84	58 , 45
toluene	92	91
toluene-d_8 (surrogate)	98	***100***
1,2,3-trichlorobenzene	180	182 , 145
1,2,4-trichlorobenzene	180	182 , 145
1,1,1-trichloroethane	97	99 , 61
1,1,2-trichloroethane	83	97 , 85
trichloroethene	95	97 , 130 , 132
trichlorofluoromethane	101	103
1,2,3-trichloropropane	75	77
1,1,2-trichloro-1,2,2-trifluoroethane	101	151 , 153
2,2,4-trimethyl pentane	57	56 , 41
1,2,4-trimethylbenzene	105	120
1,3,5-trimethylbenzene	105	120
vinyl acetate	43	86
vinyl chloride	62	64

Appendix A

Primary and Secondary Ions (Cont.)

Compound Name	Characteristic Ion(s)	
	Primary	Secondary
o-xylene	106	91
p/m-xylenes	106	91

Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

5.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., ion abundance, etc.).

5.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.3. No samples shall be analyzed without a valid LOD.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Initial Calibration (IC)

5.3.1. The IC is deemed valid if the %RSD for each analyte (except CCC) is ≤ 15%, the %RSD for each CCC is ≤ 30%, and the average RRF for each SPCC is as follows:

SPCC	Average RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

5.3.2. If the %RSD criterion for an analyte is not met, employ one of the following calibration options.

5.3.2.1. The first calibration option is linear least squares regression with equal weighting factor. The IC is deemed valid if the correlation coefficient, r, is ≥ 0.995.

5.3.2.1.1. Calibration may not be forced through the origin.

5.3.2.2. The second calibration option is quadratic least squares regression with equal weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.990.

5.3.2.2.1. This option requires at least six calibration levels.

5.4. Initial Calibration Verification (ICV)

5.4.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

5.4.2. If any project-specific analyte does not meet the %D, internal standard response and/or retention time criteria, the initial calibration is deemed unacceptable for sample analysis to begin. Document the unacceptable result, re-prepare, and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective actions, which may include replacement of standard solutions or instrument maintenance, and recalibrate.

5.5. Continuing Calibration Verification (CCV)

5.5.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%, and the daily RRF for each SPCC is as follows:

SPCC	Daily RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

5.5.2. If any project-specific analyte does not meet the %D, internal standard response and/or retention time criteria, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result, re-prepare, and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective actions and recalibrate.

5.5.3. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.6. Retention Time Window

5.6.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration.

5.6.1.1. Absolute retention time window for each analyte/surrogate is determined from the elution time of the analyte/surrogate in the midpoint calibration standard.

5.6.1.2. Document the serial number of the analytical column associated with the retention time window.

5.6.1.3. Record the retention time in minutes for each analyte/surrogate to three decimal places.

5.7. Event Based Quality Control (MBs and LCS/LCSDs)

5.7.1. Method Blanks (MBs)

5.7.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.7.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.7.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.7.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.7.1.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

5.7.1.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.7.2. Laboratory Control Samples (LCS/LCSDs)

5.7.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound in aqueous and solid matrices are listed in Appendix C.

5.7.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.7.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.7.2.3. All project-specific analytes of concern must be within control limits. No marginal exceedance is allowed for any project-specific analyte of concern. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.8. Matrix Based Quality Control (Surrogates, Internal Standards, and MS/MSDs)

5.8.1. Surrogates

5.8.1.1. The lower and upper acceptance limits for %REC of each surrogate compound in aqueous and solid matrices are listed in Appendix C.

5.8.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.8.2. Internal Standards

5.8.2.1. If the EICP area of any internal standard in each standard, sample, and blank is not within −50% to +100% from that in the midpoint calibration standard for the most recent initial calibration, the mass spectrometer must be inspected for malfunctions and corrective action effected.

5.8.2.2. If the retention time of any internal standard in each standard, sample, and blank is not within ± 30 seconds from that in the midpoint calibration standard for the most recent initial calibration, the gas chromatograph must be inspected for malfunctions and corrective action effected.

5.8.2.3. Following corrective action, reanalysis of samples analyzed while the system was malfunctioning is required.

5.8.2.4. If corrective action fails in a field sample, the results shall be reported with the appropriate data qualifier (Q-flag) for the specific analyte(s) associated with the failed internal standard.

5.8.3. Matrix Spikes (MS/MSDs)

5.8.3.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous and solid matrices are listed in Appendix C. The RPD is ≤ 30%.

5.8.3.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.8.3.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

6. PROCEDURE

6.1. Standard and sample purge vessels are loaded in the following or other logical order:

1) Tuning Standard / Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicate (LCSD)
4) Method Blank (MB)
5) Samples (up to 20 per batch, excluding QC check samples and MBs)

6) Matrix Spike (MS)
7) Matrix Spike Duplicate (MSD)

6.1.1. Item 6: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.1.1.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.1.2. Item 7: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Appendix C

CONTROL LIMITS FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Aqueous Matrix

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
1,1,1,2-Tetrachloroethane	80	130	75	135
1,1,1-Trichloroethane	65	130	55	145
1,1,2,2-Tetrachloroethane	65	130	55	140
1,1,2-Trichloroethane	75	125	65	135
1,1-Dichloroethane	70	135	60	145
1,1-Dichloroethene	70	130	55	140
1,1-Dichloropropene	75	130	65	140
1,2,3-Trichlorobenzene	55	140	45	155
1,2,3-Trichloropropane	75	125	65	130
1,2,4-Trichlorobenzene	65	135	55	145
1,2,4-Trimethylbenzene	75	130	65	140
1,2-Dibromo-3-chloropropane	50	130	35	145
1,2-Dibromoethane	80	120	75	125
1,2-Dichlorobenzene	70	120	60	130
1,2-Dichloroethane	70	130	60	140
1,2-Dichloropropane	75	125	65	135
1,3,5-Trimethylbenzene	75	130	65	140
1,3-Dichlorobenzene	75	125	65	130
1,3-Dichloropropane	75	125	65	135
1,4-Dichlorobenzene	75	125	65	130
2,2-Dichloropropane	70	135	60	150
2-Butanone	30	150	10	170
2-Chlorotoluene	75	125	65	135
2-Hexanone	55	130	45	140
4-Chlorotoluene	75	130	65	135
4-Methyl-2-pentanone (MIBK)	60	135	45	145
Acetone	40	140	20	160
Benzene	80	120	75	130
Bromobenzene	75	125	70	130
Bromochloromethane	65	130	55	140
Bromodichloromethane	75	120	70	130
Bromoform	70	130	60	140
Bromomethane	30	145	10	165
Carbon disulfide	35	160	15	185
Carbon tetrachloride	65	140	55	150
Chlorobenzene	80	120	75	130
Chlorodibromomethane	60	135	45	145
Chloroethane	60	135	50	145
Chloroform	65	135	50	150
Chloromethane	40	125	25	140
cis-1,2-Dichloroethene	70	125	60	135
cis-1,3-Dichloropropene	70	130	60	140

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Aqueous Matrix (Cont.)

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Dibromomethane	75	125	65	135
Dichlorodifluoromethane	30	155	10	175
Ethylbenzene	75	125	65	135
Hexachloro-1,3-butadiene	50	140	35	160
Isopropylbenzene	75	125	65	135
m,p-Xylene	75	130	65	135
Methyl tert-butyl ether (MTBE)	65	125	55	135
Methylene chloride	55	140	40	155
Naphthalene	55	140	40	150
n-Butylbenzene	70	135	55	150
n-Propylbenzene	70	130	65	140
o-Xylene	80	120	75	130
p-Isopropyltoluene	75	130	65	140
sec-Butylbenzene	70	125	65	135
Styrene	65	135	55	145
tert-Butylbenzene	70	130	60	140
Tetrachloroethene	45	150	25	165
Toluene	75	120	70	130
trans-1,2-Dichloroethene	60	140	45	150
trans-1,3-Dichloropropene	55	140	40	155
Trichloroethene	70	125	60	135
Trichlorofluoromethane	60	145	45	160
Vinyl chloride	50	145	35	165

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Solid Matrix

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
1,1,1,2-Tetrachloroethane	75	125	65	135
1,1,1-Trichloroethane	70	135	55	145
1,1,2,2-Tetrachloroethane	55	130	40	145
1,1,2-Trichloroethane	60	125	50	140
1,1-Dichloroethane	75	125	65	135
1,1-Dichloroethene	65	135	55	150
1,1-Dichloropropene	70	135	60	145
1,2,3-Trichlorobenzene	60	135	50	145
1,2,3-Trichloropropane	65	130	50	140
1,2,4-Trichlorobenzene	65	130	55	140
1,2,4-Trimethylbenzene	65	135	55	145
1,2-Dibromo-3-chloropropane	40	135	25	150
1,2-Dibromoethane	70	125	60	135
1,2-Dichlorobenzene	75	120	65	125
1,2-Dichloroethane	70	135	60	145
1,2-Dichloropropane	70	120	65	125
1,3,5-Trimethylbenzene	65	135	55	145
1,3-Dichlorobenzene	70	125	65	135
1,3-Dichloropropane	75	125	70	130
1,4-Dichlorobenzene	70	125	65	135
2,2-Dichloropropane	65	135	55	145
2-Butanone	30	160	10	180
2-Chlorotoluene	70	130	60	140
2-Hexanone	45	145	30	160
4-Chlorotoluene	75	125	65	135
4-Methyl-2-pentanone (MIBK)	45	145	30	165
Acetone	20	160	10	180
Benzene	75	125	65	135
Bromobenzene	65	120	55	130
Bromochloromethane	70	125	60	135
Bromodichloromethane	70	130	60	135
Bromoform	55	135	45	150
Bromomethane	30	160	10	180
Carbon disulfide	45	160	30	180
Carbon tetrachloride	65	135	55	145
Chlorobenzene	75	125	65	130
Chlorodibromomethane	65	130	55	140
Chloroethane	40	155	20	175
Chloroform	70	125	65	135
Chloromethane	50	130	40	140
cis-1,2-Dichloroethene	65	125	55	135
cis-1,3-Dichloropropene	70	125	65	135

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Solid Matrix (Cont.)

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Dibromomethane	75	130	65	135
Dichlorodifluoromethane	35	135	15	155
Ethylbenzene	75	125	65	135
Hexachloro-1,3-butadiene	55	140	40	155
Isopropylbenzene	75	130	70	140
m,p-Xylene	80	125	70	135
Methylene chloride	55	140	40	155
Naphthalene	40	125	25	140
n-Butylbenzene	65	140	50	150
n-Propylbenzene	65	135	50	145
o-Xylene	75	125	70	135
p-Isopropyltoluene	75	135	65	140
sec-Butylbenzene	65	130	50	145
Styrene	75	125	65	135
tert-Butylbenzene	65	130	55	145
Tetrachloroethene	65	140	55	150
Toluene	70	125	60	135
trans-1,2-Dichloroethene	65	135	55	145
trans-1,3-Dichloropropene	65	125	55	140
Trichloroethene	75	125	70	130
Trichlorofluoromethane	25	185	10	215
Vinyl chloride	60	125	45	140

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix C

DoD Control Limits of Surrogate Compounds in Aqueous Matrix

Analyte	Control Limit	
	Lower	Upper
1,2-Dichloroethane-d_4	70	120
4-Bromofluorobenzene	75	120
Dibromofluoromethane	85	115
Toluene-d_8	85	120

DoD Control Limits of Surrogate Compounds in Solid Matrix

Analyte	Control Limit	
	Lower	Upper
4-Bromofluorobenzene	85	120
Toluene-d_8	85	115

Appendix D

ADDITIONAL QUALITY CONTROL CRITERIA FOR BP PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Additional Quality Control Criteria for BP Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The spike standard solutions shall contain all anticipated target analytes.

3.2. The use of a standard from a second lot as the second source standard is acceptable if written warranties demonstrating that the standards from two different lots are not prepared from the same reference materials are obtained from the manufacturer. "Manufacturer" refers to the producer of the standard, not the vendor.

4. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

4.1. Holding time begins at the date and time the sample is collected as documented on the chain of custody record.

4.2. Organic extracts must be stored in the same type of vials (amber glass or clear glass) as the associated standard solutions at the appropriate storage temperatures.

4.3. Properly labeled (e.g., date installed, cold storage unit number, etc.) storage blanks must be initiated and analyzed on a bi-weekly basis for each cold storage unit (refrigerator and freezer) used to store BP samples.

4.3.1. Any field and/or trip blanks submitted by BP must be stored in the same cold storage unit units as the samples that they are intended to be associated with (even if the matrices are different).

5. QUALITY CONTROL

5.1. Method Detection Limit (MDL)

5.1.1. MDL study should be performed annually for each analyte and matrix.

5.1.2. MDL verification must be performed immediately following an MDL study.

5.1.2.1. MDL verification sample must be spiked at the calculated MDL value.

5.1.2.2. MDL verification is deemed valid if all analytes in the verification sample are recovered.

5.1.3. At a minimum, the MDL study shall be performed on a single instrument, and the calculated MDL value must be confirmed by analyzing an MDL verification sample on all instruments used to analyze BP samples.

5.2. Initial Calibration (IC)

5.2.1. In addition to the standard initial calibration criteria, the %RSD for benzene, ethylbenzene, toluene, o-xylene, p/m-xylenes, each oxygenated compound, and each surrogate must be ≤ 15%.

5.2.1.1. The oxygenated compounds are DIPE, ETBE, MTBE, TAME, TBA, and ethanol.

5.2.2. Do not force the curve equation through zero.

5.3. Initial Calibration Verification (ICV)

5.3.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

5.4. Continuing Calibration Verification (CCV)

5.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and after every 10 analyses or portion thereof within a 12-hour shift.

5.4.2. Documentation for multiple (more than one) injection trials of CCV standards must include the reason for the multiple trials, the corrective action and which trial was used and why.

5.5. Minimum Relative Response Factor

5.5.1. For IC, ICV, and CCV, the RRF of benzene, ethylbenzene, toluene, o-xylene, p/m-xylenes, each oxygenated compound, and each surrogate must be evaluated.

5.5.1.1. The RRF of each of the following analytes is as follows:

Analyte	RRF
benzene	> 0.300
ethylbenzene	> 0.300
toluene	> 0.300
o-xylene	> 0.300
p/m-xylene	> 0.300
oxygenate (except TBA)	> 0.300
TBA	> 0.100
ethanol	> 0.100
surrogate	> 0.200

5.6. Event Based Quality Control (LCS/LCSDs and MBs)

5.6.1. Method Blanks (MBs)

5.6.1.1. Contamination observed in the MB at a concentration greater than 1/2 of the RL is acceptable if either one of the following conditions is met.

5.6.1.1.1. No contaminant is detected in the associated samples.

5.6.1.1.2. The concentration of the contaminant in the associated samples is greater than 10 times the concentration in the MB.

6. PROCEDURE

6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and after every 10 analyses or portion thereof within a 12-hour shift. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume.

6.2. Standard and sample purge vessels are loaded in the following or other logical order:

1) Tuning Standard / Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicate (LCSD)
4) Method Blank (MB)
5) Samples (up to 10 analyses, excluding CCV analyses)
6) Matrix Spike (MS)
7) Matrix Spike Duplicate (MSD)

6.2.1. Item 2: The LCS is a known matrix that has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

6.2.1.1. One LCS is required every day preparatory methods (i.e., methanol extractions, purge-and-trap extractions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation event.

6.2.2. Item 3: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD).

6.2.3. Item 4: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

6.2.3.1. One MB is required every day preparatory methods (i.e., methanol extractions, purge-and-trap extractions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation event.

6.2.4. Item 6: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.2.4.1. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently within an 8-hour preparation event.

6.2.4.2. The sample selected for spiking must be one of the samples collected for the specific BP project. If 10 or fewer BP samples are received, and no sample is designated for MS/MSD analyses, then a non-BP sample may be used.

6.2.5. Item 7: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

6.2.6. If solvent, instrument, or rinse blanks are placed in the sequence, the appropriate surrogate and internal standard working standard solution shall be injected or manually added to the aforementioned blanks.

6.3. Data Interpretation

6.3.1. Qualitative identification of each analyte/surrogate is based on retention time of the sample component, and on comparison of the sample mass spectrum, after background correction, with the characteristic ions in a reference mass spectrum.

6.3.1.1. All ions for an analyte/surrogate that are present in the reference spectrum at a relative intensity greater than 10% must be present in the sample spectrum.

6.3.1.1.1. The relative intensity of the most abundant ion in the reference spectrum is 100%.

6.3.2. Target analytes are identified as present when the following criteria are met.

6.3.2.1. The intensities of the characteristic ions of an analyte maximize within one scan of each other.

6.3.2.2. The relative intensities of the characteristic ions in the sample spectrum agree within ± 30% of the relative intensities of these ions in the reference spectrum.

6.3.3. Apply methanol/water dilution factor correction for the calculation of the target analyte concentration for a methanol extracted solid sample reported on an "as-received" basis.

7. REFERENCES

7.1. Technical Requirements for Environmental Laboratory Analytical Services, BP Laboratory Management Program (LaMP), Revision 09, July 30, 2007.

Title : **EPA METHOD 8270C, SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY / MASS SPECTROMETRY (GC/MS)**

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Revision 4.8 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ **MANAGEMENT** 11/07/12 **DATE**

_____ **QA DEPARTMENT** 11-07-12 **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 8270C, Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS).

2. APPLICABLE MATRICES

2.1. This method is applicable to water/aqueous matrices, soil/solids, oil, sludges and hazardous waste.

3. DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for this method are as follows:

Soil/Solid	Water	Oil
0.5 mg/kg (wet-weight)	10 µg/L	50 mg/kg

3.2. The EQLs will be proportionally higher for sample extracts which require dilution or cleanup.

3.3. Operation of the instrument in Selected Ion Monitoring (SIM) mode will allow a lower EQL to be achieved for a specific analyte or suite of analytes. Optimization for a specific analyte or suite of analytes may be accompanied by other extractive or analytical modifications. Reference the appendices for available options and EQLs.

4. SCOPE AND APPLICATION

4.1. EPA Method 8270C is used to determine the concentration of a large number of semi-volatile organic compounds in various matrices. The method can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivitization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. The following compounds may be determined by this method:

Base/Neutral Extractables

acenaphthene	2-chloronaphthalene	fluorene
acenaphthylene	4-chlorophenyl phenyl ether	hexachlorobenzene
anthracene	chrysene	hexachloro-1,3-butadiene
azobenzene	dibenz(a,h)anthracene	hexachlorocyclopentadiene
benzidine	1,2-dichlorobenzene	hexachloroethane
benzo(a)anthracene	1,3-dichlorobenzene	indeno(1,2,3-cd)pyrene
benzo(b)fluoranthene	1,4-dichlorobenzene	isophorone
benzo(k)fluoranthene	3,3'-dichlorobenzidine	naphthalene
benzo(a)pyrene	diethyl phthalate	nitrobenzene
benzo(g,h,i)perylene	dimethyl phthalate	n-nitrosodimethylamine
benzyl butyl phthalate	di-n-butyl phthalate	n-nitrosodiphenylamine
bis(2-chloroethyl)ether	di-n-octyl phthalate	n-nitrosodi-n-propylamine
bis(2-chloroethoxy)methane	2,4-dinitrotoluene	phenanthrene
bis(2-ethylhexyl)phthalate	2,6-dinitrotoluene	pyrene
bis(2-chloroisopropyl)ether	1,2-diphenylhydrazine	1,2,4-trichlorobenzene

4-bromophenyl phenyl ether fluoranthene
2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

Acid Extractables

4-chloro-3-methylphenol	4,6-dinitro-2-methylphenol	pentachlorophenol
2-chlorophenol	2,4-dinitrophenol	phenol
2,4-dichlorophenol	2-nitrophenol	2,4,6-trichlorophenol
2,4-dimethylphenol	4-nitrophenol	

Hazardous Substances

aniline	dibenzofuran	2-nitroaniline
benzoic acid	2-methylnaphthalene	3-nitroaniline
benzyl alcohol	2-methylphenol	4-nitroaniline
4-chloroaniline	4-methylphenol	2,4,5-trichlorophenol

Others

pyridine	1-methylnaphthalene

Pesticides

aldrin	4,4'-DDE	endrin
α-BHC	4,4'-DDT	endrin aldehyde
β-BHC	4,4'-DDD	heptachlor
γ-BHC (lindane)	dieldrin	heptachlor epoxide
δ-BHC	endosulfan I	methoxychlor
α-chlordane	endosulfan II	toxaphene
γ-chlordane	endosulfan sulfate	

PCBs

aroclor-1016	aroclor-1242	aroclor-1260
aroclor-1221	aroclor-1248	aroclor-1262
aroclor-1232	aroclor-1254	

4.2. Upon client request, additional target analytes may be added to this analysis. However, it needs to be demonstrated that any added compounds lend themselves to EPA Method 8270C determination, either by regulatory reference or validation studies.

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph / mass spectrometer (GC/MS) and skilled in the interpretation of mass spectra.

5. METHOD SUMMARY

5.1. EPA Method 8270C describes chromatographic procedures that will allow for the separation of the semi-volatile organic compounds in the extract and their qualitative and quantitative analysis by mass spectrometry. Detection is achieved using a mass selective detector either in Total Ion Scan (TIC) mode for full list reporting or Selected Ion Monitoring (SIM) mode for lower EQL reporting for selected analytes.

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory methods include the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510C	SOP-M200
Continuous Liquid-Liquid Extraction	3520C	SOP-M201
Soxhlet Extraction	3540C	SOP-M203
Pressurized Fluid Extraction	3545A	SOP-M204
Ultrasonic Extraction	3550B	SOP-M202
Waste Dilution	3580A	SOP-M205
TCLP	1311	SOP-M226
SPLP	1312	SOP-M227
STLC (California)	T22.11.5.All	SOP-M228

5.3. Solid samples are extracted via EPA Methods 3540C or 3550B using methylene chloride, or via EPA Method 3545A using methylene chloride. Liquid samples are extracted via EPA Methods 3510C or 3520C at a neutral pH using methylene chloride. Oil samples are prepared in accordance with EPA Method 3580A using methylene chloride as the diluent. Solid samples for TCLP, SPLP, or STLC analysis are extracted using the appropriate extractant with the leachate then prepared by either separatory funnel or liquid-liquid extraction.

5.4. The extracts that are dirty and dark in color are subjected to Florisil cleanup.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the

applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. ***Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.***

6.13. ***Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.***

6.14. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.15. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.16. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.17. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte

concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.18. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.19. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.20. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.21. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.22. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.23. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.24. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.26. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.27. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.28. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination. In addition, sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2. Interference can also occur when "dirty" samples leave residue in the injector or analytical column. To minimize this effect, a guard columns should be used and cut frequently or replaced. Also, the analytical column can be "baked" after such samples.

7.3. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.4. Plastics contain significant amounts of leachable phthalate esters and must not be used during any stage of analytic processing.

7.5. The following provides information regarding possible target analyte losses/interferences during analytic processing:

7.5.1. The base-neutral extraction may cause significantly reduced recoveries of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

7.5.2. Benzidine is subject to oxidative losses during extract concentration and poor chromatographic behavior.

7.5.3. Under the alkaline condition step of sample preparation, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.

7.5.4. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

7.5.5. Depending upon chromatographic conditions and instrument setup, n-nitrosodimethylamine may be difficult to separate from the solvent.

7.5.6. N-nitrosodiphenylamine decomposes in the GC inlet and cannot be separated from diphenylamine.

7.5.7. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 4-chloroaniline, all nitroanilines, and benzyl alcohol are subject to erratic chromatographic

behavior. This effect is especially pronounced where the system contains high-boiling residue.

7.5.8. Pyridine may perform poorly (degrade) at normal injection port temperatures.

7.6. As a matter of routine prior to injection, all dirty or dark colored sample extracts for GC/MS determination are subjected to column Florisil cleanup. In this procedure, a glass column is packed with Florisil and topped with a water adsorbent. The methylene chloride solvent separates the target analytes from interferants by allowing the target analytes to elute through the column. Meanwhile, the Florisil retains the interferants.

8. SAFETY

8.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.2. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

8.3. The following compounds covered by this method have been tentatively classified as known or suspected human carcinogens: benzo(a) anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a) pyrene, dibenz(a,h) anthracene, and n-nitroso-dimethylamine. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when analysts handle high concentrations of these compounds.

9. ►EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Agilent 6890N Gas Chromatograph or equivalent configured with splitless injection port and Agilent 7673/7683 Series Autoinjector and PC based data system.

9.2. Mass Spectrometer: Agilent 5973/5973N Mass Selective Detector (MSD) or equivalent capable of scanning from 35 to 500 amu every one second or less, utilizing a 70-V nominal electron energy in the electron-impact ionization (EI) mode. The MS is directly coupled (capillary direct) to the column via a heated interface.

9.2.1. The MSD must be capable of producing a mass spectrum for DFTPP which meets all of the criteria in Section 12.1.1. when 1 µL of the tuning standard (50 ng of DFTPP) is injected.

9.3. ***Instrument Software***

9.3.1. Requires a PC based data system or equivalent.

9.3.2. Agilent Environmental MSD ChemStation Version E.02 or equivalent.

9.4. ***Instrument Maintenance and Troubleshooting***

9.4.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.4.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.5. Analytical Column: 30-m × 0.25-mm ID, 0.5-µm (or 0.25-µm) film thickness, silicone coated fused-silica capillary column, HP-5 MS or equivalent.

9.6. Carrier Gas: High purity helium.

9.7. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with N.I.S.T. Traceable Certification.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Methylene chloride, CH_2Cl_2, pesticide grade or equivalent.

10.1.2. Acetone, CH_3COCH_3, pesticide grade or equivalent.

10.1.3. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v). Prepare the solution by dissolving granular $Na_2S_2O_3$ (reagent grade or equivalent) in reagent water.

10.1.4. Reagent water, interferant free.

10.1.5. Sand, washed, sea or standard Ottawa.

10.1.6. All reagents must be inspected and documented prior to use.

10.2. Standards

10.2.1. Tuning standard solution containing 50 ppm each of decafluorotriphenylphosphine (DFTPP), benzidine, pentachlorophenol, and 4,4'-DDT in methylene chloride.

10.2.1.1. Inject 1 µL of the tuning standard for hardware tuning.

10.2.2. Pre-certified stock standard solutions, each in sealed glass ampules, containing 200/2000 ppm of each target analyte, 5000 ppm of each base/neutral surrogate, 10000 ppm of each acid surrogate, and 2000 ppm of each internal standard are used to prepare calibration and check standards.

10.2.3. Calibration standard solutions containing various concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride are used to prepare calibration standards.

10.2.3.1. The calibration standards are prepared as follows:

Analyte		Standard Compound Concentration (ppm)						
base/neutrals		5	10	20	50	80	120	160
acids	2.5*	5/10*	10/20*	20/40*	50/100*	80/160*	120/240*	160/320*
internal standards	40	40	40	40	40	40	40	40
surrogates		5	10	20	50	80	120	160

* 3/4-Methylphenol only.

10.2.3.2. The 10-ppm calibration standard is considered part of the initial multi-point calibration if an analyte yields poor response from the 5-ppm calibration standard.

10.2.3.3. The system performance check compounds (SPCCs) are n-nitrosodi-n-propylamine, hexachlorocyclopentadiene, 2,4-dintrophenol, and 4-nitrophenol.

10.2.3.4. The calibration check compounds (CCCs) are phenol, 1,4-dichlorobenzene, 2-nitrophenol, 2,4-dichlorophenol, hexachlorobutadiene, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol, acenaphthene, n-nitrosodiphenylamine, pentachlorophenol, fluoranthene, di-n-octylphthalate, and benzo(a)pyrene.

10.2.3.5. The 50-, 80-, and 120-ppm standards are also used as the continuing calibration verification solutions.

10.2.4. Initial calibration verification (ICV) solution containing midpoint concentration of each target analyte, internal standard, check compound, and surrogate in methylene chloride. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.4.1. The ICV solution is prepared as follows:

Analyte	Standard Compound Concentration (ppm)
base/neutrals	80
acids	80/160*
internal standards	40
surrogates	80

* 3/4-Methylphenol only.

10.2.5. Continuing calibration verification (CCV) solutions containing mid-range concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.

10.2.5.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
base/neutrals	80
acids	80/160*
internal standards	40
surrogates	80

* 3/4-Methylphenol only.

10.2.5.2. One CCV solution is used daily.

10.2.6. Surrogate standard solution containing 400 ppm each of 2-fluorophenol, phenol-d_6, nitrobenzene-d_5, 2-fluorobiphenyl, 2,4,6-tribromophenol, and p-terphenyl-d_{14} in acetone or methylene chloride.

10.2.6.1. Add 500 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

10.2.7. Internal standard solution containing 2000 ppm each of 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} in methylene chloride.

10.2.7.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

10.2.8. Spike standard solution containing 1000 ppm each of phenol, 2-chlorophenol, 1,4-dichlorobenzene, n-nitrosodi-n-propylamine, 1,2,4-trichlorobenzene, naphthalene, 4-chloro-3-methylphenol, dimethyl phthalate, acenaphthylene, acenaphthene, 4-nitrophenol, 2,4-dinitrotoluene, fluorene, pentachlorophenol, pyrene, and benzyl butyl phthalate in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.8.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

10.2.8.2. Add 200 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

10.2.9. All working standards must be replaced after six months or sooner if comparison with check standards indicates a problem.

10.2.10. All stock standards must be inspected and documented prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1-L pre-cleaned amber glass containers with Teflon-lined closures. Soil samples should be collected in 4-oz. pre-cleaned

clear glass wide-mouth jars with Teflon-lined closures. Oil samples should be collected in 40-mL VOA vials with Teflon-lined closures.

11.1.1. Aqueous samples shall be preserved with 4 mL of 10% $Na_2S_2O_3$ solution per 1 L of sample to remove residual chlorine.

11.2. Samples should be maintained in a chilled state (≤ 6°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.3. Upon receipt, the samples are stored in a cooler at temperature ≤ 6°C . Aqueous samples must be extracted within seven (7) days of collection. An extraction holding time of 14 days applies to all non-aqueous samples.

11.4. All extracted samples are then stored in freezer at (≤-10°C) conditions and must be analyzed within a 40-day period post extraction.

12. QUALITY CONTROL

12.1. Hardware Tuning

12.1.1. Prior to running the calibration standards, the GC/MS DFTPP tuning standard must be analyzed and meet the following acceptance criteria:

Mass	Ion Abundance Criteria
51	30 – 60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40 – 60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5 – 9% of mass 198
275	10 – 30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17 – 23% of mass 442

12.1.1.1. The degradation (or percent breakdown) for 4,4'-DDT is ≤ 20%. The formula for calculating %B is listed in Section 15.10.

12.1.1.2. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible.

12.1.2. These criteria must be demonstrated every 12 hours.

12.1.3. If a tune does not meet the acceptance criteria, correct the problem and re-tune the system.

12.1.4. Whenever invasive maintenance of the GC/MS hardware is performed, the system must be re-tuned.

12.2. Initial Calibration (IC)

12.2.1. The initial multi-point calibration must be established prior to the processing of sample extracts.

12.2.2. The IC is deemed valid if the %RSD for each CCC is ≤ 30%, the %RSD for each analyte (except CCC) is ≤ 15%, and the RF_{ave} value for each SPCC is ≥ 0.050.

12.2.3. Where the %RSD for each target analyte is ≤ 15%, the response factor is assumed to be invariant, and the average response factor may be used for quantitation.

12.2.4. In those instances where the %RSD for one or more target analytes exceeds 15%, the initial calibration remains acceptable if the following conditions are met:

12.2.4.1. The mean of the %RSD values for all analytes in the calibration is ≤ 15%. The mean %RSD is calculated by summing the %RSD value for each analyte and dividing by the total number of analytes.

12.2.4.2. The mean %RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project. In other words, if the analyte is part of the calibration standard, its %RSD value is included in the evaluation.

12.2.4.3. Summary of the initial calibration data or a specific list of the target analytes for which the %RSD exceeded 15%, and the results of the mean %RSD calculation must be included in the data package.

12.2.4.4. The use of the grand mean approach will lead to greater uncertainty for those analytes for which the %RSD is > 15%. Review the associated quality control results carefully, with particular attention to the matrix spike and laboratory control sample results, to determine if the calibration linearity poses a significant concern.

12.2.4.4.1. If the grand mean approach is not acceptable due to client or project specific requirements, employ one of the other calibration options (see Section 12.2.5.), or adjust instrument operating conditions and/or the calibration range until the %RSD is ≤ 15%.

12.2.5. Other calibration options are as follows:

12.2.5.1. The first calibration option is linear least squares regression with equal weighting factor. The IC is deemed valid if the correlation coefficient, r, is ≥ 0.99.

12.2.5.2. The section calibration option is quadratic least squares regression with equal weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.99.

12.2.5.2.1. This option requires at least six calibration levels.

12.2.6. The relative retention time (RRT) of each analyte in each calibration standard should agree to within ± 0.06 RRT units.

12.2.7. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.8. The relative retention time (RRT) of each target analyte in each calibration standard should agree to within ± 0.06 RRT units.

12.2.8.1. The RRT criterion is not a requirement. However, non-compliance should be considered indicative of a problematic calibration for the affected target analytes.

12.2.9. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.9.1. If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis.

12.3. Initial Calibration Verification (ICV)

12.3.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%, and the RF value for each SPCC is ≥ 0.050.

12.3.1.1. If the calibration option is average relative response, the %D is the percent difference.

12.3.1.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

12.3.2. The %D of each non-CCC is evaluated only per client request or project specific DQOs.

12.3.2.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, the initial calibration is deemed valid if the %D for each non-CCC is ≤ 50%.

12.3.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Investigate, effect corrective actions, which may include re-preparation of standard solutions, and recalibrate, if necessary.

12.4. Continuing Calibration Verification (CCV)

12.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter during analysis.

12.4.2. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%, and the RF value for each SPCC is ≥ 0.050.

12.4.2.1. If the calibration option is average relative response, the %D is the percent difference.

12.4.2.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

12.4.3. The %D of each non-CCC is evaluated only per client request or project specific DQOs.

12.4.3.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, the initial calibration is deemed valid if the %D for each non-CCC is ≤ 50%.

12.4.4. The internal standard responses and retention times for the CCV must be evaluated immediately during or after data acquisition.

12.4.4.1. If the retention time for any internal standard changes by more than 30 seconds from the midpoint standard level of the most recent initial calibration, the chromatographic system must be inspected for malfunctions and corrective action must be effected.

12.4.4.2. If the EICP area for any internal standard changes by a factor of two (−50% to +100%) from the midpoint standard level of the most recent initial calibration, the system must be inspected for malfunctions and corrective action effected.

12.4.4.3. Following corrective action, re-analysis of samples analyzed while the system was malfunctioning is required.

12.4.5. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Effect corrective action and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, recalibrate or demonstrate acceptable performance with two consecutive CCVs.

12.4.5.1. To demonstrate acceptable performance with two consecutive CCVs, the concentrations of the two CCV standards must be at two different levels within the calibration range. In addition, the concentration of one CCV standard shall be below the mid level.

12.5. Event Based Quality Control (LCS/LCSDs and MBs)

12.5.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.5.2. The acceptance criteria for LCS/LCSD compounds are as follows:

12.5.2.1. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.5.2.2. All LCS/LCSD compounds must be within acceptance limits. However, if a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside of control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary.

12.5.2.3. ME is defined as being beyond the LCS control limit (3 standard deviations), but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean.

12.5.2.4. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than 11 analytes.

12.5.2.5. The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number of Analytes Allowed in ME of the LCS Control Limit
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

12.5.2.6. Marginal exceedances must be random. If the same analyte exceeds the LCS control limit 2 out of 3 consecutive LCS, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

12.5.3. Ideally, the concentration of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.5.3.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

12.5.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-extracted and/or re-analyzed.

12.6. Matrix Based Quality Control (Surrogates, Internal Standards, and MS/MSDs)

12.6.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD), surrogates added to each sample, and internal standards added to each sample.

12.6.2. The acceptance criteria for surrogate spike compound recoveries are as follows:

12.6.2.1. The lower and upper acceptance limits for %REC of each surrogate spike compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.2.2. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

12.6.2.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration or a problem may have occurred during extraction or cleanup. The data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.6.2.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.6.2.4.1. Check the internal standard and surrogate spiking solutions for degradation and contamination.

12.6.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same extract should be re-analyzed.

12.6.2.4.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate

recoveries and the sample data reported with qualification.

12.6.2.4.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.2. If the MB surrogates are unacceptable, all associated sample data must invalidated and all associated samples re-extracted and re-analyzed.

12.6.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

12.6.3. The acceptance criteria for internal standard compounds are as follows:

12.6.3.1. The internal standard responses (area counts) for all samples including QC check samples and method blanks must be monitored.

12.6.3.2. If the area count of any internal standard in a sample or blank changes by a factor of two (−50% to +100%) from the area count of the corresponding internal standard determined in the daily CCV within the same 12-hour period, corrective action must be taken.

12.6.3.2.1. The samples including QC check samples and method blanks should be re-analyzed, the CCV solution should be checked for proper concentrations and re-analyzed, or the data should be qualified.

12.6.4. The acceptance criteria for MS/MSDs compounds are as follows:

12.6.4.1. The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.6.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.5. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.7. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-extracted and re-analyzed.

12.8. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Prior to the analysis of sample or QC extracts, the GC/MS system must be hardware tuned and an acceptable multi-point calibration established. The acceptance criteria for the parameters are listed in Sections 12.1. and 12.2.

13.1.1. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP.

13.1.2. The spectrometer must produce a mass spectrum that meets all criteria when 50 ng of DFTPP is introduced in GC/MS.

13.1.3. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not background-subtract part of the DFTPP peak.

13.1.4. Benzidine and pentachlorophenol should be present at their normal responses and no peak tailing should be present. If the benzidine and/or pentachlorophenol responses are low or peak tailing exists, effect corrective action and retune/recalibrate prior to analyzing any samples. Corrective action may include but not be limited to 1) replacing the injection port liner, 2) cleaning the injection port, or 3) clipping the analytical column.

13.1.5. 4,4'-DDT is included in the tune solution to check for degradation. The acceptance criteria for degradation of 4,4'-DDT to DDE and DDD is less than or equal to 20%. If 4,4'-DDT degradation exceeds 20%, effect corrective action and re-tune the system prior to analyzing any samples. Corrective action may include but not be limited to 1) replacing the injection port liner, 2) cleaning the injection port, or 3) clipping the guard column.

13.2. Initial Calibration

13.2.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.2.

13.2.2. After obtaining an acceptable multi-point calibration curve and prior to processing samples, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.3.

13.2.3. The initial multi-point calibration and ICV should include all anticipated target analytes for the duration of the use of the initial calibration.

14. PROCEDURE

14.1. Instrument Setup

14.1.1. Use the following GC/MS operating conditions as guidance to establish the GC/MS temperature program and flow rate necessary to separate the analytes of interest.

Description	GC/MS Operating Condition
Carrier gas flow rate	1 mL/min at 7.15 psi
Initial temperature	40°C, hold 1.50 min
Temperature program	40°C to 280°C at 22.00°C/min 280°C to 310°C at 5.00°C/min
Final temperature	310°C, hold 6.00 min
Transfer line temperature	285°C
Scan range	35~500 amu

14.1.2. Autoinjector is set to inject 1 µL of sample or QC extract.

14.2. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter during analysis. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.4.

14.2.1. If a failed CCV is the first of the day, corrective action must be effected prior to analyzing any samples.

14.2.2. If not, effect corrective action and reanalyze all samples since the last acceptable CCV.

14.3. Following extraction by one of the methods specified in Section 5.2., the extracts for the QC and actual environmental samples are received in autoinjector vials. The autoinjector vials are then loaded onto the GC/MS sample tray.

14.4. Sample vials are loaded in the following or other logical order:

1) Tuning Standard
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 20 per batch)

7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)

14.4.1. Item 1: An acceptable tune demonstrates satisfactory hardware performance. A tune meeting the acceptance criteria is required daily prior to sample analysis and every 12 hours thereafter during analysis.

14.4.2. Item 2: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. Only the CCCs and SPCCs are monitored for acceptance. An acceptable CCV is required daily prior to sample analysis and every 12 hours thereafter during analysis.

14.4.3. Item 3: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.3.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid and oil samples, the LCS consists of the specified compounds spiked into washed sea sand.

14.4.3.2. One LCS is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.4. Item 4: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.4.5. Item 5: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (i.e., surrogates, internal standards, etc.).

14.4.5.1. For aqueous samples, the MB consists of clean reagent water. For solid and oil samples, the MB consists of washed sea sand.

14.4.5.2. An MB is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. It should be noted, however, that as necessary (e.g., after high level samples), additional MBs may be placed in the sequence.

14.4.5.3. When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of methylene

chloride must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.4.6. Item 6: Up to 20 sample extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrumentation is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

14.4.7. Item 7: The MS is an actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.7.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.5.

14.4.7.2. One MS is required for every batch of 20 samples per matrix or portion thereof extracted concurrently.

14.4.8. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.5. Ensure that a sufficient amount of methylene chloride is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles. Specifically, ensure that the solvent rinse bottles are full and waste bottles are empty at the beginning of the sequence.

14.6. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the run log book.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. Evaluate the area count of each internal standard compound in all samples including QC check samples and method blanks.

14.8.1.1. If the area count of any internal standard in the sample or blank changes by a factor of two (−50% to +100%) from the area count of the corresponding internal standard determined in the daily CCV within the same 12-hour period, corrective action must be taken.

14.8.1.1.1. The samples including QC check samples and method blanks should be re-analyzed, the CCV solution should be checked for proper concentrations and re-analyzed, or the data should be qualified.

14.8.2. The qualitative identification of each analyte determined by this method is based on the 1) elution of the sample component at the same relative retention time (RRT) as the standard component and 2) comparison of the sample mass spectrum, after background correction if necessary, with characteristic ions in a reference mass spectrum.

14.8.2.1. The reference mass spectrum should be obtained from the GC/MS within the same 12-hour period as the sample analysis.

14.8.2.2. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum.

14.8.3. Analytes should be identified as present when the following criteria are met:

14.8.3.1. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target analyte at a compound-specific retention time will be accepted as meeting this criterion.

14.8.3.2. The RRT of the sample analyte is within ±0.06 RRT units of the RRT of the standard analyte.

14.8.3.3. The relative intensities of the characteristic ions agree within ± 30% of the relative intensities of these ions in the reference spectrum.

14.8.3.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different retention times. Sufficient resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.8.3.5. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component, appropriate selection of analyte spectra and background spectra is important.

14.8.3.6. Examination of extracted ion current profiles (EICPs) of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute, the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

14.8.4. When a compound has been identified, the quantitation of the compound will be based on the integrated abundance of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one with the retention time nearest that of a given analyte.

14.8.4.1. If the %RSD of a target analyte's response factor is ≤ 15%, then the concentration in the extract may be determined using the average response factor (RF_{ave}) from the initial calibration. The formula for calculating %RSD is listed in Section 15.2.

14.8.4.2. Identify and compute the concentration of each target analyte in the sample. The GC/MS data system should be programmed to perform these functions. The details provided below are for the purpose of understanding.

14.8.4.2.1. The concentration of the analyte in an aqueous sample is calculated using the concentration of the analyte in the extract, the volume of the extract, and the volume of the aqueous sample extracted. The formula for calculating the concentration is listed in Section 15.8.

14.8.4.2.2. The concentration of the analyte in a solid or oil sample is calculated using the concentration of the analyte in the extract, the volume of the extract, and the mass of the solid or oil sample extracted. The formula for calculating the concentration is listed in Section 15.9.

14.8.5. Upon request, a library search may be made for the purpose of tentative identification of compounds not associated with the calibration standards. Refer to the reporting procedure outlined in the current revision of SOP-T025.

15. CALCULATIONS

15.1. The response factor is calculated as follows:

$$RF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where: RF = response factor for target analyte being measured.

A_x = area of the characteristic ion for target analyte being measured.
C_{is} = concentration of the applicable internal standard.
A_{is} = area of the characteristic ion for the applicable internal standard.
C_x = concentration of target analyte being measured.

Note: Concentrations must be in equivalent units.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.
RF_{ave} = mean of the 5 or 6 initial RFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RF_{ave} - RF_{daily}|}{RF_{ave}} \times 100$$

where: %D = percent difference.
RF_{daily} = daily RF for the target analyte.
RF_{ave} = mean of the 5 or 6 initial RFs for the target analyte.

15.4. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte recovered in measurement 1.
C_2 = concentration of target analyte recovered in measurement 2.

Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x \times C_{is}}{A_{is} \times RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in mg/L.
A_x = area of the characteristic ion for target analyte.
C_{is} = concentration of the applicable internal standard in mg/L.
A_{is} = area of the characteristic ion for the applicable internal standard.
RF_{ave} = mean of the 5 or 6 initial RFs for the target analyte.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = volume of extract in mL.
V_A = volume of aqueous sample extracted in L.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration for a solid (or oil) sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S}$$

where: C_S = concentration of target analyte in solid (or oil) sample in mg/kg.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid (or oil) sample extracted in g.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.10. The percent breakdown is calculated as follows:

$$\%B = \frac{A_{degradation}}{A_{total}} \times 100$$

where: %B = percent breakdown of DDT.
$A_{degradation}$ = total degradation peak areas (see Note 1).
A_{total} = total peak areas (see Note 2).

Note 1: The total degradation peak areas are the areas of DDE and DDD for DDT breakdown.

Note 2: The total peak areas are the areas of DDT, DDD, and DDE for DDT breakdown.

15.11. The relative retention time of each target analyte is calculated as follows:

$$RRT = \frac{RT_x}{RT_{is}}$$

where: RRT = relative retention time of target analyte.
RT_x = retention time of target analyte.
RT_{is} = retention time of the applicable internal standard.

15.12. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and mg/kg (ppm) for oil, soil, and solid waste samples.

15.12.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

15.13. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S. All LCS/LCSD compounds must be within acceptance limits (see Section 12.5.2. for additional information).

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentration of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.3. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The lower and upper acceptance limits for %REC of each surrogate spike compound are based upon the historical average recovery ± 3S.

18.3.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

18.3.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.3. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.3.1. Check the internal standard and surrogate spiking solutions for degradation and contamination.

18.3.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample or extract should be re-analyzed.

18.3.3.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and/or re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-extracted and re-analyzed.

18.3.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S.

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically causes unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and mg/kg (ppm) for oil, soil and solid waste samples.

18.7.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If

previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries

of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8270C, USEPA, Revision 3, December 1996.

22.2. Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), Test Methods for Evaluating Solid Waste (SW-846), Pre-promulgation Version, Method 8270D, USEPA, Revision 4, February 2006.

22.3. Determinative Chromatographic Separations, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000B, USEPA, Revision 2, December 1996.

22.4. Determinative Chromatographic Separations, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000C, USEPA, Revision 3, March 2003.

22.5. Quality Control, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.6. Choosing the Correct Procedure, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, November 2000.

22.7. Organic Analytes, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, November 2000.

22.8. Semivolatile Organic Compounds (SVOCs), SW-846 Method 8270, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Requirements for Low Level N-Nitrosodimethylamine (NDMA) Determined by EPA 8270C in the Selected Ion Monitoring (SIM) Mode.

23.2. Appendix B: Requirements for Low Level Polynuclear Aromatic Hydrocarbons (PAHs) Determined by EPA 8270C in the Selected Ion Monitoring (SIM) Mode.

23.3. Appendix C: Requirements for Low Level Organochlorine Pesticides and Polychlorinated Biphenyl (PCB) Congeners Determined by EPA 8270C in the Selected Ion Monitoring (SIM) Mode.

23.4. Appendix D: Additional Quality Control Criteria for DOD Project.

23.5. ►***Appendix E: Requirements for Low Level Polynuclear Aromatic Hydrocarbons (PAHs) and Phthalates Determined by EPA 8270C in the Selected Ion Monitoring (SIM) Mode for solid matrices.***

24. MODIFICATIONS

Calscience SOP M404 Section	Reference Document EPA Method 8270C Section	Summary of Modification
All	All	None.

25. REVISION HISTORY

Revision	Description	Author(s)	Effective Date
4.8	SOP Updated.	Y. Patel	11/12/12
	Sec.6: LOD / LOQ definations added. Sec.9 Instrument Software and maintenance reference added. Sec.10 Table of ICAL, ICV and CCV replaced. Sec.11 Samples and extract storage requirements corrected as per method. Sec. 12 Alternate calibration options added for ICAL, ICV and CCV Sec. 24 and 25 created. Appendix A, B, C, D & E updated.		

Appendix A

REQUIREMENTS FOR LOW LEVEL N-NITROSODIMETHYLAMINE (NDMA) DETERMINED BY EPA 8270C IN THE SELECTED ION MONITORING (SIM) MODE

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. Low level n-nitrosodimethylamine (NDMA) determined by EPA 8270C in the Selected Ion Monitoring (SIM) mode.

2. APPLICABLE MATRICES

2.1. This method is applicable to soil/solid matrices.

3. DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for this method are as follows:

Soil/Solid

3 µg/kg

3.2. The EQLs will be proportionally higher for sample extracts which require dilution or cleanup.

4. SAMPLE PREPARATION

4.1. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory method is the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Pressurized Fluid Extraction	3545A	SOP-M204

4.2. The initial sample aliquot mass for soil/solid sample is 20 g.

4.2.1. The final extract volume at the completion of the concentration step is 2 mL.

4.2.2. The resulting preparation factor for soil/solid sample is 10:1.

5. STANDARDS

5.1. Pre-certified stock standard neat compound, in sealed glass ampule, containing 100 mg of NDMA, is used to prepare calibration standards.

5.2. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000 ppm of NDMA, 2000 ppm of surrogate, and 1000 ppm of internal standard are used to prepare calibration and check standards.

5.3. Calibration standard solutions containing 1000 ppb of NDMA, 5000 ppb of internal standard, and 1000 ppb of surrogate in methylene chloride are used to prepare calibration standards.

5.3.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppb)				
NDMA	2	10	20	50	100
internal standard	20	20	20	20	20
surrogate	2	10	20	50	100

5.4. Initial calibration verification (ICV) solution containing 20 ppb each of NDMA, internal standard, and surrogate in methylene chloride. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.5. Continuing calibration verification (CCV) solutions containing mid-range concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.

5.5.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppb)
NDMA	20
internal standard	20
surrogate	20

5.6. One CCV solution is used daily.

5.7. Surrogate standard solution containing 1000 ppb of 1,4-dichlorobenzene-d_4 in acetone or methylene chloride.

5.7.1. Add 40 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

5.8. Spike standard solution containing 1000 ppb of NDMA in acetone or methylene chloride.

5.8.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

5.8.2. Add 40 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

5.9. Internal standard solution containing 1000 ppb of n-nitrosodimethylamine-d_6 in methylene chloride.

5.9.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

5.10. All working standards must be replaced after six months or sooner if comparison with check standards indicates a problem.

5.11. All stock standards must be inspected and documented prior to use.

6. SELECTED ION MONITORING (SIM) PARAMETERS

6.1. The MSD will focus on the following selected ions of NDMA.

Analyte	Ions
n-nitrosodimethylamine-d_6	46, 80
n-nitrosodimethylamine	42, 74
1,4-dichlorobenzene-d_4	115, 150, 152

Appendix B

REQUIREMENTS FOR LOW LEVEL POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) DETERMINED BY EPA 8270C IN THE SELECTED ION MONITORING (SIM) MODE

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. Low level polynuclear aromatic hydrocarbons (PAHs) determined by EPA 8270C in the Selected Ion Monitoring (SIM) mode.

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous and soil/solid matrices.

3. DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for this method are as follows:

Soil/Solid	Aqueous
100 µg/kg	1.0 µg/L

3.2. The EQLs will be proportionally higher for sample extracts which require dilution or cleanup..

4. SAMPLE PREPARATION

4.1. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory method is the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510C	SOP-M200
Continuous Liquid-Liquid Extraction	3520C	SOP-N201
Pressurized Fluid Extraction	3545A	SOP-M204

4.2. The initial sample aliquot volume for aqueous sample is 1000 mL, and the initial sample aliquot mass for soil/solid sample is 10 g.

4.2.1. The final extract volume at the completion of the concentration step is 2 mL.

4.2.2. The resulting preparation factor is for aqueous sample is 500:1, and for soil/solid sample is 5:1.

5. STANDARDS

5.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000 ppm of each PAH target analyte, 5000 ppm of each base/neutral surrogate, and 2000 ppm of each internal standard are used to prepare calibration and check standards.

5.2. Calibration standard solutions containing 20 ppm of each PAH target analyte, 2000 ppm of each internal standard, 20 ppm of each check compound, and 20 ppm of each surrogate in methylene chloride are used to prepare calibration standards.

5.2.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppm)				
PAHs	0.1	0.5	1.0	2.0	5.0
internal standards	5.0	5.0	5.0	5.0	5.0
CCCs	0.1	0.5	1.0	2.0	5.0
surrogates	0.1	0.5	1.0	2.0	5.0

5.2.2. The calibration check compounds (CCCs) are acenaphthene, fluoranthene, and benzo(a)pyrene.

5.3. Initial calibration verification (ICV) solution containing 1.0 ppm of each PAH / target analyte, 5.0 ppm of each internal standard, 1.0 ppm of each check compound, and 1.0 ppm of each surrogate in methylene chloride. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.4. Continuing calibration verification (CCV) solutions containing mid-range concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.

5.4.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
PAHs	1.0
internal standards	5.0
CCCs	1.0
surrogates	1.0

5.5. One CCV solution is used daily.

5.6. Surrogate standard solution containing 4.0 ppm each of nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14} in acetone or methylene chloride.

5.6.1. Add 500 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

5.7. Spike standard solution containing 4.0 ppm each of acenaphthene and pyrene in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.7.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

5.7.2. Add 500 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

5.8. Internal standard solution containing 250 ppm each of naphthalene-d_8, acenaphthene-d_{10}, chrysene-d_{12}, and perylene-d_{12} in methylene chloride.

5.8.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

5.9. All working standards must be replaced after six months or sooner if comparison with check standards indicates a problem.

5.10. All stock standards must be inspected and documented prior to use.

6. QUALITY CONTROL

6.1. Initial Calibration (IC)

6.1.1. The IC is deemed valid if the %RSD for each CCC is ≤ 30%, and the %RSD for each analyte (except CCC) is ≤ 15%.

6.2. Initial Calibration Verification (ICV)

6.2.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%.

6.3. Continuing Calibration Verification (CCV)

6.3.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%.

7. SELECTED ION MONITORING (SIM) PARAMETERS

7.1. The Mass Selective detector will focus on the following selected ions of the PAHs.

Analyte	Ions	Retention Time Range
1,4-dichlorobenzene-d_4	150, 152, 115	9.54 to 10.14 min
naphthalene-d_8	136, 68, 108	12.28 to 12.88 min
nitrobenzene-d_5	82, 54, 128	10.82 to 11.42 min
naphthalene	128, 129, 127	12.32 to 12.92 min
2-methylnaphthalene	142, 141, 115	13.98 to 14.58 min
1-methylnaphthalene	142, 141, 115	14.23 to 14.83 min
acenaphthene-d_{10}	164, 162, 80	16.71 to 17.31 min
2-fluorobiphenyl	172, 171, 85	15.02 to 15.62 min
acenaphthylene	152, 151, 76	16.28 to 16.88 min
acenaphthene	153, 154, 76	16.79 to 17.39 min
fluorene	166, 165, 82	18.20 to 18.80 min
phenanthrene-d_{10}	188, 94, 80	20.82 to 21.42 min
phenanthrene	178, 89, 76	20.88 to 21.48 min
anthracene	178, 76, 89	21.01 to 21.61 min

Analyte	Ions	Retention Time Range
fluoranthene	202, 203, 101	24.35 to 24.95 min
chrysene-d_{12}	240, 236, 120	28.59 to 29.19 min
pyrene	202, 200, 101	24.97 to 25.57 min
p-terphenyl-d_{14}	244, 122, 212	25.68 to 26.28 min
benzo(a) anthracene	228, 114, 226	28.54 to 29.14 min
chrysene	228, 114, 226	28.65 to 29.25 min
perylene-d_{12}	264, 132, 260	32.48 to 33.08 min
benzo(b) fluoranthene	252, 253, 126	31.53 to 32.13 min
benzo(k) fluoranthene	252, 253, 126	31.59 to 32.19 min
benzo(a) pyrene	252, 253, 126	32.32 to 32.92 min
indeno(1,2,3-c,d) pyrene	276, 138, 277	35.13 to 35.73 min
dibenz(a,h) anthracene	278, 279, 139	35.24 to 35.84 min
benzo(g,h,i) perylene	276, 138, 277	35.83 to 36.43 min

Appendix C

REQUIREMENTS FOR LOW LEVEL ORGANOCHLORINE PESTCIDIES AND POLYCHLORINATED BIPHENYL (PCB) CONGENERS DETERMINED BY EPA 8270C IN THE SELECTED ION MONITORING (SIM) MODE

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8270C, Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Determination of Low Level Organochlorine Pesticides and Polychlorinated Biphenyl (PCB) Congeners in Selected Ion Monitoring (SIM) Mode.

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous and soil/solid matrices.

3. DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for this method are as follows:

Soil/Solid	Aqueous
5 µg/kg	0.1 µg/L

3.2. The EQLs will be proportionally higher for sample extracts which require dilution or cleanup.

4. SAMPLE PREPARATION

4.1. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory method is the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510C	SOP-M200
Continuous Liquid-Liquid Extraction	3520C	SOP-M201
Pressurized Fluid Extraction	3545A	SOP-M204

4.2. The initial sample aliquot volume for aqueous sample is 1000 mL, and the initial sample aliquot mass for soil/solid sample is 20 g.

4.2.1. The final extract volume at the completion of the concentration step is 2 mL.

4.2.2. The resulting preparation factor is for aqueous sample is 500:1, and for soil/solid sample is 10:1.

5. STANDARDS

5.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 20 ppm of each pesticide target analyte, 20 ppm of each PCB congener target analyte, 5000 ppm of each base/neutral surrogate, and 2000 ppm of each internal standard are used to prepare calibration and check standards.

5.2. Calibration standard solutions containing 20 ppm of each pesticide target analyte (2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, DDMU, and DDNU),

20 ppm of each PCB congener target analyte, 2000 ppm of each internal standard, 20 ppm of each check compound, and 20 ppm of each surrogate in hexane are used to prepare calibration standards.

5.2.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppm)				
pesticides	0.05	0.5	1.0	2.0	5.0
PCB congeners	0.01	0.05	0.5	1.0	2.0
internal standards	5.0	5.0	5.0	5.0	5.0
surrogates	0.01	0.05	0.5	1.0	2.0

5.2.2. 1.0-ppm standard also used as the continuing calibration verification solutions.

5.3. Initial calibration verification (ICV) solution containing 1.0 ppm of each pesticide or PCB congener target analyte, 5.0 ppm of each internal standard, and 1.0 ppm of each surrogate in hexane. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.4. Continuing calibration verification (CCV) solutions containing mid-range concentrations of target analytes, internal standards, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial five-point calibration.

5.4.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
pesticides	1.0
PCB congeners	0.5
internal standards	5.0
surrogates	0.5

5.4.2. One CCV solution is used daily.

5.5. Surrogate standard solution containing 4.0 ppm of p-terphenyl-d_{14} in acetone or methylene chloride.

5.5.1. Add 500 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

5.6. Spike standard solution containing 4.0 ppm of each pesticide or 100 ppm PCB congener in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.6.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

5.6.2. Add 10 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

5.7. Internal standard solution for pesticide analysis containing 250 ppm of acenaphthene-d_{10} in methylene chloride. Internal standard solution for PCB congener analysis containing 250 ppm each of phenanthrene-d_{10} and chrysene-d_{12} in methylene chloride.

5.7.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

5.8. All working standards must be replaced after six months or sooner if comparison with check standards indicates a problem.

5.9. All stock standards must be inspected and documented prior to use.

6. QUALITY CONTROL

6.1. Initial Calibration (IC)

6.1.1. The IC is deemed valid if the %RSD for each analyte is ≤ 30%.

6.2. Initial Calibration Verification (ICV)

6.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

6.3. Continuing Calibration Verification (CCV)

6.3.1. The initial calibration is deemed valid if the %D for each pesticide analyte is ≤ 50%, and the %D for each PCB congener analyte is ≤ 20%.

7. SELECTED ION MONITORING (SIM) PARAMETERS

7.1. The Mass Selective detector will focus on the following selected ions of the pesticides.

Analyte	Ions	Retention Time
acenaphthene-d_{10}	164, 162, 80	4.088 min
DDNU	178, 248, 213	6.868 min
2,4'-DDE	246, 318, 176	9.049 min
DDMU	212, 282, 176	9.086 min
4,4'-DDE	246, 318, 176	10.088 min
p-terphenyl-d_{14}	244, 122, 212	10.130 min
2,4'-DDD	235, 165, 199	10.629 min
2,4'-DDT	235, 237, 165	11.488 min
4,4'-DDD	235, 237, 165	12.146 min

7.2. The Mass Selective detector will focus on the following selected ions of the PCB congeners.

Analyte	Congener Number	Ions	Retention Time
phenanthrene-d_{10}		188, 94, 80	9.641 min
2,4'-dichlorobiphenyl	8	222, 152	10.021 min
2,2',5-trichlorobiphenyl	18	256, 186	10.268 min
2,4,4'-trichlorobiphenyl	28	256, 186	10.496 min
2,2',5,5'-tetrachlorobiphenyl	52	292, 220	10.792 min
2,2',4,5'-tetrachlorobiphenyl	49	292, 220	10.815 min
2,2',3,5'-tetrachlorobiphenyl	44	292, 220	11.000 min
3,4,4'-trichlorobiphenyl	37	256, 186	11.114 min
2,4,4',5-tetrachlorobiphenyl	74	292, 220	11.301 min
2,3',4',5-tetrachlorobiphenyl	70	292, 220	11.380 min
2,3',4,4'-tetrachlorobiphenyl	66	292, 220	11.406 min
2,2',4,5,5'-pentachlorobiphenyl	101	326, 254	11.564 min
2,2',4,4',5-pentachlorobiphenyl	99	326, 254	11.604 min
2,3',4,4',6-pentachlorobiphenyl	119	326, 254	11.681 min
2,2',3,4,5'-pentachlorobiphenyl	87	326, 254	11.810 min
p-terphenyl-d_{14}		244, 122, 212	11.819 min
3,4,4',5-tetrachlorobiphenyl	81	292, 220	11.877 min
2,3,3',4',6-pentachlorobiphenyl	110	326, 254	11.913 min
2,2',3,5,5',6-hexachlorobiphenyl	151	360, 290	11.948 min
3,3',4,4'-tetrachlorobiphenyl	77	292, 220	12.000 min
2,2',3,4',5',6-hexachlorobiphenyl	149	360, 290	12.066 min
2,3',4,4',5'-pentachlorobiphenyl	123	326, 254	12.115 min
2,3',4,4',5-pentachlorobiphenyl	118	326, 254	12.150 min
2,3,4,4',5-pentachlorobiphenyl	114	326, 254	12.200 min
2,2',3,4,4',6,6'-heptachlorobiphenyl	184	394, 324	12.206 min
2,2',4,4',5,5'-hexachlorobiphenyl	153	360, 290	12.296 min
2,3',4,4',5',6-hexachlorobiphenyl	168	360, 290	12.330 min
2,3,3',4,4'-pentachlorobiphenyl	105	326, 254	12.387 min
2,2',3,4,4',5'-hexachlorobiphenyl	138	360, 290	12.536 min
2,3,3',4,4',6-hexachlorobiphenyl	158	360, 290	12.558 min
2,2',3,4',5,5',6-heptachlorobiphenyl	187	394, 324	12.632 min
2,2',3,4,4',5',6-heptachlorobiphenyl	183	394, 324	12.672 min
3,3',4,4',5-pentachlorobiphenyl	126	326, 254	12.704 min
2,2',3,3',4,4'-hexachlorobiphenyl	128	360, 290	12.794 min

Analyte	Congener Number	Ions	Retention Time
2,3',4,4',5,5'-hexachlorobiphenyl	167	360, 290	12.824 min
2,2',3,3',4,5',6'-heptachlorobiphenyl	177	394, 324	12.892 min
2,3,3',4,4',5-hexachlorobiphenyl	156	360, 290	13.022 min
2,3,3',4,4',5'-hexachlorobiphenyl	157	360, 290	13.087 min
2,2',3,4,4',5,5'-heptachlorobiphenyl	180	394, 324	13.138 min
chrysene-d_{12}		240, 236, 120	13.253 min
2,2',3,3',4,4',5-heptachlorobiphenyl	170	394, 324	13.433 min
2,2',3,3',4,5',6,6'-octachlorobiphenyl	201	430, 358	13.463 min
3,3',4,4',5,5'-hexachlorobiphenyl	169	360, 290	13.464 min
2,3,3',4,4',5,5'-heptachlorobiphenyl	189	394, 324	13.790 min
2,2',3,3',4,4',5,6-octachlorobiphenyl	195	430, 358	13.828 min
2,2',3,3',4,4',5,5'-octachlorobiphenyl	194	430, 358	14.125 min
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206	464, 196	14.486 min
decachlorobiphenyl	209	428, 358	14.741 min

Appendix D

ADDITIONAL QUALITY CONTROL CRITERIA FOR DOD PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8270C, Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Additional Quality Control Criteria for DoD Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. Spike standard solution containing 1000 ppm of each target analyte in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

3.1.1. The standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

3.1.2. Add 200 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

3.1.3. The spike standard solution contains all anticipated target analytes.

3.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

4. ►QUALITY CONTROL

4.1. Limit of Detection (LOD)

4.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

4.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

4.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

4.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

4.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

4.1.2.3. If these criteria are not met, perform either one of the following tasks.

4.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

4.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

4.1.3. ***No samples shall be analyzed without a valid LOD.***

4.2. ***Limit of Quantitation (LOQ)***

4.2.1. ***LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.***

4.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

4.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

4.2.2. ***LOQ verification must be performed quarterly to verify precision and bias at the LOQ.***

4.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

4.2.3. ***LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.***

4.3. Tuning

4.3.1.1. The degradation (or percent breakdown) for 4,4'-DDT is ≤ 20%. The formula for calculating %B is listed in Section 15.10.

4.3.1.2. Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2.

4.4. Initial Calibration

4.4.1. The initial multi-point calibration must be established prior to the processing of sample extracts.

4.4.2. The IC is deemed valid if the %RSD for each CCC is ≤ 30%, the %RSD for each analyte (except CCC) is ≤ 15%, and the RF_{ave} value for each SPCC is ≥ 0.050.

4.4.3. ►**If these criteria are not met ,o**ther calibration options are as follows:

4.4.3.1. The first calibration option is linear least squares regression with equal weighting factor. The IC is deemed valid if the correlation coefficient, r, is ≥ 0.995.

4.4.3.2. The section calibration option is non-linear quadratic least squares regression with equal weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.99.

4.4.3.2.1. This option requires at least six calibration levels for second order and seven levels for third order.

4.4.4. The relative retention time (RRT) of each target analyte in each calibration standard must be within ± 0.06 RRT units.

4.4.5. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

4.5. Initial Calibration Verification (ICV)

4.5.1. The initial calibration is deemed valid if the %D for each project analyte is ≤ 20%.

4.5.1.1. If the calibration option is average relative response, the %D is the percent difference.

4.5.1.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

4.5.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Investigate, effect corrective actions, which may include re-preparation of standard solutions, and recalibrate, if necessary.

4.6. Continuing Calibration Verification (CCV)

4.6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter during analysis.

4.6.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%, and the RF value for each SPCC is ≥ 0.050.

4.6.2.1. If the calibration option is average relative response, the %D is the percent difference.

4.6.2.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

4.7. Retention Time Window

4.7.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration.

4.7.1.1. Absolute retention time window for each analyte, surrogate, or internal standard is the retention time of the respective analyte, surrogate, or internal standard in the midpoint calibration standard ± 30 seconds.

4.7.1.2. Document the serial number of the analytical column associated with the retention time window.

4.8. Internal Standard Verification

4.8.1. The internal standard responses and retention times for all standards and samples must be evaluated.

4.8.1.1. If the retention time for any internal standard changes by more than 30 seconds from the midpoint standard level of the most recent initial calibration, the chromatographic system must be inspected for malfunctions and corrective action must be effected.

4.8.1.2. If the EICP area for any internal standard changes by a factor of two (−50% to +100%) from the midpoint standard level of the most recent initial calibration, the system must be inspected for malfunctions and corrective action effected.

4.8.1.3. Following corrective action, re-analysis of samples analyzed while the system was malfunctioning is required.

4.8.1.4. If corrective action fails in a sample, the results shall be reported with the appropriate data qualifier (Q-flag) for the specific analyte(s) associated with the failed internal standard.

4.9. Event Based Quality Control (LCS/LCSDs and MBs)

4.9.1. Laboratory Control Samples (LCS/LCSDs)

4.9.1.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound in aqueous matrix are as follows:

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Polynuclear Aromatics				
2-Methylnaphthalene	45	105	35	115
Acenaphthene	45	110	35	120
Acenaphthylene	50	105	40	115
Anthracene	55	110	45	120
Benzo(a)anthracene	55	110	45	120
Benzo(a)pyrene	55	110	45	120
Benzo(b)fluoranthene	45	120	35	130
Benzo(k)fluoranthene	45	125	30	135
Benzo(g,h,i)perylene	40	125	25	135
Chrysene	55	110	45	120
Dibenzo(a,h)anthracene	40	125	30	140
Fluoranthene	55	115	45	125
Fluorene	50	110	40	120
Indeno(1,2,3-c,d)pyrene	45	125	30	140
Naphthalene	40	100	30	115
Phenanthrene	50	115	40	130
Pyrene	50	130	35	140
Phenolic/Acidic				
2,4,5-Trichlorophenol	50	110	40	120
2,4,6-Trichlorophenol	50	115	40	125
2,4-Dichlorophenol	50	105	40	115
2,4-Dimethylphenol	30	110	15	125
2,4-Dinitrophenol	15	140	10	160
2-Chlorophenol	35	105	25	115
2-Methylphenol	40	110	25	120
2-Nitrophenol	40	115	25	125
3-Methylphenol / 4-Methylphenol	30	110	20	125
4,6-Dinitro-2-methylphenol	40	130	25	145
4-Chloro-3-methylphenol	45	110	35	120
4-Nitrophenol	0	125	0	145
Pentachlorophenol	40	115	25	130
Phenol	0	115	0	135
Benzoic acid	0	125	0	150
Basic				
3,3'-Dichlorobenzidine	20	110	10	125
4-Chloroaniline	15	110	10	125

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Phthalate Esters				
Bis(2-ethylhexyl)phthalate	40	125	30	140
Butyl benzyl phthalate	45	115	35	130
Di-n-butyl phthalate	55	115	45	125
Di-n-octyl phthalate	35	135	20	155
Diethyl phthalate	40	120	30	130
Dimethyl phthalate	25	125	10	145
Nitrosoamines				
N-Nitrosodi-n-propylamine	35	130	20	145
N-Nitrosodimethylamine	25	110	10	125
N-Nitrosodiphenylamine	50	110	35	120
Chlorinated Aliphatics				
Bis(2-chloroethoxy)methane	45	105	35	115
Bis(2-chloroethyl)ether	35	110	25	120
Bis(2-chloroisopropyl)ether	25	130	10	150
Hexachloro-1,3-butadiene	25	105	15	115
Hexachloroethane	30	95	15	105
Halogenated Aromatics				
1,2,4-Trichlorobenzene	35	105	25	120
1,2-Dichlorobenzene	35	100	20	115
1,3-Dichlorobenzene	30	100	20	110
1,4-Dichlorobenzene	30	100	20	110
2-Chloronaphthalene	50	105	40	115
4-Bromophenyl phenyl ether	50	115	40	125
4-Chlorophenyl phenyl ether	50	110	40	120
Hexachlorobenzene	50	110	40	120
Nitroaromatics				
2,4-Dinitrotoluene	50	120	40	130
2,6-Dinitrotoluene	50	115	35	130
2-Nitroaniline	50	115	35	125
3-Nitroaniline	20	125	10	145
4-Nitroaniline	35	120	20	130
Nitrobenzene	45	110	35	120
Neutral Aromatics				
Carbazole	50	115	35	130
Dibenzofuran	55	105	45	115
Others				
1,2-Diphenylhydrazine	55	115	45	120
Benzyl alcohol	30	110	15	125
Isophorone	50	110	40	125

4.9.1.2. The lower and upper acceptance limits for %REC of each LCS/LCSD compound in solid matrix are as follows:

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Polynuclear Aromatics				
2-Methylnaphthalene	45	105	35	115
Acenaphthene	45	110	35	120
Acenaphthylene	45	105	35	115
Anthracene	55	105	45	115
Benzo(a)anthracene	50	110	40	120
Benzo(a)pyrene	50	110	40	120
Benzo(b)fluoranthene	45	115	35	125
Benzo(k)fluoranthene	45	125	30	135
Benzo(g,h,i)perylene	40	125	25	140
Chrysene	55	110	45	120
Dibenzo(a,h)anthracene	40	125	25	140
Fluoranthene	55	115	45	125
Fluorene	50	110	40	115
Indeno(1,2,3-c,d)pyrene	40	120	25	135
Naphthalene	40	105	30	120
Phenanthrene	50	110	40	120
Pyrene	45	125	35	135
Phenolic/Acidic				
2,4,5-Trichlorophenol	50	110	40	120
2,4,6-Trichlorophenol	45	110	30	120
2,4-Dichlorophenol	45	110	35	120
2,4-Dimethylphenol	30	105	20	115
2,4-Dinitrophenol	15	130	10	150
2-Chlorophenol	45	105	35	115
2-Methylphenol	40	105	30	115
2-Nitrophenol	40	110	30	120
3-Methylphenol / 4-Methylphenol	40	105	30	120
4,6-Dinitro-2-methylphenol	30	135	10	155
4-Chloro-3-methylphenol	45	115	35	125
4-Nitrophenol	15	140	10	160
Pentachlorophenol	25	120	10	135
Phenol	40	100	30	110
Benzoic acid	0	110	0	130
Basic				
3,3'-Dichlorobenzidine	10	130	0	145
4-Chloroaniline	10	95	0	110
Phthalate Esters				
Bis(2-ethylhexyl)phthalate	45	125	35	140
Butyl benzyl phthalate	50	125	35	135
Di-n-butyl phthalate	55	110	45	120
Di-n-octyl phthalate	40	130	25	145
Diethyl phthalate	50	115	40	125
Dimethyl phthalate	50	110	40	120
Nitrosoamines				
N-Nitrosodi-n-propylamine	40	115	30	125
N-Nitrosodimethylamine	20	115	10	130

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Nitrosoamines				
N-Nitrosodiphenylamine	50	115	40	125
Chlorinated Aliphatics				
Bis(2-chloroethoxy)methane	45	110	30	120
Bis(2-chloroethyl)ether	40	105	25	115
Bis(2-chloroisopropyl)ether	20	115	10	130
Hexachloro-1,3-butadiene	40	115	25	130
Hexachloroethane	35	110	20	120
Halogenated Aromatics				
1,2,4-Trichlorobenzene	45	110	30	120
1,2-Dichlorobenzene	45	95	35	105
1,3-Dichlorobenzene	40	100	30	110
1,4-Dichlorobenzene	35	105	25	115
2-Chloronaphthalene	45	105	35	115
4-Bromophenyl phenyl ether	45	115	35	130
4-Chlorophenyl phenyl ether	45	110	35	120
Hexachlorobenzene	45	120	35	130
Nitroaromatics				
2,4-Dinitrotoluene	50	115	35	130
2,6-Dinitrotoluene	50	110	35	125
2-Nitroaniline	45	120	30	130
3-Nitroaniline	25	110	15	125
4-Nitroaniline	35	115	20	125
Nitrobenzene	40	115	30	125
Neutral Aromatics				
Carbazole	45	115	30	130
Dibenzofuran	50	105	40	110
Others				
Benzyl alcohol	20	125	10	140
Isophorone	45	110	30	125

4.9.2. Method Blanks (MBs)

4.9.2.1. The concentration of a target analyte in an MB should be ≤ ½ RL. The concentrations of common laboratory contaminants should be < RL.

4.9.2.2. If these criteria are not met, investigate and eliminate the source of contamination.

4.9.2.3. Determine whether to reprocess the samples associated with the failed MB based on the following checks:

4.9.2.3.1. The concentration of a target analyte in the MB is ≥ RL as established by the test method or by regulation, <u>and</u> is > 1/10 of the amount measured in any sample.

4.9.2.3.2. The blank contamination affects the sample results as per the test method requirements or the individual project data quality objectives.

4.9.2.4. Any sample that meets either one or both of the checks described in Section 4.6.2.3. shall be reprocessed in a subsequent preparatory batch, except when the sample analysis resulted in a non-detect.

4.9.2.4.1. If no sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

4.10. Matrix Based Quality Control (Surrogates and MS/MSDs)

4.10.1. Surrogates

4.10.1.1. The lower and upper acceptance limits for %REC of each surrogate spike compound in aqueous matrix are as follows:

Analyte	Control Limit	
	Lower	Upper
2-Fluorobiphenyl	50	110
Terphenyl-d_{14}	50	135
2,4,6-Tribromophenol	40	125
2-Fluorophenol	20	110
Phenol-d_5 / Phenol-d_6	10	115
Nitrobenzene-d_5	40	110

4.10.1.2. The lower and upper acceptance limits for %REC of each surrogate spike compound in solid matrix are as follows:

Analyte	Control Limit	
	Lower	Upper
2-Fluorobiphenyl	45	105
Terphenyl-d_{14}	30	125
2,4,6-Tribromophenol	35	125
2-Fluorophenol	35	105
Phenol-d_5 / Phenol-d_6	40	100
Nitrobenzene-d_5	35	100

4.10.2. Matrix Spikes (MS/MSDs)

4.10.2.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous matrix are as follows:

Analyte	Control Limit	
	Lower	Upper
Polynuclear Aromatics		
2-Methylnaphthalene	45	105
Acenaphthene	45	110
Acenaphthylene	50	105
Anthracene	55	110
Benzo(a)anthracene	55	110
Benzo(a)pyrene	55	110
Benzo(b)fluoranthene	45	120
Benzo(k)fluoranthene	45	125
Benzo(g,h,i)perylene	40	125
Chrysene	55	110
Dibenzo(a,h)anthracene	40	125
Fluoranthene	55	115
Fluorene	50	110
Indeno(1,2,3-c,d)pyrene	45	125
Naphthalene	40	100
Phenanthrene	50	115
Pyrene	50	130
Phenolic/Acidic		
2,4,5-Trichlorophenol	50	110
2,4,6-Trichlorophenol	50	115
2,4-Dichlorophenol	50	105
2,4-Dimethylphenol	30	110
2,4-Dinitrophenol	15	140
2-Chlorophenol	35	105
2-Methylphenol	40	110
2-Nitrophenol	40	115
3-Methylphenol / 4-Methylphenol	30	110
4,6-Dinitro-2-methylphenol	40	130
4-Chloro-3-methylphenol	45	110
4-Nitrophenol	0	125
Pentachlorophenol	40	115
Phenol	0	115
Benzoic acid	0	125
Basic		
3,3'-Dichlorobenzidine	20	110
4-Chloroaniline	15	110
Phthalate Esters		
Bis(2-ethylhexyl)phthalate	40	125
Butyl benzyl phthalate	45	115
Di-n-butyl phthalate	55	115
Di-n-octyl phthalate	35	135
Diethyl phthalate	40	120
Dimethyl phthalate	25	125
Nitrosoamines		
N-Nitrosodi-n-propylamine	35	130
N-Nitrosodimethylamine	25	110

Analyte	Control Limit	
	Lower	Upper
Nitrosoamines		
N-Nitrosodiphenylamine	50	110
Chlorinated Aliphatics		
Bis(2-chloroethoxy)methane	45	105
Bis(2-chloroethyl)ether	35	110
Bis(2-chloroisopropyl)ether	25	130
Hexachloro-1,3-butadiene	25	105
Hexachloroethane	30	95
Halogenated Aromatics		
1,2,4-Trichlorobenzene	35	105
1,2-Dichlorobenzene	35	100
1,3-Dichlorobenzene	30	100
1,4-Dichlorobenzene	30	100
2-Chloronaphthalene	50	105
4-Bromophenyl phenyl ether	50	115
4-Chlorophenyl phenyl ether	50	110
Hexachlorobenzene	50	110
Nitroaromatics		
2,4-Dinitrotoluene	50	120
2,6-Dinitrotoluene	50	115
2-Nitroaniline	50	115
3-Nitroaniline	20	125
4-Nitroaniline	35	120
Nitrobenzene	45	110
Neutral Aromatics		
Carbazole	50	115
Dibenzofuran	55	105
Others		
1,2-Diphenylhydrazine	55	115
Benzyl alcohol	30	110
Isophorone	50	110

4.10.2.2. The lower and upper acceptance limits for %REC of each MS/MSD compound in solid matrix are as follows:

Analyte	Control Limit	
	Lower	Upper
Polynuclear Aromatics		
2-Methylnaphthalene	45	105
Acenaphthene	45	110
Acenaphthylene	45	105
Anthracene	55	105
Benzo(a)anthracene	50	110
Benzo(a)pyrene	50	110
Benzo(b)fluoranthene	45	115
Benzo(k)fluoranthene	45	125
Benzo(g,h,i)perylene	40	125

Analyte	Control Limit	
	Lower	Upper
Polynuclear Aromatics		
Chrysene	55	110
Dibenzo(a,h)anthracene	40	125
Fluoranthene	55	115
Fluorene	50	110
Indeno(1,2,3-c,d)pyrene	40	120
Naphthalene	40	105
Phenanthrene	50	110
Pyrene	45	125
Phenolic/Acidic		
2,4,5-Trichlorophenol	50	110
2,4,6-Trichlorophenol	45	110
2,4-Dichlorophenol	45	110
2,4-Dimethylphenol	30	105
2,4-Dinitrophenol	15	130
2-Chlorophenol	45	105
2-Methylphenol	40	105
2-Nitrophenol	40	110
3-Methylphenol / 4-Methylphenol	40	105
4,6-Dinitro-2-methylphenol	30	135
4-Chloro-3-methylphenol	45	115
4-Nitrophenol	15	140
Pentachlorophenol	25	120
Phenol	40	100
Benzoic acid	0	110
Basic		
3,3'-Dichlorobenzidine	10	130
4-Chloroaniline	10	95
Phthalate Esters		
Bis(2-ethylhexyl)phthalate	45	125
Butyl benzyl phthalate	50	125
Di-n-butyl phthalate	55	110
Di-n-octyl phthalate	40	130
Diethyl phthalate	50	115
Dimethyl phthalate	50	110
Nitrosoamines		
N-Nitrosodi-n-propylamine	40	115
N-Nitrosodimethylamine	20	115
N-Nitrosodiphenylamine	50	115
Chlorinated Aliphatics		
Bis(2-chloroethoxy)methane	45	110
Bis(2-chloroethyl)ether	40	105
Bis(2-chloroisopropyl)ether	20	115
Hexachloro-1,3-butadiene	40	115
Hexachloroethane	35	110
Halogenated Aromatics		
1,2,4-Trichlorobenzene	45	110

Analyte	Control Limit	
	Lower	Upper
Halogenated Aromatics		
1,2-Dichlorobenzene	45	95
1,3-Dichlorobenzene	40	100
1,4-Dichlorobenzene	35	105
2-Chloronaphthalene	45	105
4-Bromophenyl phenyl ether	45	115
4-Chlorophenyl phenyl ether	45	110
Hexachlorobenzene	45	120
Nitroaromatics		
2,4-Dinitrotoluene	50	115
2,6-Dinitrotoluene	50	110
2-Nitroaniline	45	120
3-Nitroaniline	25	110
4-Nitroaniline	35	115
Nitrobenzene	40	115
Neutral Aromatics		
Carbazole	45	115
Dibenzofuran	50	105
Others		
Benzyl alcohol	20	125
Isophorone	45	110

4.10.2.3. The RPD between the MS/MSD compounds is ≤ 30%.

5. REFERENCES

5.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25 2010.

Appendix E

REQUIREMENTS FOR LOW LEVEL POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) AND PTHTHALATES DETERMINED BY EPA 8270C IN THE SELECTED ION MONITORING (SIM) MODE FOR SOLID MATRICES

Calscience Environmental Laboratories, Inc.

1. ►METHOD IDENTIFICATION

1.1. ***Low level polynuclear aromatic hydrocarbons (PAHs) and Phthalates determined by EPA 8270C in the Selected Ion Monitoring (SIM) mode for solid matrices.***

2. APPLICABLE MATRICES

2.1. ***This method is applicable to soil/solid matrices.***

3. DETECTION LIMITS

3.1. ***The estimated quantitation limits (EQLs) for this method are as follows:***

Soil/Solids

2 - 10 µg/kg

3.2. ***The EQLs will be proportionally higher for sample extracts which require dilution or cleanup.***

4. SAMPLE PREPARATION

4.1. ***Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory method is the following:***

4.2.

Type of Sample Preparation	*EPA Method No.*	*SOP No.*
Pressurized Fluid Extraction	*3545A*	*SOP-M204*

4.3. ***The initial sample aliquot mass for soil/solid sample is 100 g.***

4.3.1. ***The final extract volume at the completion of the concentration step is 2 mL.***

4.3.2. ***The resulting preparation factor for soil/solid sample is 50:1.***

5. PROCEDURE MODIFICATIONS FOR LOW LEVEL REPORTING IN SOLID MATRICES

5.1. ***Sample Preparation***

5.1.1. ***Utilizing SOP M204 "EPA Method 3545, Pressurized Fluid Extraction (PFE)" the sample weight and final extract volume are modified as follows:***

5.1.2. ***Sample weight: Increased from 20 g to 100g***

5.1.3. ***Final extract volume: No change, remains 2 ml.***

6. STANDARDS

6.1. ***Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000 ppm of each PAH / phthalate target analyte, 5000 ppm of each base/neutral surrogate, and 2000 ppm of each internal standard are used to prepare calibration and check standards.***

6.2. ***Calibration standard solutions containing 200 ppm of each PAH / phthalate target analyte, 2000 ppm of each internal standard and 200 ppm of each surrogate in methylene chloride are used to prepare calibration standards.***

6.2.1. ***The calibration standards are prepared as follows:***

Analyte	Standard Compound Concentration (ppm)						
PAHs / Phthalates	0.1	0.5	5.0	8.0	10.0	15.0	20.0
internal standards	5.0	5.0	5.0	5.0	5.0	5.0	5.0
CCCs	0.1	0.5	5.0	8.0	10.0	15.0	20.0
surrogates	0.1	0.5	5.0	8.0	10.0	15.0	20.0

6.2.2. ***The calibration check compounds (CCCs) are acenaphthene, fluoranthene, benzo(a)pyrene and Di-n-Octyl Phthalate.***

6.3. ***Initial calibration verification (ICV) solution containing 10 ppm of each PAH / phthalate target analyte, 5.0 ppm of each internal standard, 10 ppm of each check compound, and 10 ppm of each surrogate in methylene chloride. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.***

6.4. ***Continuing calibration verification (CCV) solutions containing mid-range concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.***

6.4.1. ***The CCV solutions are prepared as follows:***

Analyte	Standard Compound Concentration (ppm)
PAHs / Phthalates	10.0
internal standards	5.0
CCCs	10.0
surrogates	10.0

6.5. ***One CCV solution is used daily.***

6.6. ***Surrogate standard solution containing 400 ppm each of nitrobenzene-d_5, 2-fluorobiphenyl and p-terphenyl-d_{14} in acetone or methylene chloride.***

6.6.1. ***Add 50 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.***

6.7. ***Spike standard solution containing 200 ppm each of PAHs and phthalates in acetone or methylene chloride. The spike standard solution must be of a***

source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

6.7.1. ***This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).***

6.7.2. ***Add 100 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.***

6.8. ***Internal standard solution containing 250 ppm each of naphthalene-d_8, acenaphthene-d_{10}, chrysene-d_{12}, phenanthrene-d_{10} and perylene-d_{12} in methylene chloride.***

6.8.1. ***Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.***

6.9. ***All working standards must be replaced after six months or sooner if comparison with check standards indicates a problem.***

6.10. ***All stock standards must be inspected and documented prior to use.***

7. QUALITY CONTROL

7.1. ***Initial Calibration (IC)***

7.1.1. ***The IC is deemed valid if the %RSD for each CCC is ≤ 30%, and the %RSD for each analyte (except CCC) is ≤ 15%.***

7.2. ***Initial Calibration Verification (ICV)***

7.2.1. ***The initial calibration is deemed valid if the %D for each CCC is ≤ 20%.***

7.3. ***Continuing Calibration Verification (CCV)***

7.3.1. ***The initial calibration is deemed valid if the %D for each CCC is ≤ 20%.***

8. SELECTED ION MONITORING (SIM) PARAMETERS

8.1. ***The Mass Selective detector will focus on the following selected ions of the PAHs and Phthalates.***

Analyte	Ions	Retention Time Range (min)
naphthalene-d_8	136,68	6.11 to 6.45
nitrobenzene-d_5	82, 54,128	5.38 to 5.49
naphthalene	128, 129, 127	6.09 to 6.49
2-methylnaphthalene	142, 141	6.92 to 7.12
1-methylnaphthalene	142, 141	7.04 to 7.37
acenaphthene-d_{10}	164, 162, 160	8.01 to 8.39
2-fluorobiphenyl	172, 171	7.29 to 7.62
acenaphthylene	152, 151, 153	7.86 to 8.18
acenaphthene	153, 154, 152	8.12 to 8.35
fluorene	166, 165, 167	8.59 to 8.99
phenanthrene-d_{10}	188, 94, 80	9.69 to 9.95
phenanthrene	178, 176, 179	9.69 to9.91
anthracene	178, 176, 179	9.82 to 10.05
fluoranthene	202, 203, 101	11.01 to 11.34
chrysene-d_{12}	240, 236, 120	12.70 to 13.02
pyrene	202, 200, 203	11.25 to 11.60
p-terphenyl-d_{14}	244, 122, 212	11.95 to 11.76
benzo(a) anthracene	228, 229, 226	12.64 to 12.86
chrysene	228, 229, 226	12.79 to 13.11
perylene-d_{12}	264, 265, 260	14.78 to 15.38
benzo(b) fluoranthene	252, 253, 125	14.27 to 14.99
benzo(k) fluoranthene	252, 253, 125	14.41 to 14.61
benzo(a) pyrene	252, 253, 125	14.84 to 15.16
indeno(1,2,3-c,d) pyrene	276, 138, 277	17.02 to 17.19
dibenz(a,h) anthracene	278, 279, 139	16.99 to 17.35
benzo(g,h,i) perylene	276, 138, 277	17.50 to 17.84
Dimethyl phthalate	163, 164, 194	7.79 to 8.13
Diethy phthalate	149, 177, 150	8.60 to 8.85
di-n-butyl phthalate	149, 150, 104	10.34 to 10.71
Butyl benzyl phthalate	149, 91, 206	12.02 to 12.34
bis(2-Ethyl hexyl) phthalate	149, 279, 167	12.79 to 13.15
di-n-octyl phthalate	149, 279, 150	13.70 to 14.04

Title : **EPA METHOD 8330, NITROAROMATICS AND NITRAMINES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY**

Document No. : SOP-M414
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ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
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YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. EPA Method 8330, Nitroaromatics and Nitramines by High Performance Liquid Chromatography.

2. APPLICABLE MATRICES

2.1. This method is applicable to water, soil, and solid wastes.

3. ►DETECTION LIMITS

3.1. The ***reporting*** limits (***RLs***) for this method are as follows:

	Water	***Soil***
Explosives	***2 µg/L (low-level)*** ***40 µg/L (high-level)***	***200 µg/kg (wet-weight)***

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution.

3.3. ***Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.***

4. SCOPE AND APPLICATION

4.1. EPA Method 8330 is used to determine the concentrations of explosives residues in various matrices. The following compounds can be determined by this method:

Compound	Abbreviation
2-amino-4,6-dinitrotoluene	2-Am-DNT
4-amino-2,6-dinitrotoluene	4-Am-DNT
1,3-dinitrobenzene	1,3-DNB
2,4-dinitrotoluene	2,4-DNT
2,6-dinitrotoluene	2,6-DNT
hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX
methyl-2,4,6-trinitrophenylnitramine	Tetryl
nitrobenzene	NB
2-nitrotoluene	2-NT
3-nitrotoluene	3-NT
4-nitrotoluene	4-NT
octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX
1,3,5-trinitrobenzene	1,3,5-TNB
2,4,6-trinitrotoluene	2,4,6-TNT

4.2. Upon client request, additional target analytes may be added to this analysis. However, it needs to be demonstrated that any added compounds lend themselves to Method 8330 determination, either by regulatory reference or validation studies.

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of high performance liquid chromatograph (HPLC), skilled in the interpretation of high performance liquid chromatograms, and experienced in handling explosive materials.

5. METHOD SUMMARY

5.1. EPA Method 8330 describes chromatographic procedures that will allow for the trace analysis of explosive residues in the extract and their qualitative and quantitative analysis by high performance liquid chromatography. Detection is achieved using a UV detector.

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory methods include the following:

5.2.1. Methods for Aqueous Samples

5.2.1.1. Low-Level Salting-Out Method with no Evaporation: Aqueous samples of low concentration are extracted by a salting-out extraction procedure with acetonitrile and sodium chloride. The concentrated extract is diluted 1:1 (v/v) with reagent water. An aliquot is separated on a C18 reversed phase column, determined at 254 nm, and confirmed on a CN or Biphenyl reversed phase column.

5.2.1.2. High-Level Direct Injection Method: Aqueous samples of higher concentration can be diluted 1:1 (v/v) with methanol or acetonitrile (if HMX is an important target analyte, methanol is preferred), filtered, then separated on a C18 reversed phase column, determined at 254 nm, and confirmed on a CN or Biphenyl reversed phase column.

5.2.2. Method for Soil/Sediment Samples

5.2.2.1. Soil and sediment samples are extracted using acetonitrile in an ultrasonic bath at room or below room temperature, filtered, diluted with reagent water, then separated on a C18 reversed phase column, determined at 254 nm, and confirmed on a CN or Biphenyl reversed phase column.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts,

digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.

6.12. Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.27. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

6.28. Term Specific to Trace Analysis of Explosives

6.28.1. Salting Out: A technique which promotes phase separation through the addition of a salt to make the aqueous phase of an emulsion too polar to support a less polar phase.

7. INTERFERENCES

7.1. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination. In addition, sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.3. 2,4-DNT and 2,6-DNT elute at similar retention times (retention time difference of 0.2 minutes). A large concentration of one isomer may mask the response of the other isomer. If it is not apparent that both isomers are present (or are not detected), an isomeric mixture should be reported.

7.4. Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All aqueous samples expected to contain Tetryl should be diluted with acetonitrile prior to filtration and acidified to pH < 3. All samples expected to contain Tetryl should not be exposed to temperatures above room temperature.

7.5. Degradation products of Tetryl appear as a shoulder on the 2,4,6-TNT peak. Peak heights rather than peak areas should be used when Tetryl is present in concentrations that are significant relative to the concentration of 2,4,6-TNT.

8. SAFETY

8.1. Extra caution should be taken when handling the analytical standard neat materials for the explosives, and when handling soil or waste samples which are highly contaminated with the explosives. Follow the instruction for drying the neat materials at ambient temperatures.

8.2. It is advisable to screen soil or waste samples using EPA Methods 8515 or 8510 to determine whether high concentrations of explosives are present. Soil samples containing as much as 2% of 2,4,6-TNT have been safely ground. Samples

containing higher concentrations should not be ground in the mortar and pestle or a mechanical grinder.

8.2.1. EPA Method 8515 is for 2,4,6-TNT; however, other nitroaromatics will also cause a color to be developed and provide a rough estimation of their concentrations.

8.2.2. EPA Method 8510 is for RDX and HMX; however, mixtures of RDX (and/or related compounds with 2,4,6-TNT) will cause an orange color, rather than a pink color to form.

8.3. Visual observation of a soil sample is also important when the sample is taken from a site expected to contain explosives. Lumps of material that have a chemical appearance should be suspect and not ground.

8.3.1. Explosives are generally a very finely ground grayish-white material.

8.3.2. Chunks of TNT-based explosives that have been exposed to light are generally reddish-brown to orange in color.

8.4. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.5. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

8.6. Some of the compounds covered by this method have been tentatively classified as known or suspected human carcinogens. Primary standards of these compounds must be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when analysts handle high concentrations of these compounds.

9. ►EQUIPMENT AND SUPPLIES

9.1. High Performance Liquid Chromatograph: Agilent 1100 Series Liquid Chromatograph or equivalent configured with ***the following components***.

9.1.1. Isocratic pump, ***consisting of two-channel, dual-plunger in-series pump, Agilent G1310A Isocratic Pump or equivalent***.

9.1.2. ***Thermostatted column compartment, MetaChem Technologies Inc. MetalTherm™ HPLC Column Temperature Control or equivalent.***

9.1.3. Solvent cabinet.

9.1.4. Autosampler, ***Agilent G1313A Standard Autosampler or equivalent***.

9.2. ***Instrument Software***

9.2.1. ***Agilent ChemStation for LC Version A.10.01[1635] or equivalent.***

9.3. ***Instrument Maintenance and Troubleshooting***

9.3.1. ***Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.***

9.4. Primary Detection Channel

9.4.1. Detector: Agilent 1100 Series Multiple Wavelength Detector.

9.4.2. Analytical Column: 250-mm × 4.6-mm ID, 5-µm particle size, reversed phase, Restek Ultra C18 or equivalent.

9.4.3. Mobile Phase: Methanol (HPLC grade or equivalent) and reagent water at 56:44 (v/v) ratio.

9.5. Confirmation Detection Channel

9.5.1. Detector: Agilent 1100 Series Multiple Wavelength Detector.

9.5.2. Analytical Column: 250-mm × 4.6-mm ID, 5-µm particle size, silica-based reversed phase, Dionex Acclaim Explosives E2 or equivalent.

9.5.3. ***Mobile Phase: Methanol (HPLC grade or equivalent) and reagent water at 50:50 (v/v) ratio.***

9.6. Sample Preparation

9.6.1. Ultrasonic bath, capable of temperature control.

9.6.2. Vortex mixer.

9.6.3. Balance, top loading, capable of weighing to the nearest 0.01 g.

9.6.4. Oven, forced air, without heating.

9.6.5. Magnetic stirrer.

9.6.6. Stirring bars or pellets, Teflon.

9.6.7. Volumetric flasks, 100-mL and 1-L, round bottom, Class A.

9.6.8. Graduated cylinders, 10-mL, 25-mL, 250-mL, 500-mL, and 1-L, Class A.

9.6.9. Pipet, Pasteur, disposable.

9.6.10. Mortar and pestle (or mechanical grinder), steel.

9.6.11. Sieve, 10-mesh.

9.6.12. pH Indicator paper, narrow range (0.0 – 3.0).

9.6.13. Scintillation vial, 40-mL, clear glass, disposable.

9.6.14. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.6.15. Syringe filtration apparatus:

9.6.15.1. Syringe, disposable.

9.6.15.2. Filter, 0.45-µm effective pore size, 25-mm diameter, hydrophobic PTFE (Teflon) membrane and polypropylene housing, disposable, Pall 4501 Acrodisc Syringe Filter or equivalent.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Methanol, CH_3OH, HPLC grade or equivalent.

10.1.2. Acetonitrile, CH_3CN, HPLC grade or equivalent.

10.1.3. Sodium chloride, NaCl, anhydrous, reagent grade or equivalent.

10.1.4. Sodium chloride, NaCl, 325-g/L or 32.5% (w/v). Prepare the solution by dissolving anhydrous NaCl in reagent water.

10.1.5. Calcium chloride, $CaCl_2$, 5-g/L or 0.5% (w/v). Prepare the solution by dissolving anhydrous $CaCl_2$ (reagent grade or equivalent) in reagent water.

10.1.6. Hydrochloric acid, HCl, 1:1 (v/v). Prepare the solution by diluting concentrated HCl (reagent grade or equivalent) with reagent water.

10.1.7. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v). Prepare the solution by dissolving granular $Na_2S_2O_3$ (reagent grade or equivalent) in reagent water.

10.1.8. Reagent water, interferant free, nano-pure.

10.1.9. Sand, washed, sea or standard Ottawa, < 10-mesh.

10.1.10. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. ►Standards

10.2.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 1000/2000 ppm of each target analyte, and 1000 ppm of surrogate are used to prepare calibration and check standards.

10.2.2. Calibration standard solution containing 20 ppm of each target analyte and 20 ppm of surrogate in acetonitrile is used to prepare calibration standards.

10.2.2.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppm)				
nitroaromatics/nitramines	0.02	1.0	2.0	5.0	10.0
surrogate	0.02	1.0	2.0	5.0	10.0

10.2.2.2. The ***2.0***-ppm standard is also used as the continuing calibration verification solution.

10.2.2.3. The calibration standards must be prepared fresh on the day of calibration.

10.2.3. Initial calibration verification (ICV) solution containing 2.0 ppm of each target analyte and 2.0 ppm of surrogate in acetonitrile. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.4. Continuing calibration verification (CCV) solution containing ***2.0 ppm of each target analyte and 2.0 ppm of*** surrogate in acetonitrile. The CCV solution is of a source same as that used for the initial five-point calibration.

10.2.5. Surrogate standard solution containing 1000 ppm of 1,2-dinitrobenzene (1,2-DNB) in methanol.

10.2.5.1. Add 20 µL of the surrogate standard to each aqueous sample including the quality control (QC) check samples and method blanks prior to extraction.

10.2.5.2. Add 80 µL of the surrogate standard to each solid sample including the quality control (QC) check samples and method blanks prior to extraction.

10.2.6. Spike standard solution containing 1000 ppm of each target analyte in acetonitrile. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.6.1. The standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

10.2.6.2. Add 20 µL of the spike standard to each aqueous MS/MSD and LCS/LCSD sample prior to extraction.

10.2.6.3. Add 80 µL of the spike standard to each solid MS/MSD and LCS/LCSD sample prior to extraction.

10.2.6.4. The spike standard solution contains all anticipated target analytes.

10.2.7. All working standards must be replaced after 30 days ***(unless specified otherwise)*** or sooner if ***routine QC or*** comparison with check standards indicates a problem.

10.2.7.1. Store all working standards under dark and refrigerated conditions.

10.2.8. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2.8.1. ***Check all opened stock standards frequently for signs of degradation or evaporation.***

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1-L pre-cleaned amber glass containers with Teflon-lined closures. ***Collect all samples in duplicate.***

11.1.1. ***If the aqueous sample is known or suspected to contain residual chlorine, add 4 mL of the 10% $Na_2S_2O_3$ solution per 1 L of sample. The 10% $Na_2S_2O_3$ solution may be added to the sample container prior to sample collection.***

11.1.2. ***If MS/MSD analyses are required, collect one sample in quadruplicate.***

11.2. Solid samples should be collected in 4-oz ***or 8-oz*** pre-cleaned clear glass wide-mouth jars, ***or 6-in decontaminated stainless steel or brass sleeves*** with Teflon-lined closures.

11.3. Samples ***shall*** be maintained in a chilled state (≤ 4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.4. Upon receipt, the samples are stored in a ***0~6***°C cooler. All samples expected to contain Tetryl should not be exposed to temperature above the room temperature.

11.4.1. Aqueous samples must be extracted within 7 days of sample collection.

11.4.2. Non-aqueous samples must be extracted within 14 days of sample collection.

11.4.3. All extracts are then stored under dark and refrigerated (***0~6***°C) conditions and must be analyzed within 40 days post extraction.

12. ►QUALITY CONTROL

12.1. Initial Calibration (IC)

12.1.1. The initial five-point calibration must be established prior to the processing of sample extracts.

12.1.2. The IC is deemed valid if the %RSD for each analyte is ≤ 20%.

12.1.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.1.3.1. ***If the RSD of any analyte is unacceptable, review the results (e.g., proper identification, area count, response factor, etc.) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards.***

12.1.3.2. ***If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis to rule out problems due to random chance.***

12.1.3.2.1. ***In some cases, replace the calibration standard may be necessary.***

12.1.3.3. ***If a calibration standard is replaced and/or reanalyzed, recalculate the RSD, and document the rationale for re-analysis.***

12.2. Initial Calibration Verification (ICV)

12.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

12.2.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). ***Document the unacceptable result and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable***, investigate, effect corrective action, which may include re-preparation of standard solutions ***or instrument maintenance***, and recalibrate.

12.3. Continuing Calibration Verification (CCV)

12.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.3.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

12.3.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. ***Document the unacceptable result*** and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, ***effect corrective action and*** recalibrate.

12.4. Retention Time Window

12.4.1. Establishment of retention time window width is accomplished by making three injections of CCV standards throughout the course of a 72-hour period. Serial injections over a shorter period of time may result in narrow retention time window width that does not accurately account for variations over several days.

12.4.1.1. Retention time window width is ± 3S (where S is the standard deviation of the three retention times for that analyte/surrogate) ***or ± 0.030 minute, whichever is greater***.

12.4.2. Establishment of retention time window position is accomplished by using the ***midpoint calibration standard once per initial calibration, and by using a*** CCV standard at the beginning of an analytical sequence.

12.4.2.1. ***When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S or ± 0.030 minute, whichever is greater.***

12.4.2.2. ***When initial calibration is <u>not</u> performed***, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the CCV standard ± 3S ***or ± 0.030 minute, whichever is greater***.

12.4.3. Retention time for each analyte/surrogate ***in the calibration verification standard*** is verified as follows:

12.4.3.1. ***When initial calibration is performed, the ICV standard and all CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the midpoint calibration standard.***

12.4.3.2. ***When initial calibration is <u>not</u> performed***, all succeeding CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the first CCV standard.

12.4.3.3. If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and/or position, if necessary.

12.5. Event Based Quality Control (MBs and LCS/LCSDs)

12.5.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB) and a laboratory control sample and laboratory control sample duplicate (LCS/LCSD).

12.5.2. ***The acceptance criteria for MBs are as follows:***

12.5.2.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

12.5.2.2. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.5.2.3. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples ***re-processed and/or*** re-analyzed.

12.5.3. The acceptance criteria for LCS/LCSD compounds are as follows:

12.5.3.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 40% and 160%, respectively. The RPD is ≤ 20%.

12.5.3.1.1. ***If historical data is available, the lower and upper acceptance limits for %REC and RPD of***

each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.5.3.2. All LCS/LCSD compounds must be within acceptance limits. However, if a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside of control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary.

12.5.3.3. ME is defined as being beyond the LCS control limit (3 standard deviations), but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean.

12.5.3.4. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than 11 analytes.

12.5.3.5. The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number of Analytes Allowed in ME of the LCS Control Limit
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

12.5.3.6. Marginal exceedances must be random. If the same analyte exceeds the LCS control limit 2 out of 3 consecutive LCS, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

12.6. Matrix Based Quality Control (Surrogates and MS/MSDs)

12.6.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and surrogates added to each sample.

12.6.2. The acceptance criteria for surrogate spike compound recoveries are as follows:

12.6.2.1. The lower and upper acceptance limits for %REC of each surrogate compound are 40% and 160%, respectively.

12.6.2.1.1. ***If historical data is available, the lower and upper acceptance limits for %REC of each surrogate compound are based upon the historical average recovery ± 3S that is updated at least annually.***

12.6.2.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

12.6.2.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration or a problem may have occurred during extraction. The data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgement, this data should be used in conjunction with other available QC information.

12.6.2.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.6.2.4.1. Check the surrogate standard solutions for degradation and contamination.

12.6.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recoveries, the same extract should be re-analyzed.

12.6.2.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be ***re-processed*** and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.1. If, upon ***re-processing*** and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all

associated samples ***re-processed*** and re-analyzed.

12.6.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

12.6.3. The acceptance criteria for MS/MSD compounds are as follows:

12.6.3.1. The lower and upper acceptance limits for %REC of each MS/MSD compound are 40% and 160%, respectively. The RPD is ≤ 20%.

12.6.3.1.1. ***If historical data is available, the lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.***

12.6.3.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.6.3.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.4. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.7. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples ***re-processed*** and re-analyzed.

12.8. Additional information regarding internal quality control checks is provided in SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. Top Loading Balance

13.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights ***as outlined in the current revision of SOP-T043***.

13.1.2. Calibration shall be within ± 2% ***or ± 0.02 g, whichever is greater***. If the values are not within these limits, recalibrate the balance.

13.2. ***Chromatograph*** Initial Calibration

13.2.1. Establish an acceptable five-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.2.1.1. Recalibration is required for the following maintenance procedures.

13.2.1.1.1. Change, replace, or reverse the analytical column.

13.2.2. After obtaining an acceptable five-point calibration curve and prior to processing ***field or*** QC sample extracts, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.2.

13.2.3. The initial five-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

13.3. ***Retention Time Window***

13.3.1. Retention time window width for each analyte/surrogate is generated by running three CCV standards over a 72-hour period. Retention time window width determination shall be performed at method set-up, following column changes, after major instrument maintenance or when a significant retention time shift is suspected.

13.3.2. Document the serial number of the analytical column associated with the retention time window study.

13.3.3. ***Record the retention time in minutes for each analyte/surrogate to three decimal places.***

14. ►PROCEDURE

14.1. Aqueous Sample Preparation

14.1.1. Screen waste samples with the high-level method (1–50 mg/L) to determine if the low-level method (< 1 mg/L) is required. Most groundwater samples should be processed by the low-level method.

14.1.2. Low-Level Method (Salting-Out Extraction)

14.1.2.1. Add 251.3 g of sodium chloride and 770 mL of an aqueous sample into a 1-L volumetric flask. Record the volume of the sample to the nearest 1 mL.

14.1.2.1.1. The MB/LCS/LCSD consists of 770 mL of clean reagent water, and the MS/MSD consists of 770 mL of aqueous sample in each analytical batch selected for spiking.

14.1.2.2. Add the surrogate standard solution to all samples, matrix spikes, laboratory control samples, and method blanks.

14.1.2.3. Add the spike standard solution to all matrix spikes and laboratory control samples.

14.1.2.4. Place the 1-L volumetric flask on a magnetic stirrer and add a stirring bar to mix the contents at maximum speed until the salt is completely dissolved.

14.1.2.5. Add 164 mL of acetonitrile into the 1-L volumetric flask while the solution is being stirred and continue to stir for 15 minutes. Turn off the stirrer and allow the phases to separate for 10 minutes.

14.1.2.6. Remove the acetonitrile extract (upper layer) with a Pasteur pipet and transfer it to a 100-mL volumetric flask. The inclusion of a few drops of salt water at this point is unimportant.

14.1.2.7. Repeat the extraction one more time using 10 mL of fresh acetonitrile (Sections 14.1.2.5. through 14.1.2.6.). Combine the two extracts.

14.1.2.8. Place the 100-mL volumetric flask containing acetonitrile extracts on a magnetic stirrer and add a stirring bar to mix the contents.

14.1.2.9. Add 84 mL of 325-g/L NaCl solution into the 100-mL volumetric flask while the solution is being stirred and continue to stir for 15 minutes. Turn off the stirrer and allow the phases to separate for 10 minutes.

14.1.2.10. Remove the acetonitrile extract (upper layer) with a Pasteur pipet and transfer it to a 10-mL or 25-mL graduated cylinder. Minimize the amount of water transferred with the acetonitrile. The water contains a high concentration of sodium chloride that produces a large peak at the beginning of the chromatogram, where it could interfere with the HMX determination.

14.1.2.11. Repeat the extraction one more time using 1.0 mL of fresh acetonitrile (Sections 14.1.2.9. through 14.1.2.10.). Combine the two extracts.

14.1.2.12. Record the volume of the acetonitrile extract to the nearest 0.1 mL. The resulting extract volume is about 4.5–6.5 mL.

14.1.2.12.1. It should be noted that the RL for each sample differs due to the variation of extract volume.

14.1.2.13. Perform 1:1 dilution with equal volumes of the acetonitrile extract (Section 14.1.2.12.) and reagent water.

14.1.2.13.1. If Tetryl is a suspected analyte, perform the dilution with reagent water or acetonitrile and adjust the diluted extract with 1:1 HCl to pH < 3.

14.1.2.14. Mix the solution thoroughly and collect it in an autosampler vial.

14.1.2.14.1. If the diluted extract is turbid, filter it through a Teflon filter using a disposal syringe. Discard the first 0.5-mL filtrate and collect the remainder in an autosampler vial.

14.1.3. High-Level Method

14.1.3.1. Add 5.0 mL of an aqueous sample into a clean scintillation vial. Record the volume of the sample to the nearest 0.1 mL.

14.1.3.1.1. The MB/LCS/LCSD consists of 5.0 mL of clean reagent water, and the MS/MSD consists of 5.0 mL of aqueous sample in each analytical batch selected for spiking.

14.1.3.2. Add the surrogate standard solution to all samples, matrix spikes, laboratory control samples, and method blanks.

14.1.3.3. Add the spike standard solution to all matrix spikes and laboratory control samples.

14.1.3.4. Add 5.0 mL of acetonitrile into the scintillation vial. Cap the vial with a Teflon-lined cap.

14.1.3.4.1. If HMX is a suspected analyte, use 5.0 mL of methanol instead of acetonitrile to improve quantitation.

14.1.3.5. Shake the solution thoroughly and filter it through a Teflon filter using a disposal syringe. Discard the first 3.0-mL filtrate and collect the remainder in an autosampler vial.

14.2. Soil/Sediment Sample Preparation

14.2.1. Dry soil/sediment samples in air at room temperature or colder to a constant weight. Do not expose the samples to direct sunlight.

14.2.2. Grind and homogenize a dried soil/sediment sample thoroughly in an acetonitrile-rinsed mortar and pestle to pass a 10-mesh sieve.

14.2.2.1. Screen the samples via EPA Methods 8515 or 8510 prior to grinding in a mortar and pestle (Section 8.2. and Section 8.3.).

14.2.3. Add 10.0 g of a dried, homogenized soil/sediment sample into a clean scintillation vial. Record the mass of the sample to the nearest 0.1 g.

14.2.3.1. The MB/LCS/LCSD consists of 10.0 g of washed sea sand, and the MS/MSD consists of 10.0 g of solid sample in each analytical batch selected for spiking.

14.2.4. Add the surrogate standard solution to all samples, matrix spikes, laboratory control samples, and method blanks.

14.2.5. Add the spike standard solution to all matrix spikes and laboratory control samples.

14.2.6. Add 20.0 mL of acetonitrile into the scintillation vial. Cap the vial with a Teflon-lined cap.

14.2.7. Vortex swirl the vial for 1 minute, then place it in a cooled (< 30°C) ultrasonic bath for 18 hours. After sonication, allow the solution to settle for 30 minutes.

14.2.8. Remove 5.0 mL of supernatant (acetonitrile extract) with a Pasteur pipet and transfer it to a clean scintillation vial.

14.2.9. Perform 1:1 dilution with equal volumes of the acetonitrile extract (Section 14.2.8.) and 5-g/L $CaCl_2$ solution. Mix the solution thoroughly and let it stand for 15 minutes.

14.2.10. Filter the solution through a Teflon filter using a disposal syringe. Discard the first 3.0-mL filtrate and collect the remainder in an autosampler vial.

14.3. Thoroughly document all aspects of the extraction in an extraction logbook. This logbook includes:

14.3.1. Extraction date, start time, and end time.

14.3.2. Sample matrix, initial volume or mass, and final volume.

14.3.3. Extraction solvent lot (or identification) number and volume.

14.3.4. Surrogate lot (or identification) number, concentration, and volume added.

14.3.5. Standard lot (or identification) number, concentration, and volume added.

14.3.6. Dilution solvent name and lot (or identification) number.

14.3.7. Final extract volume.

14.3.8. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

14.4. Instrument Setup

14.4.1. UV detection wavelength is set at 254 nm.

14.4.2. Autosampler is set to inject 100 µL of sample or QC extract.

14.4.3. The mobile phase flow for the primary column is set at 1.0 mL/min, and the temperature is set at 30°C.

14.4.3.1. The mobile phase flow rate can be checked by collecting solvent into a graduated cylinder.

14.4.4. Purge the autosampler and all solvent lines prior to analysis.

14.4.4.1. Pass at least 15 void volumes of mobile phase through the column and continue until the baseline is level at the UV detector's greatest sensitivity.

14.5. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence. If the QC and retention time criteria are met, the initial calibration is assumed to be valid and sample

analysis may resume. The acceptance criteria are listed in Section 12.3. and Section 12.4.3.

14.5.1. If a failed CCV is the first of the day, effect corrective action prior to analyzing any samples.

14.5.2. If ***a failed CCV is <u>not</u> the first of the day***, effect corrective action and reanalyze all samples since the last acceptable CCV.

14.6. Following extraction by one of the methods specified in Section 5.2., the extracts for the QC and actual environmental samples are received in autosampler vials. The autosampler vials are then loaded onto the HPLC sample tray.

14.7. ***Standard and*** sample vials are loaded in the following or other logical order:

1) Instrument Blank (IB)
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 20 per batch, excluding QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

14.7.1. Item 1: The IB is a vial of acetonitrile used to determine whether the HPLC system is free of interferants. Additional instrument blanks may also be added elsewhere in the sequence, as necessary (i.e., after suspected high level samples). ***IB is optional.***

14.7.2. Items 2 and 9: A CCV is used to verify the acceptance of the initial five-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

14.7.2.1. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample extract re-analyses that would be required in the event of an unacceptable CCV.

14.7.3. Item 3: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.7.3.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid samples, the LCS consists of the specified compounds spiked into washed sea sand.

14.7.3.2. One LCS is required every day ***preparatory methods (i.e., extractions, filtrations, etc.)*** are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.7.4. Item 4: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.7.5. Item 5: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (i.e., surrogates, etc.).

14.7.5.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of washed sea sand.

14.7.5.2. One MB is required every day ***preparatory methods (i.e., extractions, filtrations, etc.)*** are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.7.5.3. When samples that are ***processed*** together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of acetonitrile must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.7.6. Item 6: Up to 20 sample ***(excluding QC check sample and method blank)*** extracts per batch. Complex extracts should be sufficiently diluted to ensure that instrument is not contaminated. Dilution of extracts will result in increased reporting limits.

14.7.6.1. ***All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.***

14.7.7. Item 7: The MS is an actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.7.7.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement

is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.5.

14.7.7.2. One MS is required for every batch of 20 samples per matrix or portion thereof ***processed*** concurrently.

14.7.8. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.7.9. ***Solvent blanks may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration sample extracts), to check for potential carryover or cross-contamination.***

14.8. Ensure that a sufficient amount of methanol/water is present in the mobile phase bottle(s) and that a sufficient unused volume exists in the waste bottles at the beginning of the sequence.

14.9. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook ***or on the sequence table printout***.

14.10. Initiate the sequence.

14.11. Data Interpretation

14.11.1. Establish the daily retention time window for each analyte/surrogate (see Section 12.4.2.1. ***and Section 12.4.2.2.***).

14.11.1.1. Tentative identification of an analyte/***surrogate*** occurs when a peak from a sample extract falls within the daily retention time window.

14.11.1.2. Use the succeeding CCV standards analyzed throughout the course of an analytical sequence within a 12-hour shift to evaluate retention time stability (see Section 12.4.3.). If any analyte(s)/***surrogate(s)*** in the CCV standard fall outside of their daily retention time window(s), determine the cause of the problem and effect appropriate corrective action.

14.11.1.2.1. If any analyte(s)/***surrogate(s)*** in the CCV standard fall outside of their daily retention time window(s), then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.

14.11.2. Quantitation of a target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample extract and the calibration standards.

14.11.2.1. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak(s) can be determined.

14.11.2.2. Determine the concentration based on the initial calibration curve.

14.11.2.2.1. Calculate the concentration of each target analyte in a sample extract using the average of the initial RFs and the area of the characteristic peak. The formula for calculating concentration is listed in Section 15.7.

14.11.2.3. If the instrument response exceeds the calibration range, dilute the extract and reanalyze.

14.11.3. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

14.11.3.1. ***When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.***

14.11.3.2. ***When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially integrating a peak, etc.), manual integrations performed by the analyst are necessary.***

14.11.3.3. ***Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.***

15. CALCULATIONS

15.1. The response factor is calculated as follows:

$$RF = \frac{A_x}{C_x}$$

where: RF = response factor for target analyte being measured.
A_x = area of the characteristic peak(s) for target analyte being measured.
C_x = concentration of target analyte being measured in µg/L.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.

RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RF_{ave} - RF_{daily}|}{RF_{ave}} \times 100$$

where: %D = percent difference.
RF_{daily} = daily RF for the target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.4. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x}{RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in µg/L.
A_x = area of the characteristic peak(s) for target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
V_A = volume of aqueous sample extracted in mL.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid sample extracted in g.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.10. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and µg/kg (ppb) for soil and solid waste samples.

15.11. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. ►If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples ***re-processed*** and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 40% and

160%, respectively. The RPD is ≤ 20%. All LCS/LCSD compounds must be within acceptance limits (see Section 12.5.2. for additional information).

18.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.3. The acceptance criteria for surrogate compound recoveries are predetermined. The lower and upper acceptance limits for %REC of each surrogate compound are 40% and 160%, respectively.

18.3.1. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

18.3.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.3. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.3.1. Check the surrogate standard solutions for degradation and contamination.

18.3.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample or extract should be re-analyzed.

18.3.3.3. ►If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be ***re-processed*** and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.1. If, upon ***re-processing*** and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all

associated samples ***re-processed*** and re-analyzed.

18.3.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD compounds are predetermined. The lower and upper acceptance limits for %REC of each MS/MSD compound are 40% and 160%, respectively. The RPD is ≤ 20%.

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and µg/kg (ppb) for soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8330, USEPA, Revision 0, September 1994.

22.2. *Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8330B, USEPA, Revision 2, October 2006.

22.3. *Determinative Chromatographic Separations*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000C, USEPA, Revision 3, March 2003.

22.4. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.5. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, November 2000.

22.6. *Organic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, November 2000.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Additional Quality Control Criteria for ***Department of Defense*** Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8330 Revision 0 are noted.

Calscience SOP M414 Section	Reference Document EPA Method 8330 Section	Summary of Modification
9.4.	7.2	Mobile phase methanol to water ratio is modified.
14.2.	7.1.2.2	Solid sample mass and solvent for extraction are modified.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
2.3	Section 6: Add LOD/LOQ definitions. Section 9: Update the list of equipment and supplies. Section 10: Insert reference to verification logbook. Section 13: Add calibration requirement for changing column.	K. Chang	02/03/12

Revision	Description	Author(s)	Effective Date
2.3	Section 14: Specify the number of samples per analytical batch. Appendix A: Update DoD quality control requirements and criteria.	K. Chang	02/03/12
2.4	Section 3: Revise reporting limits and add reference to detection limits. Section 9: Update the list of equipment and supplies. Section 10: Revise CCV standard preparation and add standard checking procedure. Section 11: Update sampling requirements. Section 12: Update quality control procedure and criteria. Section 13: Add reference to SOP-T043 for support equipment and revise calibration criteria. Section 14: Revise analytical and manual integration procedures. Section 18: Revise terminology. Section 25: Add revision history. Appendix A: Delete Section 3. of the appendix.	K. Chang	03/21/12

Appendix A

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8330, Nitroaromatics and Nitramines by High Performance Liquid Chromatography – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The spike standard solution shall contain all anticipated target analytes.

3.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

4. QUALITY CONTROL

4.1. Limit of Detection (LOD)

4.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

4.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

4.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

4.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

4.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

4.1.2.3. If these criteria are not met, perform either one of the following tasks.

4.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

4.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

4.1.3. No samples shall be analyzed without a valid LOD.

4.2. Limit of Quantitation (LOQ)

4.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

4.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

4.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

4.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

4.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

4.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

4.3. Initial Calibration Verification (ICV)

4.3.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

4.4. Continuing Calibration Verification (CCV)

4.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

4.4.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

4.4.3. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

4.5. Retention Time Window

4.5.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a low-to-midpoint CCV standard at the beginning of an analytical sequence.

4.5.1.1. When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S.

4.5.1.2. When initial calibration is not performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the low-to-midpoint CCV standard ± 3S.

4.5.2. Retention time for each analyte/surrogate in the calibration verification standard is verified as follows:

4.5.2.1. When initial calibration is performed, the ICV standard and all CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the midpoint calibration standard.

4.5.2.2. When initial calibration is not performed, all succeeding CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the first CCV standard.

4.5.2.3. If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and/or position, if necessary.

4.6. Event Based Quality Control (MBs and LCS/LCSDs)

4.6.1. Method Blanks (MBs)

4.6.1.1. The MB is considered to be contaminated if one of the following conditions is met.

4.6.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

4.6.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

4.6.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

4.6.1.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

4.6.1.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific

analyte(s) in all samples associated with the failed MB.

4.6.2. Laboratory Control Samples (LCS/LCSDs)

4.6.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound in aqueous matrix are listed below.

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
2-Am-DNT	50	155	35	170
4-Am-DNT	55	155	40	170
1,3-DNB	45	160	30	175
2,4-DNT	60	135	50	145
2,6-DNT	60	135	50	150
RDX	50	160	35	180
Tetryl	20	175	10	200
NB	50	140	35	155
2-NT	45	135	30	150
3-NT	50	130	35	145
4-NT	50	130	35	145
HMX	80	115	75	120
1,3,5-TNB	65	140	50	150
2,4,6-TNT	50	145	35	160

4.6.2.2. The lower and upper acceptance limits for %REC of each LCS/LCSD compound in solid matrix are listed below.

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
2-Am-DNT	80	125	75	130
4-Am-DNT	80	125	75	130
1,3-DNB	80	125	70	135
2,4-DNT	80	125	75	130
2,6-DNT	80	120	70	130
RDX	70	135	65	145
Tetryl	10	150	0	172
NB	75	125	70	130
2-NT	80	125	70	130
3-NT	75	120	70	130
4-NT	75	125	70	135
HMX	75	125	65	135
1,3,5-TNB	75	125	65	135
2,4,6-TNT	55	140	45	155

4.6.2.3. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

4.6.2.3.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

4.6.2.4. All project-specific analytes of concern must be within control limits. No marginal exceedance is allowed for any project-specific analyte of concern. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

4.7. Matrix Based Quality Control (Surrogates and MS/MSDs)

4.7.1. Matrix Spikes (MS/MSDs)

4.7.1.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous and solid matrices are listed below. The RPD is ≤ 30%.

Analyte	Aqueous Matrix Control Limit		Solid Matrix Control Limit	
	Lower	Upper	Lower	Upper
2-Am-DNT	50	155	80	125
4-Am-DNT	55	155	80	125
1,3-DNB	45	160	80	125
2,4-DNT	60	135	80	125
2,6-DNT	60	135	80	120
RDX	50	160	70	135
Tetryl	20	175	10	150
NB	50	140	75	125
2-NT	45	135	80	125
3-NT	50	130	75	120
4-NT	50	130	75	125
HMX	80	115	75	125
1,3,5-TNB	65	140	75	125
2,4,6-TNT	50	145	55	140

5. PROCEDURE

5.1. Instrument Setup

5.1.1. The mobile phase flow for the confirmation column is set at 1.0 mL/min, and the temperature is set at 30°C.

5.1.1.1. The mobile phase flow rate can be checked by collecting solvent into a graduated cylinder.

5.2. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

5.3. Standard and sample vials are loaded in the following or other logical order:

1) Instrument Blank (IB)

2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 10 per batch, excluding QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

5.3.1. Items 2 and 9: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

5.3.2. Item 6: Up to 10 sample (excluding QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

5.3.3. Item 7: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

5.3.3.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

5.3.4. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

5.4. Data Interpretation

5.4.1. Tentative identification of a target analyte occurs when a peak from a sample extract falls within the analyte's retention time window. Confirmation is necessary when the composition of samples is not well characterized. Qualitative confirmation techniques are by second column with dissimilar stationary phase, HPLC/UV data at two different wavelengths where UV spectra are generated with a diode array detector, or HPLC data from two different detectors.

5.4.2. Second column confirmation is made on a "confirmation" channel configured with a column of dissimilar stationery phase and a second detector. The principle is that the retention time of the target analyte will differ between the primary and confirmation column and, unless the detected compound is the particular target analyte, it will not be observed within both retention time windows.

5.4.2.1. Report the higher result between the primary and confirmation column. The RPD between results must be ≤ 40%.

5.4.2.1.1. If one result is significantly higher (e.g., > 40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are observed, examine the baseline parameters established by the instrument data system (or operator) during peak integration.

5.4.2.1.2. If no anomalies are observed, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the higher result. This approach is conservative relative to protection of the environment. The data user should be advised of the disparity between the results on the two columns.

5.4.2.2. In cases where a peak is not observed in the confirmation column's retention time window, the analyte is reported as "ND."

5.4.2.3. A calibration curve and retention time window for each analyte/surrogate are also established and maintained for the confirmation channel. The calibration and quality control requirements for the confirmation channel are identical to those of the primary channel.

5.4.2.4. The flagging criteria and data reporting procedure for second column confirmation are as follows:

5.4.2.4.1. If RPD is > 40%, apply the appropriate data qualifier (J-flag) and document in the case narrative.

5.4.2.4.2. Follow project-specific reporting requirements when reporting data.

5.4.2.4.2.1. If project-specific reporting requirements are unavailable, apply method-specific reporting requirements.

5.4.2.4.2.2. If method-specific reporting requirements are unavailable, report the results from the primary column or detector, unless there is a scientifically valid and documented reason for not doing so.

5.4.2.4.3. Identify unconfirmed results with the appropriate data qualifiers and document in the case narrative.

5.4.3. Confirmation is required for all positive results unless the samples meet all of the following requirements:

5.4.3.1. All samples (liquid or solid) come from the same source (e.g., same monitoring well). However, samples of the same matrix from the same site but from differing sources (e.g., different monitoring wells) are not exempted.

5.4.3.2. All chemical parameters have been previously analyzed, identified, and confirmed by a second column with dissimilar stationary phase, HPLC/UV data at two different wavelengths where UV spectra are generated with a diode array detector, or HPLC data from two different detectors. Documentation of such must be maintained.

5.4.3.3. The resulting chromatograms are relatively simple and do not contain complex or overlapping peaks.

5.4.3.4. Chromatograms are largely unchanged from those for which confirmation was carried out.

6. REFERENCES

6.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Title : **►ORGANOTINS by KRONE et al., (1989) via GC/MS and Selected Ion Monitoring (SIM)**

Document No. : SOP-M442
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Revision 3.0 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 08/14/14
MANAGEMENT **DATE**

_____ 08-14-14
QA DEPARTMENT **DATE**

1. ►METHOD IDENTIFICATION

1.1. Organotins by Krone et al., (1989) ***via*** GC/MS ***and Selected Ion Monitoring (SIM).***

2. ►APPLICABLE MATRICES

2.1. This method is applicable for water/aqueous, soil/solids, marine sediments and ***tissue matrices.***

3. ►DETECTION LIMITS

3.1. The estimated ***reporting*** limits (RLs) for this method are 3ng/L for aqueous samples, 3µg/kg (wet weight) for soil, sediment or tissue samples ***as supported by the MDL study and low cal point.*** The RLs will be proportionally higher for samples that require dilution.

3.2. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedures on establishing detection and reporting limits.

4. ►SCOPE AND APPLICATION

4.1. ***This method is used to determine the concentration of Organotin organic compounds in various matrices using GCMS in Selected Ion Monitoring (SIM) mode.***

4.2. The following compounds may be determined by this method:

Tetrabutyltin Tributyltin Dibutyltin Monobutyltin

4.3. Eurofins Calscience routinely reports Tributyltin. In the event that one or more of the additional analytes are required, please refer to section 12.6.2.

4.4. This method is restricted to use by or under the supervision of analysts experienced in the use of GC/MS and skilled in the interpretation of mass spectra ***and SIM mode.***

5. ►METHOD SUMMARY

5.1. This method describes chromatographic procedures that will allow for the separation and derivitization of the compounds in the extract and for their qualitative and quantitative analysis by mass spectrometry. Detection is achieved using a mass selective detector in Selected Ion Monitoring (SIM) mode.

5.2 Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample ***as outlined in section 14. Analytical data reported will indicate "SOP M442" as the extraction method.***

5.2.1 Additional extraction procedures may be used provided the associated MDL study displays that the procedure is sufficiently sensitive to achieve the low reporting limits required by this method.

5.3 Sample clean-up using mercury, silica gel and/or alumina is performed as warranted by the look of the extract or chromatographic performance. Please refer to section 14.2.

5.4 Samples are extracted using 0.1% Tropolone in Hexane, the extracts are concentrated and derivitized via Pentylmagnesium bromide Grignard reagent, and direct injected into the GC/MS system.

5. DEFINITIONS

5.1. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

5.2. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

5.2.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours.

5.2.2. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

5.3. Derivitization: A technique which transforms a chemical compound into a product (the reaction's derivate) of similar chemical structure, called a derivative.

5.4. Grignard Reagent: A Grignard reagent has a formula RMgX where X is a halogen, and R is an alkyl or aryl (based on a benzene ring) group.

5.5. Grignard Reaction: A organometallic chemical reaction in which alkyl, vinyl, or aryl-magnesium halides (Grignard reagents) add to a carbonyl group in an aldehyde or ketone. This reaction is an important tool for the formation of carbon–carbon bonds.

5.6. Holding Times: The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

5.7. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

5.8. Laboratory Control Sample: A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

5.9. Mass-to-Charge Ratio (m/z): The dimensionless quantity formed by dividing the mass of an ion in unified atomic mass units by its charge number (regardless of sign).

5.10. Matrix Spike: A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

5.11. Matrix Spike Duplicate: A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

5.12. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

5.13. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

5.14. Please refer to the current revision of the Eurofins Calscience, Inc. Quality Systems Manual for additional terms and definitions.

6. ►COMMENTS AND INTERFERENCES

6.1. Chemists are responsible for reviewing the chemist worksheet for special instructions as related to sample preparation, analysis and/or reporting.

6.2. This process uses a Grignard reaction to complete the derivitization. The process must be kept away from exposure to air and moisture in order to have a complete reaction as both water and air will rapidly destroy the reagent by protonolysis or oxidation. Reagents used for this reaction must be stored in sealed containers and kept moisture free.

6.3. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination. In addition, sample syringes should be thoroughly rinsed with solvent between sample injections.

6.4. Interference can also occur when "dirty" samples leave residue in the injector or column. To minimize this effect, guard columns should be used and cut or replaced frequently. Also, the column can be "baked" after such samples.

6.5. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7. SAFETY

7.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals and samples.

7.2. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

8. ►EQUIPMENT AND SUPPLES

8.1. A gas chromatography system comprised of the following:

8.1.1. Gas Chromatograph: Agilent 6890N Gas Chromatograph configured with an Agilent 7683 autoinjector, or equivalent.

8.1.2. Mass Spectrometer: Agilent 5973Network Mass Selective Detector (MSD), Agilent 5975B MSD, Agilent 5975C MSD, or equivalent capable of scanning from 35 to 270amu every 1 second or less, using 70 volts (nominal) electron energy in the electron-impact ionization (EI) mode, and configured with the following components:

8.1.3. Electron-ionization ion source.

8.1.4. Hyperbolic quadrupole mass filter.

8.1.5. High energy dynode (HED) electron multiplier (EM) detector.

8.1.6. Column: HP-5 MS, 30m x 0.25mm ID, 0.25µ film thickness, silicone-coated fused-silica capillary column, or equivalent.

8.2. Instrument Software

8.2.1. Requires a PC based data system or equivalent.

8.2.2. Agilent MSD ChemStation Version E.02.00.493, Agilent MSD ChemStation Version E.02.01.1177, or equivalent equipped with NIST mass spectral library.

8.3. Instrument Maintenance and Troubleshooting

8.3.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting. Additional information can be found in the user manual or operating guide for the specific instrument.

8.4. Calibrated balance (+/- 0.01gms)

8.5. Separatory funnels, 2L, pear-shaped, borosilicate glass or transparent polytetrafluoroethylene (PTFE), with PTFE stopcock and PTFE stopper or screw cap, Kimax Squibb Separatory Funnel, Nalgene Squibb Transparent FEP Separatory Funnel, or equivalent.

8.6. Shaker, 40–400rpm variable speed, 0–60min mechanical timer, Thermo Scientific Lab-Line MaxQ 3000 Open-Air Shaker Model SHKA3000 or equivalent.

8.7. Nitrogen Blowdown apparatus - Nitrogen, N_2, 99.998%, compressed, Praxair 4.8 grade or higher.

8.8. Pipettes, Pasteur, glass, disposable.

8.9. pH paper test strips for pH of 2.

8.10. Ice Bath

8.11. Graduated cylinders, glass, 100mL, 1000mL, 2000mL, or other capacity, Class 'A'.

8.12. Erlenmeyer flasks, 250mL or other capacity, glass.

8.13. Spatula, stainless steel

8.14. Glass wool, borosilicate glass fiber without binder resin, Pyrex® or equivalent.

8.15. Kuderna-Danish (K-D) apparatus:

8.15.1. Concentrator tube, 10-mL, 19/22 joint size, graduated, without hooks, borosilicate glass, Kimble Kontes 570051-1025 or equivalent.

8.15.2. Evaporation flask, 250-mL or 500-mL, 24/40 top joint size, 19/22 bottom joint size, borosilicate glass, Kimble Kontes 570011-0250, Kimble Kontes 570037-0500, or equivalent.

8.15.2.1. Attach evaporation flask to concentrator tube with clamps.

8.15.3. Snyder column, three-ball macro, 24/40 joint size, without hooks, borosilicate glass, Kimble Kontes 503000-0121 or equivalent.

8.15.4. Snyder column, two-ball micro, 19/22 joint size, without hooks, borosilicate glass, Kimble Kontes 569011-0219 or equivalent.

8.15.5. Clamps, fitting 19/22 joint size, polyacetal, Kimble Kontes 675300-0019 or equivalent.

8.15.6. Stopper, pennyhead, fitting 19/22 joint size, ground glass, Kimble Kontes 850500-1922 or equivalent.

8.16. Filtration apparatus:

8.16.1. Hirsch funnel, short-stemmed, glass.

8.16.2. Glass Wool

8.16.3. Filter paper, untreated or silicone-treated, 150mm or 185mm diameter, Whatman, Whatman 1PS Phase Separator, or equivalent.

8.16.3.1. Rinse silicone-treated filter paper with 5–10ml of the extraction solvent prior to filtering sample extract. Discard the rinsate in the appropriate waste stream.

8.17. Clean-up Apparatus:

8.17.1. Cartridges, solid-phase extraction (SPE)

8.17.2. Vacuum manifold, 24-port, Restek Resprep™ 24-port SPE Manifold, or equivalent, equipped with the following components:

8.17.2.1. Valves (stopcocks), flow control, polypropylene.

8.17.2.2. Valve attachments, polypropylene.

8.17.2.3. Lid, polypropylene.

8.17.2.4. Needle attachments, polypropylene.

8.17.2.5. Sample guides, polypropylene.

8.17.2.6. Vacuum chamber, glass, with vacuum regulator.

8.18. Boiling stones, Teflon.

8.19. Beakers, 2000ml or other capacity, glass.

8.20. Thermometer, calibrated.

8.21. Water bath, heated, capable of temperature control within ± 5°C.

8.22. VOA vials, 28mm × 95mm (40ml capacity), screw top, clear or amber glass, with Teflon- or aluminum foil-lined open top or closed top screw caps and Teflon-lined septa, EPA VOA Vial or equivalent.

8.23. Storage vials, 15mm × 45mm (4ml capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

8.24. Autoinjector/Autosampler vials, 12mm × 32mm (2ml capacity), crimp top, clear glass, with aluminum crimp caps and Teflon-lined septa, disposable.

8.25. Vial inserts, 300µL, clear glass, with conical bottom and spring.

8.26. Syringes, 10µL, 25µL, 50µL, 100µL, 250µL, and 500µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent.

9. ►REAGENTS AND STANDARDS

9.1. Reagents

9.1.1. Hexane, pesticide grade

9.1.2. Tropolone (2-Hydroxy-2,4,6-cycloheptatrien-1-one), reagent grade, Aldrich or equivalent.

9.1.2.1. A 0.1% Tropolone solution is made by adding 1 gram Tropolone to 1 liter of hexane (or other equivalent volumes).

9.1.3. Diatomaceous earth, 60−100-mesh (nominal), white pellets, Varian Chem Tube Hydromatrix™ P/N 198004 or equivalent.

9.1.4. 1:1 Hydrochloric Acid Solution, trace metals grade

9.1.4.1. Prepared by adding equal parts of trace metal grade HCl to reagent grade water. May also be purchased.

9.1.5. Pentylmagnesium Bromide (Grignard Reagent), reagent grade, Aldrich or equivalent.

9.1.6. Sodium Sulfate, reagent grade

9.1.7. Silica gel SPE Cartridge 6mL/1g packing, Restek part # 24038 or equivalent.

9.1.8. Silica gel SPE Cartridge 15ml/5g packing, Restek Part # 26065, or equivalent.

9.1.9. Alumina SPE Cartridge 6ml/2g packing, 60-325 mesh, Supelco part #57083-U, or equivalent.

9.1.10. Silica gel, SiO_2, 60−200-mesh (nominal), white powder, Davisil® grade 62, reagent grade, EMD SX0143U, or equivalent.

9.1.10.1. ***Prior to the first use, activate silica gel by baking at 130°C for at least 16 hours in a shallow tray, loosely covered with aluminum foil. Allow to cool before use.***

9.1.10.2. ***Store the unused, activated silica gel in a desiccator. Re-activate the silica gel at 130°C for at least 12 hours as needed prior to further use.***

9.1.10.2.1. ***Do not heat silica gel above 160°C, for silica gel oxidizes at higher temperatures.***

9.2. Standards

9.2.1. ***Tuning Standard:***

9.2.1.1. Tuning standard solution containing 50ppm of decafluorotriphenyl-phosphine (DFTPP) in methylene chloride. (The solution may also contain benzidine, pentachlorophenol, and 4,4'-DDT, however, these compounds are not used in the evaluation of the instrument.)

9.2.1.1.1. Inject 1µL of the tuning standard for hardware tuning.

9.2.2. Internal Standard:

9.2.2.1. Pre-certified stock standard solution in sealed glass ampules, containing the internal standard, Tetra-n-propyltin, at 2000µg/ml, in methylene chloride. Accustandard #OMT-005, or equivalent.

9.2.2.2. The working internal standard is made up at a concentration of 5µg/ml in hexane

9.2.2.2.1. The internal standard, Tetrapropyltin, is spiked at a level of 100ng/ml or 10µl of 5ng/ml solution into 0.5ml of extract for all QC and samples.

9.2.3. Surrogate Standard:

9.2.3.1. Pre-certified stock standard solution in sealed glass ampules, containing the surrogate, Tripentyltin Chloride, at 2000µg/ml, in methylene chloride. Tripentyltin chloride will derivatize to Tripentyltin.

9.2.3.2. Accustandard #OMT-004, for the primary source and Restek # 31477 for the secondary source, or equivalent.

9.2.4. Initial Calibration Standards:

9.2.4.1. Pre-certified stock standard solution in sealed glass ampules, containing each target compound in organometallic butyltin chloride form (tributyltin chloride, tetrabutyltin, dibutyltin dichloride and butyltin trichloride) at 2000µg/ml, in methylene chloride. Accustandard #OMT-001, or equivalent. These compounds will derivatize to tributyltin, tetrabutyltin, monobutyltin and dibutyltin.

9.2.5. Initial Calibration Verification (ICV) standard:

9.2.5.1. Pre-certified stock standard solution in sealed glass ampules, containing each target compound in organometallic butyltin chloride form (tributyltin chloride, tetrabutyltin, dibutyltin dichloride and butyltin trichloride) at 2000µg/ml, in methylene chloride. Restek #31472, or equivalent. These compounds will derivatize to tributyltin, tetrabutyltin, monobutyltin and dibutyltin.

9.2.5.2. The ICV solution must be of a source differing from that used for the initial five point calibration.

9.2.5.3. The ICV is also used for the LCS and MS spike.

9.2.6. Derivitization of Calibration Standards (ICAL and ICV):

9.2.6.1. Calibration standards will need to be derivitized prior to calibration of the instrument using the following procedure:

9.2.6.1.1. Make a 1ug/ml Organotin Chlorides mixture containing Tetrabutyltin, Tributyltin Chloride, Dibutyltin Chloride, Monobutyltin Chloride and the surrogate Tripentyltin Chloride by dilution from the 2000ug/ml commercial stock solutions using Hexane.

9.2.6.1.2. Take 5ml of a 1ug/ml Organotin Chlorides mixture and add to a 40ml VOA vial.

9.2.6.1.3. Add 0.80ml Pentylmagnesium Bromide.

9.2.6.1.3.1. In order to limit oxidation during derivitization, eliminate the air present in the vial with nitrogen.

9.2.6.1.3.2. Add the Pentylmagnesium Bromide to the vial, turn on the nitrogen such that a gentle stream is emitted and introduce the stream to the vial for approximately 10 seconds. Quickly cap the vial. Turn off the nitrogen.

9.2.6.1.4. Place capped vial on orbital shaker, secure and shake for 60 minutes.

9.2.6.1.5. Place vial in ice bath and add 1:1 HCL until the precipitates are dissolved.

9.2.6.1.6. Pipette off the upper hexane layer and adjust the final volume to 10ml with hexane.

9.2.6.1.7. The resulting solution contains each of the four Organotins and the surrogate at a concentration of 0.5ug/ml.

9.2.6.2. Follow the same process for the ICV using the second source standards.

9.2.7. Initial calibration standards are made up in hexane, as follows:

Analyte	Standard Concentration in ng/ml					
	ICAL 1	ICAL 2	ICAL 3	ICAL 4	ICAL 5	ICV
Tetrabutyltin	3	50	100	200	400	100
Tributyltin	3	50	100	200	400	100
Dibutyltin	3	50	100	200	400	100
Monobutyltin	3	50	100	200	400	100
Tripentyltin (Surr)	3	50	100	200	400	100

9.2.8. Lab Control Sample (LCS) / Matrix Spike (MS) sample standard:

9.2.8.1. Using the ICV source, make up a working spike solution containing 1000ng/ml each of tributyltin chloride, tetrabutyltin, dibutyltin dichloride and butyltin trichloride in hexane.

9.2.8.2. Add 200µL of this solution to the aqueous LCS and MS / MSD.

9.2.8.2.1. The spiked compounds are quantified at 200ng/ml on column, equivalent to 200ng/L in the sample for aqueous matrices

9.2.8.3. Add 1000µL of this solution to the solid/***tissue*** LCS and MS/MSD.

9.2.8.3.1. The spiked compounds are quantified at ***200***ng/kg on column, equivalent to 100ug/kg in solid matrices.

10. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

10.1. Aqueous samples should be collected in 1L pre-cleaned amber glass containers with Teflon-lined closures.

10.2. Soil samples should be collected in 4oz. pre-cleaned clear wide mouth jars with Teflon-lined closures.

10.3. Samples should be maintained in a chilled state (≤0-6°C) post sample collection until received at the laboratory. Upon receipt, the samples are stored in a 4°C cooler.

10.4. Aqueous samples must be extracted within seven (7) days of collection.

10.5. Solid samples must be extracted within 14 days of collection.

10.6. All sample extracts are then stored under refrigerated (4°C) conditions and must be analyzed within a 40 day period following extraction.

11. ►QUALITY CONTROL

11.1. Hardware Tuning

11.1.1. Prior to running the calibration standards, the GC/MS DFTPP tuning standard must be analyzed and meet the following acceptance criteria:

Mass	*Ion Abundance Criteria*
51	*30 – 60% of mass 198*
68	*< 2% of mass 69*
70	*< 2% of mass 69*
127	*40 – 60% of mass 198*
197	*< 1% of mass 198*
198	*Base peak, 100% relative abundance*
199	*5 – 9% of mass 198*
275	*10 – 30% of mass 198*
365	*> 1% of mass 198*
441	*Present but less than mass 443*
442	*> 40% of mass 198*
443	*17 – 23% of mass 442*

11.2. Initial Calibration:

11.2.1. The initial minimum of a five point calibration curve (3, 50, 100, 200 and 400ng/ml with 100ng/ml of IS in each) must be established prior to the processing of sample extracts.

11.2.2. The %RSD for each target analyte should be less than or equal to 20%.

11.2.2.1. Where the %RSD is ≤20%, then the relative response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation. In those instances where the RSD for one or more analytes exceeds 20%, the initial calibration remains acceptable if the following conditions are met:

11.2.2.2. The mean of the RSD values for all analytes in the calibration is less than or equal to 20%. The mean RSD is calculated by summing the RSD value for each target analyte and dividing by the total number of analytes.

11.2.2.3. The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project. In other words, if the target analyte is part of the calibration standard, its RSD value is included in the evaluation.

11.2.2.4. The analyst must include a summary of the initial calibration data or a specific list of those compounds for which the RSD exceeded 20% and the results of the mean RSD calculation in the data package.

11.2.2.5. Alternatively, if the %RSD of a target analytes relative response factor is >20%, a regression line fitted to the initial calibration should be used for determination of the extract concentration.

11.2.2.5.1. The acceptance criteria for the curve is $r \geq 0.995$.

11.2.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

11.2.4. The relative retention time (RRT) should agree to within 0.06 RRT units. This is not a requirement but non-compliance should be considered indicative of a problematic calibration for the affected target analytes.

11.3. Initial Calibration Verification (ICV):

11.3.1. Immediately following the initial calibration standards the ICV must be analyzed.

11.3.2. The ICV is deemed valid if the %D (difference or drift) for the target compounds is ≤ 20%. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin.

11.3.2.1. Make up a new ICV standard and reanalyze one time to confirm that the standard is acceptable. If the ICV still fails to meet acceptance criteria, recalibrate the instrument.

11.3.2.1.1. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least

one of the solutions is no longer intact (representative of the stated concentration). Investigate, effect corrective actions, which may include re-preparation of standard solutions, and recalibrate.

11.4. Continuing Calibration Verification (CCV):

11.4.1. Following establishment of a valid initial calibration, a CCV standard must be analyzed at the start of the analytical sequence and every 12 hours thereafter during analysis.

11.4.2. The CCV is deemed valid if the %D for the target compounds is ≤ 20%. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin.

11.4.2.1. Make up a new CCV standard and reanalyze one time to confirm that the standard is acceptable. If the CCV still fails to meet acceptance criteria, recalibration is warranted.

11.4.2.1.1. If the CCV is above the upper control limit and the associated samples are non-detect, the MB is non-detect and the LCS recoveries are within acceptance criteria, sample data may be reported with narration.

11.4.3. The internal standard responses and retention times in the CCV must be evaluated immediately after or during data acquisition.

11.4.3.1. If the retention time for any internal standard changes by more than 30 seconds from the mid-point standard level of the most recent initial calibration, the chromatographic system must be inspected for malfunctions and corrective action must be effected.

11.4.3.2. If the EICP area for any internal standard changes by a factor of two (-50% to +100%) from the mid-point standard level of the most recent initial calibration, the system must be inspected for malfunctions and corrective action effected. Following corrective action, re-analysis of samples analyzed while the system was malfunctioning is required.

11.4.4. If these criteria are not met, than all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed. If a failed CCV is the first of the day, corrective action must be effected prior to analyzing any samples.

11.4.5. It is a useful diagnostic tool to monitor internal standard retention times and area counts in all samples, spikes, blanks, and standards to check drifting method performance and monitor system trends.

11.5. Internal Standards (Field and QC Samples):

11.5.1. If the area count of any internal standard in a field or QC sample changes by a factor of two (−50% to +100%) from the area count of the corresponding internal standard determined in the daily CCV within the same 12-hour period, corrective action must be taken.

11.5.2. The affected field and/or QC samples should be re-analyzed, the CCV solution should be checked for proper concentrations and re-analyzed, or the data should be qualified.

11.6. Event Based Quality Control (MBs and LCSs):

11.6.1. Method Blank (MB):

11.6.1.1. The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (i.e., surrogates, internal standards, etc.).

11.6.1.1.1. For aqueous samples, the MB consists of organic free water. For solid and tissue samples, the MB ***consists of a matrix such as tilapia, corn oil or chicken.***

11.6.1.2. A MB is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. It should be noted, however, that as necessary (e.g., after high level samples), additional instrument or solvent blanks may be placed in the sequence.

11.6.1.2.1. When samples that are extracted together are analyzed on separate instruments and/or at different times, the MB associated with those samples must be analyzed on one of the instruments. A solvent blank should be analyzed on the other instruments to demonstrate that the instrument is not introducing contaminants to the samples.

11.6.1.3. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

11.6.1.3.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

11.6.1.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

11.6.2. Lab Control Sample (LCS):

11.6.2.1. The LCS is a known matrix which has been spiked with a known concentration of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

11.6.2.1.1. Although all four analytes are included in the spike mixture, only Tributyltin and Tetrabutyltin are routinely evaluated and reported.

11.6.2.1.2. If a full list spike is required by client or project, the standards must be made up fresh prior to extraction.

11.6.2.2. A LCS is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

11.6.2.3. The acceptance criteria for LCS compounds vary depending upon historical data. The upper and lower acceptance limits for each LCS compound are based upon the historical average recovery ±3S. All LCS compounds must be within acceptance limits. If one or more LCS compounds are not acceptable, the problem must be identified and corrected.

11.6.2.3.1. Client or project-specific criteria may be required. Confirm with the Testcode and/or special instructions on the chemist worksheet.

11.6.2.4. If the problem was not related to the extraction process, then the LCS and all associated QC sample extracts must be re-analyzed. If the failure was associated with the extraction process, then all associated samples must be re-extracted and re-analyzed in a new QC batch.

11.6.2.5. Prepare an LCS/LCSD when there is insufficient sample available to prepare an MS/MSD.

11.7. Sample Based Quality Control (MS/MSDs, Surrogates ***and Internal Standards***):

11.7.1. Matrix Spike / Matrix Spike Duplicate (MS/MSD)

11.7.1.1. One MS/MSD pair is required for every batch of 20 samples per matrix or portion thereof extracted concurrently.

11.7.1.1.1. In the event that there is insufficient sample volume/mass for an MS/MSD, prepare and analyze an LCS/LCSD to provide precision and accuracy measurements for the associated samples.

11.7.1.2. The MS and MSD are made up of the actual sample matrix spiked with known concentrations of specific target analytes. The MS contains the following four compounds: Tetrabutyltin, Tributyltin, Dibutyltin and Monobutyltin. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

11.7.1.2.1. Although all four analytes are included in the spike mixture, only Tributyltin and Tetrabutyltin are routinely evaluated and reported.

11.7.1.2.2. If a full list spike is required, the standards must be made up fresh prior to extraction.

11.7.1.3. The acceptance criteria for MS/MSD compounds vary depending upon historical data. The upper and lower acceptance limits for each spike compound are based upon the historical average recovery ±3S.

11.7.1.3.1. Client or project-specific criteria may be required. Confirm with the Testcode and/or special instructions on the chemist worksheet.

11.7.1.4. The purpose of a MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The MS in combination with the MSD can be used to assess the precision of the analytical measurements as well. The measurement is expressed as relative percent difference (RPD). The formulas for calculating %REC and %RPD are listed in Section 15.

11.7.1.5. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix.

The MS/MSD data shall be reported with the corresponding sample data.

11.7.1.6. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

11.7.1.7. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS. Specifically, an acceptable LCS usually supports matrix interference.

11.7.2. Surrogate:

11.7.2.1. The acceptance criteria for surrogate spike compound recovery may vary depending upon historical data. The upper and lower acceptance limits for the surrogate spike compound is based upon the historical average recovery ± 3S.

11.7.2.1.1. Client or project-specific criteria may be required. Confirm with the Testcode and/or special instructions on the chemist worksheet.

11.7.2.2. If the surrogate compound recovery is acceptable, report the surrogate and sample data without qualification.

11.7.2.3. If the surrogate recovery is not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration or a problem may have occurred during extraction. The data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

11.7.2.4. By itself, an unacceptable surrogate recovery does not invalidate sample data. The following must be accomplished if surrogate recovery is not acceptable.

11.7.2.4.1. Check the internal standard and surrogate spiking solutions for degradation and contamination.

11.7.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same extract should be re-analyzed.

11.7.2.4.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recovery and the sample data reported with qualification.

11.7.2.4.3.1. If, upon re-extraction and re-analysis, the surrogate recovery remains unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recovery and the sample data reported with qualification.

11.7.2.4.3.2. If the MB surrogates are unacceptable, all associated sample data must invalidated and all associated samples re-extracted and re-analyzed assuming there is sufficient sample and holding time remaining. Otherwise, qualify data and address in the narrative.

11.7.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

11.8. Additional information regarding internal quality control checks is provided in SOP-T020.

12. CALIBRATION AND STANDARDIZATION

12.1. Top Loading Balance

12.1.1. Verify the calibration of the top loading balance at a minimum of two points that bracket the intended range of use: 0.1g, 1g, 100g, and/or 2000g using Class 2 weights as outlined in the current revision of SOP-T043.

12.1.2. If control limits are not specified, calibration shall be within ± 2% or ± 0.02 g, whichever is greater.

12.1.3. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

12.2. Thermometer

12.2.1. Calibrate the thermometer using a NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

12.3. Prior to the analysis of sample or QC extracts, the GC/MS system must be tuned and have an initial five-point calibration established.

12.3.1. Calibration standards must be derivitized prior to analysis.

12.4. To verify and validate the calibration, an initial calibration verification (ICV) standard must be analyzed immediately following the calibration standards.

12.4.1. The ICV shall be at mid-concentration containing all target analytes and shall be of a source other than that of the initial calibration. The acceptance criteria for the ICV is listed in Section 12, Quality Control.

13. ►PROCEDURE

13.1. Sample Preparation

13.1.1. Aqueous Matrices:

13.1.1.1. Mark the level of an aqueous sample on the outside of the sample bottle with a sharpie.

13.1.1.1.1. Alternatively, zero a top loading balance, and weigh the aqueous sample including the sample bottle. Record the mass to the nearest 1g. ***The difference between the full and empty bottle is equal to the amount of volume, assuming that 1ml = 1 gram.***

13.1.1.2. Quantitatively transfer the whole aqueous sample from the sample bottle into a clean separatory funnel. Fill the sample bottle up to the mark with water, transfer to a graduated cylinder and record the amount of sample extracted on the preparation log.

13.1.1.2.1. For MB and LCS measure exactly 1000mL of clean reagent water.

13.1.1.2.2. For MS/MSD, measure exactly 1000mL of aqueous sample selected for spiking.

13.1.1.2.3. ***If there is insufficient sample for an MS/MSD, prepare an LCSD in the same manner as the LCS.***

13.1.1.3. Adjust sample to pH <2 with 1:1 HCL. Confirm with pH paper.

13.1.1.4. Add 0.2ml of a 1ug/ml surrogate solution to all QC and field samples.

13.1.1.5. Add 0.2ml of a 1ug/ml spike standard solution to the LCS and MS/MSD samples.

13.1.1.6. Extract three consecutive times using fresh 60ml aliquots of 0.1% Tropolone in Hexane.

13.1.1.6.1. Extract for a minimum of two minutes each time.

13.1.1.7. Following each extraction, collect the extract in a Kuderna Danish concentrator, passing through ***Sodium Sulfate in a glass funnel (use glass wool to plug the stem)*** to remove water.

13.1.1.8. Once all three extracts have been collected, attach a three ball Schneider column to the KD flask, place in a heated water bath and concentrate down until the extract reaches a volume of between 4 and 5ml in the KD tube.

13.1.1.8.1. Allow the concentrate to cool in the KD apparatus.

13.1.1.9. Once cooled, transfer to a 40ml vial and make up to a final volume of 5ml by adding additional Hexane, or blowing down with a gentle stream of nitrogen. Use a reference vial for comparison of the final volume.

13.1.1.10. Extract is ready for derivitization.

13.1.1.11. Derivitization:

13.1.1.11.1. Add 0.2ml of 2 Molar (2M) Pentylmagnesium Bromide and shake for approximately 60 minutes.

13.1.1.11.1.1. In order to limit oxidation during this process, be sure to eliminate the amount of air in the vial used for derivitization. Do this by adding a blanket of nitrogen to the vial before capping and shaking.

13.1.1.11.1.2. Add the Pentylmagnesium Bromide to the vial, turn on the nitrogen such that a gentle stream is emitted and introduce the stream to the vial for approximately 10 seconds. Quickly cap the vial. Turn off the nitrogen.

13.1.1.11.2. Place vial in an ice bath, and add 1:1 HCL until the precipitates are dissolved.

13.1.1.11.3. Pipette off the Hexane layer and concentrate to 1 ml using nitrogen.

13.1.1.12. Transfer 0.5ml of the extract to an autosampler vial and add 10µl of the internal standard (5ug/ml). The extract is now ready for analysis.

13.1.2. Soil/Sediment/***Tissue*** Matrices:

13.1.2.1. Measure 10gm of sample into a 250ml Erlenmeyer beaker.

13.1.2.2. Adjust sample to pH <2 using 1:1 HCL and add drying agent, Hydromatrix diatomaceous earth, to absorb moisture.

13.1.2.3. Add 1ml of a 1ug/ml surrogate solution to all QC and field samples.

13.1.2.4. Add 1ml of a 1ug/ml spike standard solution to the LCS and MS/MSD samples.

13.1.2.5. Add 60ml of 0.1% Tropolone in Hexane to all QC and samples.

13.1.2.6. Cover the beakers with para-film or foil and place on the Labline Orbit shaker.

13.1.2.7. Secure and shake for 15 min at an intensity setting of 3.

13.1.2.8. Repeat these same steps again with an additional 60ml aliquot of the Tropolone/Hexane mix. Shake for 10 min. Repeat a third time.

13.1.2.9. Following each extraction, collect the extract in a Kuderna Danish concentrator, passing through ***Sodium Sulfate in a glass funnel (use glass wool to plug the stem)*** to remove water.

13.1.2.10. Once all three extracts have been collected, attach a three ball Schneider column to the KD flask, place in a heated water bath and concentrate down until the extract reaches a volume of between 3 and 4ml in the KD tube.

13.1.2.10.1. Allow the concentrate to cool in the KD apparatus.

14.1.1.11. Once cooled, transfer to a 40ml vial and make up to a final volume of 4ml by adding additional Hexane, or blowing down with a gentle stream of nitrogen. Use a reference vial for comparison of the final volume.

14.1.1.12. Extract is ready for derivitization.

14.1.1.13. Derivitization:

14.1.1.13.1. Add 0.2ml of 2 Molar (2M) Pentylmagnesium Bromide and shake for approximately 60 minutes.

14.1.1.13.1.1. In order to limit oxidation during this process, be sure to eliminate the amount of air in the vial used for derivitization. Do this by adding a blanket of nitrogen to the vial before capping and shaking.

14.1.1.13.1.2. Add the Pentylmagnesium Bromide to the vial, turn on the

nitrogen such that a gentle stream is emitted and introduce the stream to the vial for approximately 10 seconds. Quickly cap the vial. Turn off the nitrogen.

14.1.1.13.2. Place vial in an ice bath, and add 1:1 HCL until the precipitates are dissolved.

14.1.1.13.3. Pipette off the hexane layer and adjust volume to 4ml.

14.1.1.13.4. Transfer 0.5ml of the extract to an autosampler vial and add 10µl of the internal standard (5ug/ml). The extract is now ready for analysis.

14.2. Extract Cleanup Procedures

14.2.1. If after derivitization the cleanup of sample extracts is warranted, proceed with the following:

14.2.1.1. Aqueous and low level solid samples or tissue samples with <5% lipids: 1g Silica gel/2g Alumina. Mercury for presence of sulfur in sediments and solids, waters.

14.2.1.2. Tissue samples with % lipids >5% or high level solid samples: 5g Silica gel/2g Alumina, Mercury for presence of sulfur in sediments and solids.

14.2.2. Sulfur Cleanup:

14.2.2.1. Pipette approximately 1−2ml of the hexane extract into a clean 2 or 4ml vial.

14.2.2.2. Add 2−3 drops of mercury to the extract, and cap the vial. Record the mercury identification number in the extraction logbook. (Add more drops of mercury if an elevated level of sulfur is observed – yellow or dark color.)

14.2.2.3. Place the vial on the shaker vial tray, set the shaker speed rotary dial to 10 and agitate the contents of the vial for 1-2 hours.

14.2.2.4. Remove from the shaker and allow the black mercury sulfide precipitate to settle.

14.2.2.4.1. If the precipitate does not settle, place the vial in a centrifuge tube, and centrifuge at low speed for 1−2 min or until the precipitate has settled.

14.2.2.5. Pipette the sulfur-cleaned up extract (supernatant) into a clean 2 or 4ml vial for additional cleanup using silica gel/alumina, if warranted, or into a crimp-top autosampler vial if ready for analysis. The supernatant must be clear and free of the mercury sulfide particles. Label appropriately.

14.2.3. Silica/Alumina Column Cleanup:

14.2.3.1. ***Cartridge prep for 'Low Level' Cleanup (waters, solids or lipids <5%)***

14.2.3.1.1. ***Unseal a 6ml (2g) Alumina SPE cartridge and attach it to the valve of the vacuum manifold.***

14.2.3.1.2. ***Weigh out 1 gram of loose silica gel and add to the top of the alumina bed in the SPE cartridge.***

14.2.3.1.2.1. ***Alternately, stack/attach a 1 gram silica gel cartridge to a 2g alumina cartridge.***

14.2.3.1.3. ***Proceed to section 14.2.3.3.***

14.2.3.2. ***Cartridge prep for 'High Level' Cleanup (Sediments, or lipids >5%)***

14.2.3.2.1. Unseal a 15ml (5g) Silica Gel SPE cartridge and a 6ml (2g) Alumina SPE cartridge.

14.2.3.2.2. ***Stack/attach the silica gel cartridge on top of the alumina cartridge and attach it to the valve of the vacuum manifold.***

14.2.3.2.3. ***Proceed to section 14.2.3.3.***

14.2.3.3. ***Cleanup process for all sample types:***

14.2.3.3.1. ***Place a waste vial below the sample guide.***

14.2.3.3.2. ***Turn on the vacuum pump and set the vacuum to 10-in (254mm) Hg.***

14.2.3.3.3. ***Slowly open the flow control valve for each column or cartridge. Control the flow rate by adjusting the valve.***

14.2.3.3.4. ***Condition (i.e., rinse) the column or cartridge with 20ml of hexane. The elution rate should be approximately 2ml/min.***

14.2.3.3.5. ***Allow the hexane to flow through the sorbent bed until the meniscus of the solvent is just above the surface of the silica gel. This will settle and pack the loose silica gel.***

14.2.3.3.6. ***Close the valve to stop solvent flow, and discard the hexane eluate. Do not turn off the vacuum.***

14.2.3.3.6.1. ***Do not allow the column to become dry. If the column becomes dry, repeat the conditioning procedure.***

14.2.3.3.7. ***Remove the waste container, label a clean 40ml VOA vial and place it below the sample guide for each column or cartridge.***

14.2.3.3.8. ***Load 1.0ml of the extract onto the column using a 1.0ml syringe, or other volumetric device.***

14.2.3.3.9. ***Slowly open the valve and start collecting the extract at approximately 2ml/min.***

14.2.3.3.10. ***When the meniscus of the extract is just above the surface of the packing, slowly add 20ml of hexane in 1−2ml increments.***

14.2.3.3.10.1. ***Add each increment of hexane when the meniscus of the solvent is just above the surface of the silica gel. Do not expose the surface of silica gel to air.***

14.2.3.3.11. ***Monitor the silica gel/alumina packing during elution. If any channeling, streaking, or change is observed, replace the cartridge and re-process the extract.***

14.2.3.3.12. ***Allow the hexane to flow through the column until the meniscus of the solvent is just above the surface of silica gel. Close the valve to stop solvent flow and turn off the vacuum. The eluted extract is the silica gel cleaned up extract.***

14.2.3.3.13. ***Concentrate the cleaned up extract to 1.0ml under a gentle stream of nitrogen. Bring to final volume with additional hexane as needed. Use a reference vial for comparison of the final volume as needed.***

14.2.3.3.14. ***Transfer the cleaned up extract into a clean crimp-top autosampler vial and label appropriately. The extract may now be analyzed.***

14.3. Analysis

14.3.1. Following establishment of a valid initial calibration, a CCV must be analyzed every 12 hours thereafter during analysis. If the criteria are met for this CV, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria for the CV is listed in Section 12, Quality Control.

14.3.2. The sample vials may loaded in the following order or in any other acceptable order.

1) Continuing Calibration Verification (CCV) (every 12 hours)
2) Laboratory Control Sample (LCS)
3) Method Blank (MB)
4) Samples (up to 20 per batch)
5) Matrix Spike (MS)
6) Matrix Spike Duplicate (MSD)

14.3.3. Ensure that a sufficient amount of Hexane is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles.

14.3.4. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. Print, stamp, complete the information and file the run log in the associated run log book.

14.3.5. Initiate the sequence.

14.3.6. Data Interpretation

14.3.6.1. The qualitative identification of analytes determined by this method is based on:

1) Elution of the sample component at the same relative retention time (RRT) as the standard component and

2) Comparison of the sample mass spectrum, after background correction if necessary, with characteristic ions in a reference mass spectrum. The reference mass spectrum should be obtained from the GC/MS within the same 12 hour period as the sample analysis.

14.3.7. The respective scanned ions for the four quantified analytes are as follows:

14.3.7.1. Tetrabutyltin: ***291, 289, 287***
Tributyltin: ***305, 303, 301***
Dibutyltin: ***319, 317, 305***
Monobutyltin: ***319, 317, 333***

14.3.8. Target analytes should be identified as present when:

14.3.8.1. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search

routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target analyte at a compound-specific retention time will be accepted as meeting this criterion.

14.3.8.2. The RRT of the sample target analyte is within ±0.06 RRT units of the RRT of the standard target analyte.

14.3.8.3. The relative intensities of the characteristic ions agree with 30% of the relative intensities of these ions in the reference spectrum.

14.3.8.4. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one target analyte. When gas chromatographic peaks obviously represent more than one sample component, appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles (EICPs) of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute, the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

14.3.9. When a compound has been identified, the quantitation of the compound will be based on the integrated abundance of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte.

14.3.9.1. If the %RSD of a target analyte's relative response factor is ≤20%, then the concentration in the extract may be determined using the average response factor (RF_{ave}) from the initial calibration. The formula for calculating RF_{ave} is listed in Section 15.

14.3.9.2. Alternatively, if the %RSD of a target analyte's relative response factor is >20%, a regression line fitted to the initial calibration should be used for determination of the extract concentration.

14.3.9.2.1. Identify and compute the concentration of each target analyte in the sample. The GC/MS data system should be programmed to perform these functions. The details provided in the below subsections are for the purpose of understanding.

14.3.9.2.2. The concentration of the analyte in an aqueous sample is calculated using the concentration of the analyte in the extract, the volume of the extract, and the volume of sample extracted. The formula

for calculating the concentration is listed below in section 10, Calculations.

14.3.9.2.3. The concentration of the analyte in the solid of the sample is calculated using the concentration of the analyte in the extract, the volume of the extract, and the weight of the subsample. The formula for calculating the concentration is listed below in Section 15, Calculations.

15. ►CALCULATIONS

15.1. Response factors are calculated as follows:

$$RF = \frac{(A_x \times C_{is})}{(A_{is} \times C_x)}$$

where: RF = response factor for target analyte being measured.
A_x = area of the characteristic ion for target analyte being measured.
A_{is} = area of the characteristic ion for the applicable internal standard.
C_{is} = concentration of the specific internal standard in ng/µL.
C_x = concentration of the target analyte being measured in ng/µL.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the average RFs for the target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.3. The percent difference of each CCC is calculated as follows:

$$\%D = \frac{(C_I - C_c)}{C_I} \times 100$$

where: %D = percent difference (or percent drift) of CCC.
C_I = CCC standard concentration.
C_c = measured concentration.

Note: Concentrations must be in equivalent units.

15.4. The recovery of LCS compounds is calculated as follows:

$$\%REC_{LCS} = \left(\frac{C_{recovered}}{C_{added}}\right) \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS.
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The recovery of the MS compounds is calculated as follows:

$$\%REC_{MS} = \left(\frac{C_{recovered} - C_{sample}}{C_{added}}\right) \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements(C_1&C_2).
C_1 = concentration of target analyte recovered in measurement 1.
C_2 = concentration of target analyte recovered in measurement 2.

15.7. Compound concentration in the extract is calculated as follows:

$$C_{ex}\ (\mu g/L) = \frac{(A_x \times C_{is})}{(A_{is} \times RF_{ave})}$$

where: C_{ex} = concentration of target analyte in extract in µg/L.
A_x = area of the characteristic ion for target analyte.
C_{is} = concentration of the specific internal standard in ng/ml.
A_{is} = area of the characteristic ion for the applicable internal standard.
RF_{ave} = mean of 5 initial RFs for a compound.

15.8. Sample concentration for aqueous samples is calculated as follows:

$$C_A\ (ng/L) = \frac{(C_{ex} \times V_{ex})}{V_o}$$

where: C_A = concentration of the target analyte in the aqueous sample in ng/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = extract volume in mls.
V_o = volume of aqueous sample extracted in L.

15.9. Sample concentration for solid, sediment ***or tissue*** samples is calculated as follows:

$$C_s\ (\mu g/kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

where: C_s = concentration of the target analyte in the solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = extract volume in mls.
W_s = weight of solid sample extracted in gms.

15.10. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: ***C_S = concentration of target analyte in solid sample in µg/kg.***
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid sample solvent extracted in g.
C_{ss} = solids content in %.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.11. All concentrations shall be reported in ng/L for water samples and µg/kg for soil and sediment samples.

15.11.1. If required by client or project, dry weight corrected data can be reported.

15.12. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses, lab coats and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Please refer to Section 12 of this SOP or directly to SOP T020 for information related to data assessment and acceptance criteria for the routine QC elements: MB, LCS, MS/MSD, Surrogates and Internal Standards.

18.1.1. Additional questions related to data usability should be addressed to the Group Leader, Project Manager and/or QA department.

18.2. Additional information regarding internal quality control checks is provided in SOP-T020.

18.3. All concentrations shall be reported in ng/L for water samples and µg/kg for soil and sediment samples.

18.4. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. ►CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the group leader of the appropriate department. All samples associated with an unacceptable QC set is then subject to reanalysis, depending upon the QC type in question.

20.1.1. LCS: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the group leader confirms the unacceptable result.

20.1.1.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.1.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.1.2.1. ***This applies to all cases of LCS failure with the following exception: If the LCS fails high for an analyte of concern, the CCV is within criteria or also bias high, and the associated samples are non-detect for the associated analyte(s), report the sample data as is and address in the narrative. The recoveries in the QC samples will be flagged as out of control in the report.***

20.1.1.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

20.1.2. MS/MSD: Acceptability of the MS/MSD recoveries are subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries an MS/MSD data set is does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS recoveries, to determine acceptance of the sample results.

20.1.2.1. If the LCS is also outside criteria, repreparation and analysis may be warranted (see section 20.1.1.2.1.) assuming there is sufficient sample and holding time remaining.

20.1.3. Refer to SOP T020 for additional information regarding data validity and reporting protocols.

21. WASTE MANAGEMENT

21.1. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.2. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.3. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.4. Each specific laboratory area shall maintain clearly labeled satellite waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. ►REFERENCES

22.1. Krone, C.A., Brown, D. W., Burrows, D. G., Bogar, R. G., Chan, S., Varanasi, U. (1989). A method for analysis of butyltin species and measurement of butyltins in sediment and English Sole livers from Puget Sound. *Marine Environmental Research,* (27), 1-18.

22.2. Restek Corp. (n.d.). Sample preparation and analysis of organotin compounds [Application Note]. Bellefonte, PA: Author.

22.3. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8270C, USEPA, Revision 3, December 1996.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. None.

24. MODIFICATIONS

24.1. None

25. ►REVISION HISTORY

Revision	Description	Author	Effective Date
2.0	Section 3: Add reference SOP. Section 4: Update scope Section 5: Update method summary Section 6: Update definitions. Section 7: Update comments. Section 9: Update equipment. Section 10: Update reagents/standards. Section 12: Update quality control. Section 13: Update calibration. Section 14: Update procedure. Section 24: Add modification section. Section 25: Add revision history section.	L. Scharpenberg / L. Lem	07/16/2014
3.0	Section 1: Added SIM to method title Section 2: Updated Matrices to add tissue Section 3: Changed EQL to RL Section 4: Updated scope Section 5: Updated method summary Section 7: Updated comments. Section 9: Updated equipment. Section 10: Updated reagents/standards. Section 11: Updated transport temperature Section 12: Updated quality control. Section 14: Add tissue, cleanup procedures & ions Section 18: Update data assessment Section 20: Update contingencies and usability Section 22: Update references Section 25: Update revision history	L. Scharpenberg / L. Lem	08/25/2014

Title : **SM 2540 C / EPA METHOD 160.1, TOTAL DISSOLVED SOLIDS (FILTERABLE RESIDUE, GRAVIMETRIC)**

Document No. : SOP-M713
Revision No. : 2.7
Supersedes : 2.6

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Revision 2.7 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 12/04/13
MANAGEMENT **DATE**

_____ 12-04-13
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. SM 2540 C / EPA Method 160.1, Total Dissolved Solids (Filterable Residue, Gravimetric).

2. ►APPLICABLE MATRICES

2.1. This method is applicable to drinking, surface and saline waters, domestic and industrial wastewaters.

2.2. ***Soil, solid and non-aqueous matrices may be analyzed using the extraction procedure noted in Section 14.5. and reporting as a modified method, EPA Method 160.1(M) or SM 2540 C(M).***

3. DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for this method are as follows:

Concentration (mg/L or mg/kg) in Sample	EQL (mg/L or mg/kg)
≤ 999	1.0
> 999 and ≤ 9,999	10
> 9,999 and ≤ 99,999	100
> 99,999	1000

4. SCOPE AND APPLICATION

4.1. SM 2540 C / EPA Method 160.1 are used to determine the total dissolved solids.

4.2. This method is restricted to use by or under the supervision of analysts experienced in the use of the equipment and apparatus required to execute the analysis and skilled in the interpretation of the outputs.

4.2.1. Each analyst must demonstrate the ability to generate acceptable results with this method and be approved by the applicable Group Leader prior to analyzing billable samples.

5. METHOD SUMMARY

5.1. A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated in weighed beaker and dried to a constant weight at 180°C. The increase in weight of the beaker represents the total dissolved solids.

5.2. The filtrate from the determination of total suspended solids (non-filterable residue) may be used for this method.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. ***Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1 %.***

6.10. ***Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.11. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.12. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.13. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.14. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.15. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.16. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.17. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.18. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.19. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.20. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.21. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.22. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.23. Terms Specific to Solids Analysis

6.23.1. Total Dissolved Solids: The portion of total solids that passes through a filter of 2.0-µm (or smaller) nominal pore size under specified conditions.

6.23.2. Total Solids: Material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids include total dissolved solids and total suspended solids.

6.23.3. Total Suspended Solids: The portion of total solids retained on a filter of 2.0-µm nominal pore size under specified conditions.

7. INTERFERENCES

7.1. Sampling, subsampling, and pipeting two-phase or three-phase samples may introduce serious errors. Make and keep such samples homogeneous during transfer. Use special handling to insure sample integrity when subsampling.

7.1.1. Mix small samples with a magnetic stirrer. Avoid using a magnetic stirrer if the samples contain magnetic particles.

7.1.2. If suspended solids are present, pipet with wide-bore pipets.

7.1.3. If part of a sample adheres to the sample container, document it in the logbook when evaluating and reporting results.

7.2. Some samples may dry with the formation of a crust that prevents water evaporating.

7.2.1. Limit sample to no more than 200 mg residue to prevent water-trapping crust.

7.3. Weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, gases from heat-induced chemical decomposition, and weight gains due to oxidation depend on the temperature and heating time at which the residue is dried.

7.3.1. Each sample requires close attention to desiccation after drying. Minimize opening the desiccator to prevent moist air from entering.

7.3.2. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

7.4. Residue dried at 180 ± 2°C will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulfates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of carbon dioxide may convert bicarbonate to carbonate, and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost.

7.4.1. In general, evaporating and drying water samples at 180°C yields values for dissolved solids closer to those obtained from summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature.

7.5. Residues high in oil or grease may yield questionable results because of the difficulty of drying to constant weight in a reasonable time.

7.5.1. Disperse visible floating oil and grease with a blender before withdrawing a sample aliquot for analysis.

7.6. Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.

7.7. Samples containing high concentrations of bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate.

8. SAFETY

8.1. Beakers are heated in an oven and will be hot upon removal. Use tongs to handle the weighing dishes when removing from the oven.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. ►EQUIPMENT AND SUPPLIES

9.1. Specimen containers, 4.5-oz (120-mL), with lids, high density polyethylene (HDPE) or polypropylene, disposable.

9.2. Graduated cylinders, 25-mL, 50-mL, 100-mL, or other capacity, glass, Class A.

9.2.1. Class A graduated cylinder is utilized to measure sample volume.

9.3. Graduated cylinders, 50-mL, glass, Class B.

9.3.1. Class B graduated cylinder is utilized to collect sample filtrate.

9.4. ***Volumetric flasks, 1-L, Class A***.

9.5. Blender or homogenizer.

9.6. Magnetic stirrer.

9.7. Stir bars, Teflon coated.

9.8. Stir bar retriever, magnetic.

9.9. Transfer pipets, wide-bore, glass or plastic, disposable.

9.10. Spatula, stainless steel.

9.11. Vacuum filtration apparatus:

9.11.1. Vacuum apparatus.

9.11.2. Buchner funnel, 100-mm diameter, 320-mL capacity, porcelain with fixed perforated plate, capable of supporting a 90-mm diameter filter, CoorsTek Fixed Plate Buchner Funnel or equivalent.

9.11.3. Filtration flask, 1000-mL or other capacity, glass, with tubulation.

9.11.4. Filter paper, 1.5-µm effective pore size, 90-mm diameter, borosilicate glass microfiber, binder free, Whatman Grade 934-AH Glass Microfiber Filter or equivalent.

9.12. Ultrasonic bath, VWR Scientific Aquasonic Model 550T or equivalent.

9.13. Drying oven, thermostatically controlled, forced draft, capable of maintaining 180 ± 2°C.

9.14. Hot plate, capable of maintaining 80−100°C.

9.15. Muffle furnace, capable of maintaining 550 ± 50°C.

9.16. ***Instrument Software***

9.16.1. ***Not applicable.***

9.17. ***Instrument Maintenance and Troubleshooting***

9.17.1. ***Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.***

9.17.2. ***Additional information can be found in the user manual or operating guide for the specific instrument.***

9.18. Thermometer, calibrated, capable of monitoring temperatures at 90 ± 10°C and 180 ± 2°C.

9.19. Desiccator, containing indicating-type desiccant.

9.20. Forceps or tongs, stainless steel.

9.21. Gloves, heat resistant.

9.22. Wash bottle, 500-mL, 1000-mL, or other capacity, low density polyethylene (LDPE).

9.23. Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.

9.24. ***Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.***

9.25. Beakers, ***100***-mL or 150-mL, glass.

9.26. Paper towels.

9.27. Tray, plastic.

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, deionized.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. ***Sodium chloride, NaCl, white crystalline solid, reagent grade or equivalent.***

10.1.4. All reagents (except reagent water) must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. ***Sodium chloride stock standard solution, 1000ppm.***

10.2.1.1. ***Dissolve 1.0000 ± 0.0100 g NaCl in reagent water and dilute to 1L in a volumetric flask.***

10.2.2. ***Sodium chloride working solution, 100ppm***

10.2.2.1. ***Measure 100mL of the 1000ppm NaCl stock solution with a graduated cylinder and dilute to 1L in a volumetric flask.***

10.2.3. ***All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1-L pre-cleaned high density polyethylene (HDPE) or clear glass containers with Teflon-lined closures.

11.1.1. No preservation chemicals are required.

11.2. Solid samples should be collected in 4-oz or 8-oz pre-cleaned clear glass wide-mouth jars (preferable), or 6-in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.3. Samples should be maintained in a chilled state, ***0-6°C, not frozen,*** post sample collection until received at the laboratory, ***where they are stored under refrigerated conditions.***

11.3.1. Aqueous and solid samples shall be analyzed as soon as feasible to minimize microbiological decomposition of solids. The maximum holding time is within 7 days of sample collection.

11.4. Additional sample handling information can be found in the Sample Control SOPs.

12. ►QUALITY CONTROL

12.1. Event Based Quality Control (MBs ***and LCS/LCSDs***)

12.1.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), ***a laboratory control sample (LCS) and, in some cases, a laboratory control sample duplicate (LCSD).***

12.1.1.1. ***When requested by client, to meet project DQOs, or if insufficient sample volume is received for a sample duplicate, a laboratory control sample duplicate (LCSD) is required.***

12.1.2. ***The acceptance criteria for LCS/LCSD compounds are as follows:***

12.1.2.1. ***The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively. When an LCSD is done, the RPD is ≤ 20%.***

12.1.3. ***The*** concentration of target analyte in an MB should be ≤ ½ the respective reporting limit (RL). If the concentration of target analyte exceeds ½ its RL, the source of contamination must be investigated and, if possible, eliminated.

12.2. Matrix Based Quality Control (Sample Duplicates)

12.2.1. Matrix based quality control consists of QC samples processed using actual environmental samples. This consists of a sample duplicate.

12.2.1.1. A sample duplicate is a selected field sample re-processed and re-analyzed under the same analytical conditions as the associated samples.

12.2.1.2. ***A sample duplicate shall be analyzed for every 10 samples or portion thereof.***

12.2.2. The acceptance criteria for duplicate analyte are as follows:

12.2.2.1. The RPD is ≤ ***5***%.

12.2.2.1.1. For EPA Region 9 requirement, the RPD is < 20%.

12.2.2.2. When the RPD of the duplicate analyte is at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

12.2.2.3. If the RPD of the duplicate analyte is not within the established acceptance limits, the analytical system performance shall be suspect.

12.2.3. Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.

12.3. If the RPD of the sample duplicate is unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.4. Additional information regarding internal quality control check is provided in SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. Analytical Balance

13.1.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights ***as outlined in the current revision of SOP-T043***.

13.1.2. ***If control limits are not specified***, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. ***If control limits are specified, calibration shall be within the specified limits.*** If the values are not within these limits, recalibrate the balance.

13.2. ***Top Loading Balance***

13.2.1. ***Calibrate the top loading balance at 1 g and 100 g using Class 2 weights as outlined in the current revision of SOP-T043***.

13.2.2. ***If control limits are not specified, calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.***

13.3. Thermometer

13.3.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of ***SOP-T043, "Support Equipment – Calibration, Verification, Monitoring***."

14. ►PROCEDURE

14.1. Conductivity Determination

14.1.1. Determine the conductivity of an aqueous sample as outlined in the current revision of SOP-M702. Record the conductivity to 3 significant figures in the Total Dissolved Solids ***Logbook***.

14.1.2. Conductivity measurement is used to estimate the concentration (in mg/L) of total dissolved solids in an aqueous sample by multiplying conductivity (in µmho/cm) by an empirical factor. This factor may vary from 0.55 to 0.90, depending on the soluble components of the water and on the temperature of measurement.

14.1.2.1. Relatively high factors may be required for saline or boiler waters, whereas lower factors may apply where considerable hydroxide of free acid is present.

14.1.2.2. The factor of 0.6 is applied to all aqueous samples received at the laboratory.

14.2. Beaker Preparation

14.2.1. Using a fine point Sharpie, write an identification number on a clean ***100***-mL beaker.

14.2.1.1. Handle beaker using clean forceps or tongs throughout the course of beaker preparation.

14.2.1.2. Do not use fingers. Oils or other contaminants from fingers or gloves may change the mass of the beaker and skew the mass of the residue.

14.2.2. Heat the clean, labeled beaker in an oven at 180°C ± 2°C for one hour.

14.2.2.1. If volatile solids are to be measured, heat the beaker in a muffle furnace at 550°C ± 50°C for 15 minutes instead.

14.2.3. Remove the beaker from the oven, transfer to a desiccator, and allow to cool.

14.2.4. When cool to ambient temperature, and immediately prior to sample preparation, weigh the beaker on a calibrated analytical balance. Record the beaker identification number and the mass to the nearest 0.1 mg (or 0.0001 g).

14.2.4.1. Shut all access doors on the balance and tare. Open a single access door, remove a beaker from the desiccator, and place on the balance pan. Shut the access door and allow the digital readout to stabilize before recording the mass.

14.2.4.2. Place the beaker in a tray lined with clean paper towels for immediate use.

14.3. Filter Paper Preparation

14.3.1. If total suspended solids is to be determined in conjunction with this method, prepare filter paper as outlined in the current revision of SOP-M714.

14.4. Aqueous Sample Preparation

14.4.1. Allow an aqueous sample to reach ambient temperature.

14.4.2. Homogenize the aqueous sample by shaking the sample thoroughly. Invert the sample container at least three times while shaking.

14.4.2.1. Sample may be homogenized by stirring with a magnetic stirrer at a speed to shear large particles.

14.4.3. Quickly measure 20.0 ± 1.0 mL of the homogenized aqueous sample into a Class A graduated cylinder. Excess volume may be removed with a disposable transfer pipet. Record the volume to the nearest 0.1 mL or 3 significant figures.

14.4.3.1. For MB, measure exactly 20.0 mL of clean reagent water.

14.4.3.2. ***For LCS/LCSD, measure exactly 20.0 mL of 100ppm NaCl working solution.***

14.4.3.3. The sample volume shall yield between 2.5-mg and 200-mg dried residue. If the volume filtered fails to meet the minimum yield, increase the sample volume. If complete filtration takes

more than 10 minutes, increase the filter diameter or decrease the sample volume.

14.4.4. Proceed to Section 14.6. for filtration procedure.

14.5. Solid Sample Preparation

14.5.1. Allow a solid sample to reach ambient temperature.

14.5.2. Homogenize the solid sample as outlined in the current revision of SOP-M230.

14.5.3. Measure 3.00 ± 0.15 g of the homogenized solid sample into a clean specimen container. Record the mass to the nearest 0.01 g or 3 significant figures.

14.5.3.1. For MB, measure exactly 3.00 g of washed sea sand. Record the washed sea sand identification number.

14.5.3.2. ***For LCS/LCSD, measure exactly 3.00 g of washed sea sand. Record the washed sea sand identification number.***

14.5.3.2.1. ***Spike the sand with 2.0 mL of 1000ppm NaCl stock solution.***

14.5.3.3. The sample mass shall yield between 2.5-mg and 200-mg dried residue. If complete filtration takes more than 10 minutes, increase the filter diameter or decrease the sample mass.

14.5.4. Add 20.0 mL of clean reagent water to the solid sample. Cap the specimen container and shake vigorously.

14.5.5. Place the specimen container in an ultrasonic bath, and sonicate the solid sample for at least 30 minutes.

14.5.6. Proceed to Section 14.6. for filtration procedure.

14.6. Assemble a vacuum filtration apparatus with a clean filtration flask and Buchner funnel.

14.7. Place a filter paper in the Buchner funnel and apply vacuum.

14.7.1. Handle filter paper using clean forceps throughout the course of sample preparation and analysis.

14.8. Using wash bottle, wet the filter paper with a small volume of reagent water to seat it on the funnel, then rinse the filter paper with three successive 20-mL portions of reagent water.

14.8.1. If the filter paper was pre-prepared for the determination of total suspended solids, no rinsing with three successive 20-mL portions of reagent water is required.

14.9. Continue to apply vacuum until all traces of water have been removed. Turn the vacuum pump off and discard the washings.

14.10. Place a clean, dry 50-mL Class A or B graduated cylinder in the filtration flask to collect filtrate.

14.11. Apply vacuum and carefully decant the measured sample onto and through the filter paper without splashing. Continue filtration with the vacuum operating.

14.12. Using wash bottle, rinse the filter paper thoroughly with three successive 10-mL portions of reagent water. Allow complete drainage between washings, and continue to apply vacuum for about 3 minutes after filtration is complete or until all visible water is removed.

14.13. Turn the vacuum pump off. Carefully remove the graduated cylinder from the filtration flask using clean forceps or tongs.

14.13.1. Do not splash or spill the contents of the graduated cylinder.

14.14. Pour the filtrate (with washings) into a pre-weighed beaker.

14.14.1. Handle beaker using clean forceps or tongs throughout the course of sample preparation and analysis.

14.15. Place the beaker on a hot plate set at 80−100°C.

14.15.1. Monitor the hot plate temperature with a calibrated thermometer.

14.16. Evaporate the filtrate on the hot plate until all traces of water have been removed.

14.16.1. Evaporating on a hot plate ensures observation that no sample splattering occurs.

14.17. Once dry, transfer the beaker to an oven designated for the analysis.

14.17.1. Check the oven temperature prior to placing the beaker inside. The acceptable temperature range is 178−182°C.

14.17.2. Check the temperature log and/or the actual thermometer to be sure the oven is in proper working condition.

14.18. Dry the residue in the oven at 180 ± 2°C for at least one hour.

14.19. Remove the beaker from the oven, transfer to a desiccator and allow to cool.

14.20. When cool to ambient temperature, weigh the beaker including the dried residue on a calibrated analytical balance. Record the mass to the nearest 0.1 mg (or 0.0001 g).

14.20.1. Repeat the drying cycle (Section 14.18. to Section 14.19.) until a constant mass is obtained. The mass change shall be less than 4% of the previous mass or 0.5 mg, whichever is less.

14.21. Samples are filtered one at a time in the following or other logical order:

1) Method Blank (MB)
2) ***Laboratory Control Sample (LCS)***
3) ***Laboratory Control Sample Duplicate (LCSD), if required***
4) Samples (up to ***10***, excluding ***QC***)
5) Sample Duplicate
6) ***Samples (up to 10, excluding QC***)
7) ***Sample Duplicate***

14.21.1. Item 1: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.21.1.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of washed sea sand.

14.21.1.2. One MB is required every day preparatory procedures (i.e., filtrations, dryings, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.21.2. ***Item 2: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.***

14.21.2.1. ***For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid samples, the LCS consists of the specified compounds spiked into washed sea sand.***

14.21.2.2. ***One LCS is required every day sample preparations are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.***

14.21.3. ***Item 3: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.1.***

14.21.4. ***Items 4 and 6***: Up to ***a total of 20 field*** samples ***per batch***.

14.21.5. ***Items 5 and 7***: The sample duplicate is a selected field sample re-processed and re-analyzed under the same analytical conditions. The sample duplicate is processed concurrently with the associated samples. In the processing of the sample duplicate, reagents and procedures identical to those for actual samples are used.

14.21.5.1. The purpose of the sample duplicate is to access the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.1.

14.21.5.2. One sample duplicate is required for every 10 samples per matrix or portion thereof processed concurrently.

14.21.5.2.1. For EPA Region 9 requirement, one sample duplicate is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.22. Thoroughly document all aspects of the preparatory procedures in the Total Dissolved Solids ***Logbook***. This logbook includes, but is not limited to:

14.22.1. Preparation and analysis dates.

14.22.2. Sample volume or mass.

14.22.3. Beaker and dried residue masses.

14.22.4. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

14.23. Data Interpretation

14.23.1. Determine the total dissolved solids of a sample from the sample volume or mass, and the beaker masses before and after sample filtration. The formulas for calculating the concentration of total dissolved solids are listed in Section 15.3. and Section 15.4.

15. CALCULATIONS

15.1. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of total dissolved solids in measurement 1.
C_2 = concentration of total dissolved solids in measurement 2.

Note: Concentrations must be in equivalent units.

15.2. The preparation factor for a solid sample is calculated as follows:

$$P = \frac{V_w}{W_S}$$

where: P = preparation factor for solid sample in mL/g.
V_w = volume of reagent water used prior to sonication in mL. Unless specified otherwise, $V_w = 20$.
W_S = mass of solid sample sonicated in g.

15.3. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_{TDS} = \frac{(M_f - M_i) \times 1000}{V_A}$$

where: C_{TDS} = concentration of total dissolved solids (TDS) in mg/L.
M_f = mass of beaker and oven-dried residue in mg.
M_i = mass of beaker in mg.
V_A = volume of aqueous sample filtered in mL.

15.4. The target analyte concentration for a solid sample is calculated as follows:

$$C_{TDS} = \frac{(M_f - M_i) \times 1000}{V_x} \times P$$

where: C_{TDS} = concentration of total dissolved solids (TDS) in mg/kg.
M_f = mass of beaker and oven-dried residue in mg.
M_i = mass of beaker in mg.
V_x = volume of sonicated solid sample filtered in mL. Unless specified otherwise, $V_x = 20$.
P = preparation factor for solid sample in mL/g.

15.5. All concentrations shall be reported in mg/L (ppm) for aqueous samples and mg/kg (ppm) for solid samples.

15.6. Report TDS concentrations which are < 100 ppm to 2 significant figures, and TDS concentrations which are ≥ 100 ppm to 3 significant figures.

15.7. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009 unless specified otherwise.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. ***The*** concentration of target analyte in an MB should be ≤ ½ the respective reporting limit (RL). If the concentration of target analyte exceeds ½ its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If the target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.2. ***The acceptance criteria for LCS/LCSD compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively. The RPD is ≤ 20%. All LCS/LCSD compounds must be within acceptance limits.***

18.2.1. ***If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD (when applicable) is within acceptance limits, and all target***

analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2. ***If an LCS/LCSD pair was analyzed, both the LCS and the LCSD must be reported.***

18.3. The acceptance criteria for duplicate analyte are predetermined. The RPD is ≤ ***5%***.

18.3.1. For EPA Region 9 requirement, refer to Section 12.2.2.1.1. for acceptance criteria.

18.3.2. When the RPD of the duplicate analyte is at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

18.3.3. If the RPD of the duplicate analyte is not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.

18.5. Additional information regarding internal quality control checks is provided in SOP-T020.

18.6. All concentrations shall be reported in mg/L (ppm) for aqueous samples and mg/kg (ppm) for solid samples.

18.7. Report TDS concentrations which are < 100 ppm to 2 significant figures, and TDS concentrations which are ≥ 100 ppm to 3 significant figures.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009 unless specified otherwise.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits.

The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. ►REFERENCES

22.1. 2540 C. Total Dissolved Solids Dried at 180°C, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998 ***(Committee approval 1997)***.

22.2. 2540 C. Total Dissolved Solids Dried at 180°C, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005 ***(Committee approval 1997)***.

22.3. ***2540 C. Total Dissolved Solids Dried at 180°C, Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012 (Committee approval 1997/Edited 2011)***.

22.4. 2510 A. Conductivity, Introduction, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005 ***(Committee approval 1997)***.

22.5. ***2510 A. Conductivity, Introduction, Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012 (Committee approval 1997/Edited 2011)***.

22.6. EPA Method 160.1: Residue, Filterable (Gravimetric, Dried at 180°C), Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, USEPA, March 1983.

22.7. Total Dissolved Solids (TDS), EPA Method 160.1 (Gravimetric, Dried at 180°C, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, November 1999.

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. ***Appendix A: Procedure Outline***.

23.2. ***Appendix B: Additional Quality Control Criteria for Department of Defense Projects***.

24. ►MODIFICATIONS

24.1. The following modifications from SM 2540 C. are noted:

Calscience SOP M713 Section	Reference Document SM 2540 C Section	Summary of Modification
12.2.2.1	3d	The RPD control limit is modified.
14.15 - 14.16	3d	The filtrate evaporation procedure is modified.

24.2. The following modifications from EPA Method 160.1 are noted:

Calscience SOP M713 Section	Reference Document EPA 160.1 Section	Summary of Modification
14.4.3	7.3	The volume of aqueous sample filtered is modified.
14.15 - 14.16	7.5	The filtrate evaporation procedure is modified.
		EPA Region 9 requirements on contract required detection limit (CRDL), analytical balance check acceptance criteria, and mineral reference sample analyses are not applied.

25. ►*REVISION HISTORY*

Revision	Description	Author	Effective Date
2.7	Section 2: Update matrices. Section 6: Update definitions. Section 9: Update equipment. Section 10: Update reagents and standards. Section 11: Update sample storage. Section 12: Update QC requirements. Section 13: Update calibration. Section 14: Update procedure. Section 18: Update data assessment. Section 22: Update references. Section 23: Add appendices. Section 24: Add Modification tables. Section 25: Add Revision History.	K. Burney	12/16/2013

►*Appendix A*

PROCEDURE OUTLINE

Calscience Environmental Laboratories, Inc.

SOP-M713, Revision 2.7

SM 2540 C PROCEDURE OUTLINE

Total Dissolved Solids (Filterable Residue, Gravimetric)

PROCEDURE

1) Determine conductivity of samples and record in TDS Logbook.
2) Prepare beakers (write ID #, heat in TDS oven 1 hour, cool, weigh).
3) Homogenize aqueous sample and measure 20mL in graduated cylinder.
4) Homogenize solid sample and weigh 3.0g into specimen container; add 20mL reagent water and sonicate 30 minutes.
5) Assemble vacuum filtration apparatus and insert filter in funnel.
6) Wet with reagent water to seat; if not pre-cleaned, wash 3x with 20mL reagent water.
7) Apply vacuum until all water gone; discard washings.
8) Insert clean 50mL graduated cylinder in the filtration flask.
9) Apply vacuum and decant sample onto filter without splashing.
10) Rinse filter 3x with ~ 10mL reagent water with complete drainage in between.
11) Continue to apply vacuum for 3 minutes or until all water gone.
12) Turn off pump; carefully remove graduated cylinder with tongs or forceps.
13) Pour filtrate into pre-weighed beaker.
14) Place beaker on hot plate at 80-100°C and dry until no visible water remains.
15) Dry residue in TDS oven for at least one hour; cool in desiccator.
16) Weigh beaker and record mass.
17) Repeat drying cycle until constant mass obtained.

Special requirements for DoD projects:

Must have MB, LCS and sample duplicate.

APPROVED BY: _____

DATE: _____

SOP-M713, Revision 2.7

SM 2540 C PROCEDURE OUTLINE

Total Dissolved Solids (Filterable Residue, Gravimetric)

REAGENTS

1) Reagent water, interferant free
2) Sand, washed, sea or standard Ottawa.
3) Sodium chloride, NaCl.

QC REQUIREMENT

MB/LCS/LCSD - per batch of 20 samples
Sample Duplicate - every 10 samples

APPROVED BY: _____

DATE: _____

►*Appendix B*

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECTS

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. ***SM 2540 C / EPA Method 160.1, Total Dissolved Solids (Filterable Residue, Gravimetric) – Additional Quality Control Criteria for Department of Defense (DoD) Projects.***

2. SCOPE AND APPLICATION

2.1. ***The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.***

3. QUALITY CONTROL

3.1. ***Limit of Detection (LOD)***

3.1.1. ***LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.***

3.1.2. ***LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.***

3.1.2.1. ***LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit.***

3.1.2.2. ***LOD verification is deemed valid if the apparent signal-to-noise ratio of the analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).***

3.1.2.2.1. ***For a data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.***

3.1.2.3. ***If these criteria are not met, perform either one of the following tasks.***

3.1.2.3.1. ***Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.***

3.1.2.3.2. ***Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.***

3.1.3. ***No samples shall be analyzed without a valid LOD.***

3.2. ***Limit of Quantitation (LOQ)***

3.2.1. ***LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.***

3.2.1.1. ***The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.***

3.2.1.2. ***The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.***

3.2.2. ***LOQ verification must be performed quarterly to verify precision and bias at the LOQ.***

3.2.2.1. ***LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.***

3.2.2.2. ***LOQ verification is deemed valid if the recovery of the analyte is within the established test method acceptance criteria or client data objectives for accuracy.***

3.3. ***Event Based Quality Control (LCS and MBs)***

3.3.1. ***Laboratory Control Sample (LCS)***

3.3.1.1. ***The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. Results of the LCS are compared to established criteria and, if found to be outside of these criteria, indicates that the analytical system is "out of control."***

3.3.1.1.1. ***Any affected samples associated with an out of control LCS shall be reprocessed for re-analysis or the results reported with appropriate data qualifying codes.***

3.3.1.2. ***The LCS shall be analyzed at a minimum frequency of one per preparation batch.***

3.3.1.2.1. ***In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.***

3.3.1.3. ***The concentration of the spiked compounds shall be at the project-specific concentration of concern. If this is not specified, it shall be at or below the midpoint of the calibration curve.***

3.3.2. ***Method Blanks (MBs)***

3.3.2.1. ***The method blank is used to assess the preparation batch for possible contamination during the preparation and processing steps. The method blank shall be processed along with and under the same conditions as the associated samples to include all steps of the analytical procedure. Procedures shall be in place to determine if a method blank is contaminated.***

3.3.2.1.1. Any affected samples associated with a contaminated method blank shall be reprocessed for analysis or the results reported with appropriate data qualifying codes.

3.3.2.2. ***The method blank shall be analyzed at a minimum of 1 per preparation batch.***

3.3.2.2.1. In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

3.3.2.3. ***The MB is considered to be contaminated if one of the following conditions is met.***

3.3.2.3.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, <u>and</u> is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

3.3.2.3.2. The concentration of any common laboratory contaminant in the MB exceeds RL, <u>and</u> is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

3.3.2.3.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

3.3.2.4. ***If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the MDL.***

3.3.2.4.1. If no sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

3.4. ***Matrix Based Quality Control (Sample Duplicates)***

3.4.1. ***Sample duplicates are defined as replicate aliquots of the same sample taken through the entire analytical procedure. The results from this analysis indicate the precision of the results for the specific sample using the selected method.***

3.4.1.1. ***The sample duplicate provides a usable measure of precision only when target analytes are found in the sample chosen for duplication.***

3.4.2. ***The frequency of the analysis of sample duplicates may be determined as part of a systematic planning process (e.g., Data Quality Objectives) or as specified by the mandated test method.***

3.4.3. ***Each preparation batch of samples must contain an associated sample duplicate using the same matrix collected for the specific DoD project.***

3.4.3.1. ***In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.***

3.4.4. ***The results from sample duplicates are primarily designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD) or another statistical treatment (e.g., absolute differences). The laboratory shall document the calculation for relative percent difference or other statistical treatments..***

3.4.5. ***Results are compared to the acceptance criteria as published in the mandated test method. Where there are no established criteria, the laboratory shall determine internal criteria and document the method used to establish the limits.***

3.4.5.1. ***For sample duplicates results outside established criteria corrective action shall be documented or the data reported with appropriate data qualifying codes.***

4. *REFERENCES*

4.1. ***Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 2010.***

Ultra Trace Air Toxics SOP **BRL SOP-00405 / 10**

Ultra Trace Air Toxics

Dioxin and Furan Extracts Cleanup

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Updated SOP to reflect changes
BRL SOP-00405 rev10

Associated Documents

Document Control Documents

- Burlington SOP BRL SOP-00404 : Dioxins and Furans by HRGC HRMS in Air Samples
- Burlington SOP BRL SOP-00406 : Dioxins and Furans by HRGC HRMS in Water and Soil (EPA 8290)
- Burlington SOP BRL SOP-00408 : PCB Congeners Analysis by HRGC HRMS in Water, Soil and Air
- Burlington SOP BRL SOP-00410 : Dioxins and Furans in Water and Soil by HRGC HRMS (EPA 1613)
- Burlington FCD BRL FCD-00015 : All Parameter Hi-Res Sample Tracking Sheet
- Burlington FCD BRL FCD-00023 : Hi Res/ Low Res Sample Tracking Sheet
- Corporate WI Publish to All COR WI-00012 : Definitions
- Corporate WI Publish to All COR WI-00018 : Determination of Estimation of Analytical Uncertainty of Measurement
- Corporate WI Publish to All COR WI-00040 : Corporate Procedure for Policy Deviation Forms
- Campobello WI CAM WI-00095 : Environmental Method Validation (NELAC + DOD requirements)
- Campobello WI CAM WI-00121 : Maxxam Lab QM Supplement to Meet Requirements of DoD QSM Version 4.1
- Campobello FCD CAM FCD-00903 : FMS Proofing Information Form

Campobello FCD CAM FCD-00904 : FMS Clean-up Form

Campobello Method Summary Sheet CAM MS-00010 : BRL SOP-00405 Method Summary for DFs Sample Clean-up

Reason for Change

Date of Change July 14, 2009 **Version** 2
Section Changed Header, 1.0, 4.0.1, 4.3, 7.A-7.B, 10.1, 10.2.2, 12.0
Change Made Header updated Maxxam's name
1.0 updated current lab location
4.0.1 updated reference method 8290 to current revision
4.3 replaced SOP list with the reference to Associated Documents
7.A renumbered section by adding a prefix "A" differentiate from added option 7.B.
7.B added option "B" for Automated Sample Clean-up using POWERPREP™
10.1 updated lab's location
10.2.2. updated procedure to reflect current practice
12.0 added FCD#

Date of Change January 6, 2012 **Version** 3
Section Changed 6.3.1, 7.A.1.1, 7.A.3, 7.A.4, 7.B.1.3, 7.B.1.6, 12.0
Change Made section 6.3.1 added - listing disposable FMS columns and their part numbers.

section 7.A.1.1 - corrected reference to section 7.A.2

section 7.A.3 - added NOTE: Carbon cleanup is required for ALL Soil samples

section 7.A.4 step 14 - corrected information - changed 2mL to 1mL and changed benzene to toluene

section 7.B.1.3 - added "Example of POWERPREP setting when "Jumbo" silica column is used " and changed some of the values for the solvents

section 7.B.1.6 added "Example of Wash program for POWERPREP unit, this can vary dependent on how much cleanup is required"

section 12.0 added "BRL FCD-00023 Tracking Sheet"

Date of Change January 10, 2012 **Version** 4
Section Changed 7.A.1.2.1
Change Made Sulphuric Acid Extraction:
change all references to hexane to DCM

Date of Change January 10, 2012 **Version** 5
Section Changed 1 page Header
Change Made 1 page of the Word doc was formatted as a separate page, inadvertently rev. 4 was not reflected on 1st page, but all other pages. Rev 5 corrected for the formatting of this SOP.

Date of Change September 17, 2012 **Version** 6
Section Changed 7.A.2
Change Made Section 7.A.2 - Step 4 - added iso-octane as a keeper

Date of Change December 5, 2012 **Version** 7
Section Changed 4.0.3-4.0.5, 7.A.3
Change Made 4.0.3-4.0.5 added relevant reference methods to this section
&.A.3 added the addition of carbon clean-up to all air samples
Optional Field A Associated documents have been reviewed, and where required the CPro links were updated to reflect most current procedures in use by the HRMS laboratory

Date of Change May 8, 2013 **Version** 8
Section Changed 10.1, 10.3, 10.4
Change Made 10.1 - added BRL FCD-00023
10.3 - Added reference to CAM WI-00010
10.4 - fixed numbering
Associated documents have been reviewed, and where required the CPro links were updated to reflect most current procedures in use by the HRMS laboratory

Date of Change September 30, 2013 **Version** 9
Section Changed various
Change Made added info to section 6.1.6 re teflon tubes
Optional Field A updated preparation of raw silica gel section 6.2.12
Also added expiry dates to prepared adsorbants
Optional Field B 7.A.2 updated to reflect that adsorbants used to prepare the mixed bed silica column are now weighed. Also added the eluant is to be collected as soon as the extract is added to the column

Date of Change March 11, 2014 **Version** 10
Section Changed 6.2.4.1
Change Made changed carbon and celite mixture to current practice - 18g carbon & 82 g celite
Optional Field A Note: associated documents have been reviewed, and no changes to them are required.

Approval Status Table

Approver Source **Role for Approvers** **Parallel-Everybody** Segment

Approver	Action	Date	Comment
Betsy Cliffe	Approve	March 11, 2014 1:18 PM GMT-4	
Salima Haniff	Approve	March 3, 2014 9:20 AM GMT-5	

CLEAN-UP OF SAMPLE EXTRACTS FOR PCDD AND PCDF ANALYSIS

1.0 LOCATION:

Clean-up procedures are performed in the HRMS Preparation Laboratory.

2.0 PURPOSE:

This method is used to prepare and clean up extracts for the determination of PCDD/DF.

2.1 Principle of the Method: extracts for the determination of PCDDs and PCDFs are cleaned up and passed through a series of columns which remove, by reaction and/or selective adsorption, the bulk of the organic matrix co-extracted with the PCDDs and PCDFs.

A mixed bed column of 44% H_2SO_4/Silica gel, 33% 1M KOH/Silica gel, 10% $AgNO_3$/Silica gel is the first column the sample extract is passed through. The acid silica gel removes any oxidizable contaminants including PAHs and some organochlorine pesticides, many of which are oxidized to acids. This layer becomes highly coloured if a sample extract contains a high concentration of oxidizable material. The basic silica gel removes any acids and phenols. The high water content of the acid and base silica gel deactivates the silica to the point where the silica gel acts only as a support for the acid and base. The $AgNO_3$/Silica gel reacts with organic thio-compounds, molecular sulphur and olefins, complexing them and retaining them on the column. If the sample extract contains high concentrations of these compounds, the $AgNO_3$/Silica layer will be highly coloured.

Silica gel is used between the layers of acid, base and $AgNO_3$ silica gel. These layers hold on to polar compounds. If hexane, used as the eluting solvent, is contaminated with even a small amount of a polar solvent, the polar compounds expected to remain on the column may be eluted. If the silica gel is too active, i.e. not deactivated with at least 3% water, some of the more polar of the dioxins and furans may elute later and not within the expected elution window.

The elution order is generally based on polarity. The higher chlorinated dibenzo-p-dioxins are the least polar and elute first, followed by the less chlorinated dibenzo-p-dioxins. The dibenzofurans are more polar than the dibenzo-p-dioxins and will start eluting later and in the same general order as the dibenzo-p-dioxins based on their degree of chlorination. Overlap occurs in the elution of the dioxins and the furans. The position of chlorine atoms may increase the polarity causing it to elute later. This results in some inconsistencies in the general rule that the higher chlorinated compounds elute first. Solubility also affects the elution order. Less chlorinated, smaller molecular weight compounds are more soluble and causes the lower chlorinated PCDD and PCDF to elute earlier.

The eluent from the mixed-bed column is concentrated and passed through a column of activated alumina. This column also separates compounds based on polarity and is mainly used to separate the dioxins and furans from PCBs. PCBs do not contain oxygen atoms and thus are less polar. They will pass through the column in the first fraction. The dioxins and furans are collected in a second fraction which eluted with dichloromethane, a highly polar solvent used to strip any polar compounds held by the column. This vigorous stripping of polar compounds is possible at this point since most of the unwanted polar compounds were removed with the initial mixed bed column.

If further cleaning of the extract is required an activated charcoal column is used. The extract is loaded onto a column of charcoal supported on Celite. Dioxins and furans are removed from the column using toluene. The activated charcoal column separates the dioxins and furans from interfering compounds based on planarity. The dioxins, furans are planar and elute with the toluene. Co-planar PCBs also elute with the toluene.

2.2 Safety:

2.3.1 General Considerations: each reagent, analyte and sample should be treated as a potential health hazard and exposure should be reduced to the lowest possible level. On the basis of the available toxicological and physical properties of the PCDDs and PCDFs, these compounds should only be handled by highly trained personnel familiar with handling and cautionary procedures, and who understand the associated risks. All work related to the analysis of

PCDDs and PCDFs should be carried out within a specially designed laboratory. Refer to the appropriate MSDS for further information.

2.2.2 PCDDs and PCDFs: the 2,3,7,8-tetrachlorodibenzo-p-dioxin isomer has been found to be acnegenic, carcinogenic and teratogenic in laboratory animal studies. It is soluble in water to ~200 ppt, (ng/L), and in organic solvents to ~0.14%. At room temperature it is a solid and has a relatively low vapour pressure. The physical properties of the 135 other tetra to octa chlorinated PCDDs/PCDFs have not been well established. It is presumed that the physical properties of these congeners are generally similar to those of the 2,3,7,8-TCDD isomer.

All labware, safety clothing, and other items known to have been contaminated with PCDD/PCDF must be carefully secured and subjected to proper disposal. In the unlikely event that analytical personnel experience skin contact with PCDD/PCDF or samples containing these, the contaminated area should be immediately and thoroughly scrubbed using mild soap and water. Personnel involved in any such accident should seek medical advice.

3.0 SCOPE:

This procedure is applicable to all extracts of soil, water, air and biota for the determination of PCDDs and PCDFs at low picogram to nanogram levels by HRGC/HRMS or HRGC/LRMS.

3.1 Interferences: solvents, adsorbents, reagents, glassware and other sample processing hardware may yield artifacts or elevated baselines that may cause misinterpretation of the data. Proper cleaning of glassware is extremely important. Note that glassware may not only contaminate the samples, but may also remove the analytes of interest by adsorption on the glass surface. Method blanks are analyzed to demonstrate that all laboratory materials are free from interferences under the conditions of the analysis. The use of high purity reagents minimizes interferences.

The sensitivity of this method is dependent upon the level of interferences within a given matrix. Interferents co-extracted from the sample material will vary considerably with the matrix and the diversity of the site being sampled. PCDDs and PCDFs are often associated with other chlorinated organics, which may potentially interfere with the analysis. These include PCBs, polychlorinated methoxybiphenyls, polychlorinated hydroxy diphenylethers, polychlorinated benzylphenyl ethers, polychlorinated diphenyl ethers, polychlorinated naphthalenes, polychlorinated xanthenes, polynuclear aromatics, and pesticides.

The interfering compounds may be present at concentration levels several orders of magnitude higher than any PCDDs and PCDFs in the sample. This cleanup procedure reduces or eliminates these interferences to the maximum extent practicable in order to ensure reliable quantitation of PCDDs and PCDFs at trace levels. Despite rigorous cleanup procedures, the possibility of matrix interference will still exist. If detection limits are seriously elevated by excessive background, the sample extract may have to be re-processed or re-extracted with modified cleanup techniques.

4.0 REFERENCES:

4.0.1 US EPA SW846 8290A, Revision A, February 2007

4.0.2 Reference Method for the Determination of PCDDs and PCDFs in Pulp and Paper Mill Effluents, 4th Draft April 1991, Chemistry Division, River Road Environmental Technology Centre, Conservation and Protection, Environment Canada.

4.0.3 US EPA Method 1613, Revision B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS

4.0.4 US EPA SW846 Method 23A Version 1, Dec. 1, 1996. “Sampling Method for Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofuran Emissions from Stationary Sources.

4.0.5 US EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-9, Method for the Determination of Polychlorinated Dibenzo-p-dioxins In Ambient Air Using High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)

4.1 Analytical Testcodes:

Test codes may be created as necessary

4.2 Other Relevant SOPs – refer to Associated Documents in CPro section of this SOP

4.3 Modifications and/or Improvements from Referenced Methods:

4.3.1 EPA SW846 Method 8280A & 1613B:

- Maxxam does not partition the sample with NaCl
- Reference uses NaOH Si Gel, Maxxam uses KOH Si Gel
- Reference uses acidic alumina, Maxxam uses basic alumina
- Reference elutes alumina with 20%DCM in Hexane/DCM, Maxxam uses: 4%DCM in hexane/hexane

4.3.2 Environment Canada River Road Protocol:

- Reference uses 2% DCM in hexane, Maxxam uses 4% DCM in hexane
- Reference uses 50% DCM in Hexane, Maxxam uses straight DCM

5.0 SAMPLE HANDLING AND PRESERVATION:

Maintain the volume of any extracts to at least 2 ml in glass containers prior to cleanup by this procedure. If the cleanup is to be performed >5 days after extraction, store the extracts in teflon-sealed glass containers at 2-6 °C until clean-up.

6.0 APPARATUS AND MATERIALS:

6.1 Apparatus: equivalent labware and equipment may be purchased from other suppliers as available.

6.1.1 Pasteur Pipettes: 5¾" from VWR, Cat. No. 14673-010 and 9" Cat. No. 14673-043 or equivalent

6.1.2 Chromatography Columns: borosilicate glass, 15 mm ID, ~40 cm long with tapered ends for preparing mixed bed silica columns. Obtained from a commercial glass blower.

6.1.3 Borosilicate Glass Tubing: 14 cm long x 5.5 mm ID, for the preparation of carbon/Celite columns. Custom made by a commercial glass-blower.

6.1.4 Borosilicate Glass Vials (16 ml): with closures, used for the collection of fractions from the alumina and carbon/celite columns, rinsed with DCM prior to use. (VWR 66011-121) or equivalent

6.1.5 Borosilicate Glass Vials (35 ml): with closures, used for the collection from the mixed bed silica column, rinsed with dichloromethane prior to use. (VWR Catalogue No. 66012-066) or equivalent

6.1.6 Teflon Tubing: to fit tightly over wide end of pasteur pipettes to facilitate the addition of solvent for alumina cleanup. 6.4 mm. ID, 7.9 mm. OD, cut to ~30 cm lengths. (Canlab, Cat No. R5354-3, Nalgene 890 Teflon FEP 8050-0310 or equivalent). **Note:** keep Hi-Res Teflon tubes separate from those used for Lo-Res samples. The teflon tubing is reusable and as a minimum should be rinsed with DCM between sets of samples. The teflon tubes are stored in a 500mL cylinder filled with DCM when not in use.

6.1.7 Reacti-vials: clear glass, 1 ml, rinsed with DCM prior to use. (Kimble 60700-1) or equivalent. 5mL disposable centrifuge tubes may also be used.

6.1.8 Nitrogen Evaporator/Concentrator: Meyer N-EVAP Organomation Model 111

6.1.9 Balance: capable of measuring to within 0.1 gram

6.1.10 Bottles: 500 ml a/g wide mouth and 1 L c/g bottles with teflon lined closures for the preparation and storage of column packing materials. Rinse with DCM and air dry prior to use.

6.1.11 Glass Wool: 8 µ fiberglass

6.2 Reagents: equivalent reagents may be purchased from other suppliers as available. Other volumes of a reagent may be prepared as necessary by modifying the amount of stock used appropriate to the final volume required.

6.2.1 Activated Carbon/Charcoal: activated charcoal from Anderson Development Company, Cat. No. AX-21 or equivalent. Prior to use the raw carbon is rinsed with ~2 L of methanol using a 90 mm Buchner funnel and a 1 L vacuum flask and dried for ~72 hours at ~130 °C.

6.2.2 Basic Alumina: aluminum oxide basic powder, Brockmann Activity Grade 1, 50-200 µm (Baker no. 0539-05) or equivalent. Activated by heating for at least 18 hours at ~225 °C. Store at ~225 °C.

6.2.3 Copper Powder: reagent grade, from Anachemia, Cat. No. AC 2577 or equivalent

6.2.3.1 Activated Copper Powder: add ~1 ml of reagent grade copper powder to a 35 ml vial and add ~20 ml of concentrated HCl. Using a small Pasteur pipette, stir for ~1 min. After settling remove the HCl with the pipette. Rinse 3 times with RODI water, followed by 3 sequential rinses each of acetone and hexane. Dry using a stream of N_2. Prepare this fresh daily.

6.2.4 Celite: Celite 545 from Fisher Scientific or equivalent

6.2.4.1 Carbon/Celite Mixture: mix 18.0 ±0.01 g of activated carbon and 82.0 ±0.01g of Celite in a 250 ml bottle with a Teflon-lined screw cap. Tumble overnight, minimum 16 hr. Label with the batch number, prep date and analyst ID.

6.2.5 Nitrogen: UHP Grade from Linde or equivalent

6.2.6 RODI: Reverse Osmosis Deionized Water, (RODI), >16MΩ purity.

6.2.7 Hydrochloric Acid (HCl): reagent grade, from Anachemia, Cat. No. EG 4955 or equivalent

6.2.8 Potassium Hydroxide (KOH): reagent grade, from Caledon, Cat. No. 6160-1 or equivalent

6.2.9 Potassium Hydroxide (1.0 M KOH): weigh 56.00 ±0.01 g of KOH into a 1L volumetric flask and dilute to volume with RODI. Store in a 1L amber bottle at room temperature. Prepare as needed.

6.2.10 Solvents: dichloromethane (DCM), ethylene chloride, toluene, hexane, benzene, cyclohexane, ethyl acetate, iso-octane from Caledon or equivalent, Distilled in Glass quality

6.2.10.1 4% DCM in Hexane: using the 4% DCM in hexane labeled Oxford dispenser or equivalent, add 40 ml of DCM to the dispenser and make up to 1 L with hexane

6.2.11 Silver Nitrate: reagent grade, from Caledon, Cat. No. 7020-1 or equivalent

6.2.12 Silica Gel: 100-200 mesh, 60 A. from ICN Biomedicals, Cat. No. 02761 or equivalent

The Silica gel must be washed as follows before use:

1. Place approx. 300mL of ICN Silica Gel into a 600mL Buchner funnel and connect to a vacuum pump
2. Cover the silica gel with approx. 300mL of hexane
3. Stir the silica with a spatula or glass rod and let it settle for 2 minutes
4. Turn on the vacuum pump to remove the solvent
5. Repeat steps 2,3 & 4 2 more times using hexane – total washing with hexane = 3
6. Repeat steps 2,3 & 4 using DCM – this is also repeated 3 times

7. Transfer the washed Silica gel into a pyrex dish lined with foil (rinsed with DCM)
8. Cover pyrex dish with rinsed foil (put some vent holes in the foil cover)
9. Allow to dry in a fumehood overnight to remove solvent
10. Once the solvent is removed, place the silica in the pyrex dish in the oven at 200°C overnight

The washed silica gel is to be used for the preparation of all adsorbants used for D/F cleanups

6.2.12.1 Acid Silica Gel (44% H_2SO_4): tare an empty 1 L clear glass bottle, marked for 44% H_2SO_4. Add ~270-300 g silica gel. The amount of H_2SO_4 needed is calculated by:

Wt. H_2SO_4 needed (g) = wt. Silica Gel (g) x (44/56)

Carefully add the H_2SO_4 to the bottle, on the balance, and allow it to be absorbed. Shake by hand to loosen up the silica gel before placing on the tumbler. Record the prep date, expiry date and prep person's name on the bottle and in the Adsorbent Logbook. overnight, minimum 16hrs. Store at room temperature, prepare as needed. Expiry date is 1 month from preparation date.

6.2.12.2 Basic Silica Gel (33% KOH): tare an empty 1 L c/g bottle labeled 33% KOH. Add ~270-300 g silica gel. The amount of 1M KOH needed is calculated by:

Wt. 0.1 M KOH needed (g) = Wt. silica gel (g) * (33/67)

Carefully add 1M KOH to the bottle, on the balance, and allow it to be absorbed. Shake by hand to loosen up he silica gel before placing the bottle on the tumbler. Record prep date, expiry date and prep person's name on the bottle and in the Adsorbent Logbook. overnight, minimum 16hrs. Store at room temperature, prepare as needed. Expiry date is 1 month from preparation date.

6.2.12.3 $AgNO_3$/Silica Gel (10% $AgNO_3$): dissolve 30.00 ±0.01 g of $AgNO_3$ in a minimum amount of water in a wide mouth glass container with a Teflon-lined closure. Add 270 g of silica gel, cap and shake by hand for ~2 min. to distribute the $AgNO_3$. Cover the bottle with a suitable material to prevent light penetration. Tumble overnight, minimum 16hours. The mixture is placed in the oven at 200°C for 30 minutes. Store at room temperature in the dark and prepare as needed. Record weights, dates, prep person and supplier/lot # in the Adsorbent Logbook. Avoid light penetration of the bottle. Expiry date is 1 month from date of preparation.

6.2.13 Sodium Sulfate (Na_2SO_4): granulated, reagent grade, from Caledon, Cat. No. 8220 or equivalent

6.2.14 Sulfuric Acid (H_2SO_4): reagent grade, from Anachemia, Cat. No. EG 8750 or equivalent

6.3.1 Disposable FMS (Fluid Management Systems) Columns:

- PCB Free High Capacity with Teflon Chips (Jumbo Silica column) part # PCB-HCDS-ACD-TFC
- PCB Free Classical Silica ABN Column part # PCB-ABN-STD
- PCB Free Disposable Basic Alumina (11g) column part # PCBA-BAS-011
- PCB Free Disposable Carbon/Celite (34g_ Column part # PCBC-CCE-034

7.0 ANALYTICAL PROCEDURE:

7.A.1 Extract Preparation: the 2 ml sample extracts from BRL SOP-00407 are transferred to the first clean up column directly from the flask if no splits are required. Add a clean-up spike if required.

7.A.1.1 Normally Coloured Extracts: proceed to Section 7.A.2 if the following are applicable

- concentrated extract is not highly coloured
- does not contain a high concentration of lipids

- not expected to overload the acid silica column, i.e. based on the experience of the analyst

7.A.1.2 Highly Coloured Extracts: a further sulfuric acid extraction may be required if

- the concentrated extract is highly coloured
- the sample is known to contain a high concentration of lipids
- the sample is expected to overload the acid silica, i.e. based on the analyst's experience

7.A.1.2.1 Sulphuric Acid Extraction:

Step 1 quantitatively transfer the extract with DCM to a 15 ml glass vial
Step 2 dilute the extract to ~10 ml of hexane
Step 3 add ~4 ml of concentrated H_2SO_4 to the extract
Step 4 if the H_2SO_4 bottom layer is not highly coloured, stir or gently shake the contents
Step 5 if an emulsion forms and increasing the volume of H_2SO_4 and/or DCM does not yield 2 distinct layers, transfer the entire contents of the vial to a small separatory funnel
Step 6 increase the volumes of DCM and H_2SO_4
Step 7 remove the H_2SO_4 layer using a Pasteur pipette and collect in another 15 ml vial
Step 8 repeat the extraction with H_2SO_4 until no further colour is noticed in the H_2SO_4
Step 9 wash the collected H_2SO_4 twice with ~2 ml of DCM
Step 10 add these washes to the original extract
Step 11 concentrate the extract under a gentle stream of N_2 to ~1 ml
Step 12 process the extract as per Section 7.2

7.A.2 Mixed Bed Silica Gel Column Clean-Up: prepare these columns just prior to use

Step 1 pack the tapered end of a 15 mm ID x 40 cm glass column with a small piece of glass wool and add in the following sequence;
Prepare columns as follows:
- Glass wool plug in bottom of column
- 2.5g of Na2SO4
- 1.0g of 10% silver nitrate/silica gel
- 1.0g washed silica gel
- 3g of 33% KOH/Silica gel
- 1g of washed silica gel
- 8g 44% sulphuric acid
- 1g washed silica gel
- 2.5g Na2SO4

Step 2 rinse the packed column with 30 ml hexane and discard this eluent
Step 3 using a 9" Pasteur pipette, add the extract to the column just as the solvent reaches the top of the column bed

Transfer steps are critical. Loss of any of the extract will seriously affect recoveries.

Step 4 start to collect the eluant as soon as the extract has been loaded onto the column
Step 5 collect the eluant in a pre-rinsed 40 ml vial and add 1mL of iso-octane as a keeper
Step 6 quantitatively transfer the extract with at least three 2 ml hexane rinses, adding each rinse to the column just when the previous rinse reaches the top of the column bed
Step 7 add additional hexane in small amounts to rinse down the sides of the column
Step 8 when the vial is approximately half full, the hexane can be added in larger amount (~10 ml)
Step 9 continue this to the point where the vial is filled to the top
Step 10 concentrate the total eluent to a 2 ml final volume under a gentle stream of N_2
Step 11 cover the eluent with a teflon-lined cap if the extract will not be processed immediately

Note: if the entire sulphuric acid-silica gel layer is coloured, the column has been overloaded. Reprocess the concentrated eluent on a fresh column. Based on the experience of the analyst, the sample may be passed through a column of 44% H_2SO_4 only.

7.A.2.1 Secondary H_2SO_4 Acid/Silica Gel Clean-Up:

Step 1 pack the tapered end of a 15 mm ID x 40 cm glass column with glass wool and add the following in sequence;

- ~1 cm sodium sulfate
- 1 cm silica gel
- 9 cm of 44% sulphuric acid silica gel
- 1 cm of silica gel
- ~1 cm sodium sulfate

Step 2 prepare these columns just prior to use and rinse with 30 ml of hexane
Step 3 transfer the extract and collect the eluent in the same manner as in Section 7.2.1
Step 4 the sample may also be split and passed through multiple columns and then recombined when acid layer is clean, (this decision is based on the experience of the analyst)

Note: if the $AgNO_3$ column is highly coloured (yellow), clean it further with fresh activated copper powder prior to another column cleanup by performing the following, (see BRL SOP-00008), Sulphur Clean-up:

Step 5 add ~0.5 ml of the activated copper powder to the ~2 ml concentrated extract in the vial
Step 6 mix for at least 1 minute using a Pasteur pipette
Step 7 add more copper powder until the copper powder no longer turns black
Step 8 the extract can now be passed through the Secondary H_2SO_4 Acid/Silica Gel column

7.A.3. Basic Alumina Column Clean-Up:

Step 1 pre-rinse the Teflon tubing with ~5-10 ml DCM
Step 2 pack the tapered end of a 9" Pasteur pipette with glass wool, add the following in sequence;

- add ~0.5 cm sodium sulfate
- fill to within 1 cm of the top with hot basic alumina
- add ~0.5 cm of sodium sulfate

Step 3 fit the top of the pipette with a piece of Teflon tubing
Step 4 place column in a stand and rinse with 7 ml of hexane, discarding the eluent
Step 5 place a 15 ml borosilicate glass vial under the column
Step 6 add the sample extract to the column with a Pasteur pipette just as the wash solvent reaches the top of the column bed
Step 7 quantitatively transfer the extract with 2 rinses of ~2 ml of 4% DCM/hexane each time
Step 8 add each rinse to the column when the previous rinse just reaches the top of the column bed
Step 9 add a further 4 ml of 4% DCM/hexane for a total eluent volume of ~10 ml
Step 10 label this eluent fraction A and archive
Step 11 place a second 15 ml vial, (pre-rinsed with DCM), under the column just as the last of the hexane reaches the top of the column bed
Step 12 add 8 ml of DCM to the column using a pipette or solvent dispenser
Step 13 add 1ml of hexane or isooctane to a 9 ml total volume. This "Fraction B" contains PCDD/DF
Step 14 if carbon cleanup isn't required, concentrate the extract as in Sect. 7.5
Step 15 if carbon cleanup is required, concentrate the eluent to ~1 ml under a gentle stream of N_2

<u>NOTE: Carbon cleanup is required for ALL soil samples and ALL air samples</u>

7.A.4 Carbon/Celite Column Clean-Up:

Step 1 mark a 14 cm long piece of 5 mm ID glass tubing with a permanent marker at 7cm and 11 cm
Step 2 form a plug of glass wool at the 7 cm mark
Step 3 fill to ~half way between the 11 cm mark and the end with carbon/Celite mixture
Step 4 gently tap on the counter to bring the carbon/Celite down to the 11 cm mark

Step 5 add glass wool to form another plug
Step 6 place the columns in the stand with the larger reservoir end up
Step 7 place a 15 ml vial under the column to collect waste
Step 8 add 5 ml of toluene in 1 ml aliquots
Step 9 add 1 ml of 50:50 DCM/cyclohexane
Step 10 add 5 ml hexane in 1 ml aliquots
Step 11 add the sample, (concentrated Fraction B eluent from alumina cleanup), to the column using a Pasteur pipette just as the wash solvent reaches the top of the column bed
Step 12 transfer the extract, rinsing twice with 0.5 ml hexane, adding each rinse to the column just as the previous rinse reaches the top of the column bed, keep this vial to collect the sample portion of the eluent
Step 13 add 2 ml 50:50 DCM/hexane in 1 ml aliquots
Step 14 add 1 ml of 50:50 toluene/ethyl acetate
Step 15 discard the waste vial
Step 16 **invert column and place a piece of teflon tubing on the column**
Step 17 place the sample vial back under the column and add 14 ml of toluene, in two 7 ml portions
Step 18 this rinse contains the PCDD/DFs and is then concentrated and transferred as in Section 7.5

7.A.5 Concentration of Cleaned Extract:

Step 1 concentrate the eluent, containing PCDD/DF from the alumina column, or the eluent, containing PCDD/DF from the carbon/celite column, to ~0.5-1 ml with a gentle stream of N_2
Step 2 transfer the concentrated extract to a DCM rinsed Reacti-vial, do not fill the vial >half full
Step 3 concentrate the extract under a gentle stream of N_2 while transferring
Step 4 rinse the vial at least three times with hexane
Step 5 concentrate the extract almost to dryness

NOTE:

- Adding the rinses to the extract, at a point when the total volume in the vial is less than half full, ensures that the sides of the vial are rinsed and that the final extract will be in the bottom of the vial.

- Method spike is prepared with each batch of samples. The method spike consists of all the spiking solutions added to the blank spike.

7.B.1 Automated Sample Clean-up using POWERPREP™ (Optional)

Expiry date of elution solvents is assigned according to CAM WI-00004 unless otherwise stated in this SOP.

7.B.1.1 The elution solvents are placed at the right of the units and are installed as follows: Position 1, hexane, Position 2, 2%DCM in hexane, Position 3, 50% DCM in hexane, Position 4, 50% EtAC in toluene and Position 5, toluene.

7.B.1.2. 2%DCM in hexane and 50% DCM in hexane should be made daily or every other day at the most. 50% EtAC in toluene every month depending on consumption.

7.B.1.3. Assuming that the lines have been flushed already, connect the columns and place the sample into position according to the diagram at the front of the POWERPREP™. Note that the silica columns can only be installed only way with the red arrow pointing upwards.

NOTE: IF THE BACK PRESURE BUILDS TO 30psi, THE UNIT WILL STOP. SHUT OF THE POWERPREP AND TURN ON AGAIN, THEN FOLLOW THE PROCEDURE IN THE MANUAL.

DF CLEANUP PROGRAM FOR POWERPREP ™
Example of POWERPREP setting when "Jumbo" silica column is used

No	Flow ml/min	Volume (mL)	Description
1	10	80	Wet Si column with hexane
2	12	12.5	Flush hexane through by-pass
3	10	24	Wet Alumina Col. With hexane
4	10	24	Wet carbon Col. With hexane
5	10	240	Condition Si Column with hexane
6	12	14	Change to Toluene through by-pass
7	10	47	Pre-elute carbon with Toluene
8	12	14	Change to Et/Ac Through by pass
9	10	12	Pre-elute carbon with EtAc/Toluene
10	12	14	Change to 50% DCM/Hex Through by pass
11	10	24	Pre-elute carbon with 50% DCM/Hex
12	12	14	Change to Hex Through by pass
13	10	36	Pre-elute carbon with Hexane
14	5.0	18	Add sample Extract in Hexane
15	10	240	Elute Si Column with hexane
16	12	12	Change to 2% DCM/Hex Through by pass
17	10	72	Elute Al and Carbon column with 2% DCM/Hex
18	12	14	Change to 50% DCM/Hex Through by pass
19	10	143	Elute with 50% DCM/Hex
20	12	12	Change to Et/Ac Through by pass
21	10	4.0	Elute with EtAc/Toluene
22	10	14	Change to hexane through by-pass
23	10	12	Flush Carb col with hexane
24	12	14	Change to Toluene through by-pass
25	5.0	156	Collect PCDD/PCDF through reverse carbon Column

7.B.1.4 When the high capacity or "jumbo" silica column is employed the following steps are affected: Step 1, 70mL instead of 20mL, Step 5, 200mL, Step 14, depends on desired sample dilution and Step 15, 200mL. The same volumes here are used when both silica columns are employed as well.

When the clean up is done remove the spent columns and discard. Place the couples and connect the lines where the columns once were.

7.B.1.5 Remove the samples tube and replace with a vessel containing clean hexane.

7.B.1.6 Run the clean power prep program in order to clean out the back lines. See the following:

INTERNAL LINE WASH PROGRAM FOR POWERPREP ™

Example of Wash program for POWERPREP unit, this can vary dependent on how much cleanup is required

No	Flow ml/min	Volume (mL)	Description
1	15	40	Wash lines with 50%DCM/hexane
2	15	40	Wash carbon column lines with 50%DCM/hexane
3	15	40	Wash sample lines with 50%DCM/hexane
4	15	40	Wash PCB lines with 50%DCM/hexane
5	15	40	Wash lines with hexane
6	15	40	Wash carbon column lines with hexane
7	15	40	Wash lines with hexane
8	15	40	Wash PCB lines with hexane

Note that the final steps of the line wash are in hexane as DCM can attack the internal valve structures.

8.0 QUALITY CONTROL:

8.1 Internal Standards: refer to the appropriate analytical SOP for details.

8.2 Method Blanks: for water samples, process a method blank of RODI water with each batch of 20 samples. Process a method blank of sodium sulfate for each batch of 20 solid samples.

8.3 Blank Matrix Spikes: an aliquot, equal to or as close as possible to the method blank aliquot size is spiked with the matrix spiking solution. Refer to the analytical SOP for details on the spiking solution to use. Extract the blank spike with the samples in the batch. One blank matrix spike is analyzed for every 20 samples unless regulations or contracts require or allow a different frequency.

8.4 Matrix Duplicate: process a matrix duplicate from a random sample as required by the specific method or client's request. If possible, use a sample in which positives are expected i.e. site history indicates positives.

8.5 Matrix Spike/Matrix Spike Duplicates: spike a random aliquot, equal to or as close as possible to the sample aliquot size, with the matrix spiking solution. Refer to the analytical SOP for details on the spiking solution to use. Extract the sample matrix spike with the batch of samples. A sample matrix spike is analyzed at a frequency of 1 in 20 samples unless regulations or contracts require otherwise.

8.6 Additional Quality Control: blind duplicates, audit and performance evaluation samples may have specific instructions to be followed. They are to be treated the same as any other sample.

9.0 DATA CALCULATIONS:

9.1 Data Entry:

All lot numbers of adsorbents, solvents, spiking solutions etc. are recorded on the Job Work / tracking sheet , generated using MaxxLIMS when work on a batch of samples commences. Data is entered in MaxxLIMS for each test or group of tests logged for a set of samples ie., Lipid determination, moisture determination etc. This information is retrievable for reporting by the Project Manager to the client and is linked by Job number, Worksheet number, sample number, client id, and analytical test results.

10.0 DOCUMENTATION:

10.1 A tracking sheet is completed (see BRL FCD-00015 and BRL FCD-00023 forms) for each batch of samples. It must contain complete information i.e.; Job number, extraction date, clean up date, sample number, client name, client sample id, sample weight/volume, number of splits, amount and type of spike added, solvent lots, reagent lots,

preparation dates and any additional information pertaining to the extraction or cleanup. A photocopy is given to the instrument technician with the completed samples and the original is kept in a binder in the HRMS Prep Lab.

10.2 Analyst Logbook: maintain a logbook which contains, at a minimum, the following information.

- deviations from normal procedures required for problematic samples, (these deviations must be discussed and signed off by the appropriate Supervisor or Operations Manager. Deviations can alternatively be recorded on the sample tracking / worksheet.

10.2.1 Sample Deviation Records: Deviations must be recorded in the Job report remarks section in Maxxlims and appear on the Certificate of Analysis. Examples are as follows:

- analyzed past hold time
- sample is not homogeneous

10.2.2 Method Deviation Records: if instances arise in which the SOP may not be applicable to the nature of the sample and may require modifications to the normal methodology.

- prior to use, discuss proposed deviation with the Supervisor or Operations Manager
- if deviation is deemed appropriate, record the deviation in the QSI Policy Deviation Form and submit to the Supervisor or Operations Manager for approval. Deviation must be approved prior to its implementation.
- record the deviations for each sample in the Sample report remarks area in Maxxlims.

10.3 Standard and Reagent Preparation Tracking: record all preparations of standards and reagents in the Standard Preparation and the Reagent Preparation Logbooks. Refer to CAM WI-00010 for the required information.

10.4 Certificates of Analysis for Standards and Reagents: certificate of analyses are kept for all inorganic salts and solutions utilized in this SOP. These records will contain at a minimum the following information.

- Source of the inorganic salt or solution
- supplier information and Lot Number
- date received

11.0 WASTE MANAGEMENT:

All efforts are taken to prevent or reduce to a minimum the effect of waste disposal on the environment. All solvents are collected for shipment to a recycling facility. All recyclable plastic, glass and paper products are shipped to an appropriate recycling facility. The disposal of waste materials and samples are to carried out in accordance with protocols outlined in the SOP for the Preparation, Storage and Disposal of Reagents and Standards and the SOP for the Receipt, Handling and Disposal of Hazardous Wastes. All waste disposal will comply with the Ontario Ministry of the Environment and Energy's Sewer Guidelines and Regulation 558.

11.1 Specific Disposal Issues: contaminated sample extracts are collected and sent for disposal to an approved hazardous waste subcontractor. Excess contaminated samples are either returned to the client or submitted for disposal as noted.

12.0 APPENDIX:

- BRL FCD-00015 Tracking Sheet
- BRL FCD-00023 Tracking Sheet

Ultra Trace Air Toxics SOP **BRL SOP-00406 / 12**

Ultra Trace Air Toxics

Dioxins and Furans by HRGC HRMS in Water and Soil (EPA 8290)

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Ultra Trace Air Toxics Departments	Environmental HRMS		

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Release and Audit Schedule	
Release Schedule	When Approved ☐ **Allow Administrator to Release Document Early**
Expiration Schedule	When Superseded or Obsoleted
Audit Schedule	12 Month(s)
Special Handling on Release	
☑ **Update Completed Trainee Records**	

Insert Text

BRL SOP-00406 rev12

Associated Documents

Document Control Documents

- Burlington FCD BRL FCD-00002 : Data Review Checklist
- Burlington FCD BRL FCD-00003 : Organic Control Chart Out of Control Checklist
- Burlington FCD BRL FCD-00023 : Hi Res/ Low Res Sample Tracking Sheet
- Burlington SOP BRL SOP-00405 : Dioxin and Furan Extracts Cleanup
- Burlington SOP BRL SOP-00407 : Dioxin and Furan Extraction in Liquid and Solid Samples
- Burlington WI BRL WI-00011 : Review and Validation of Analytical Data
- Campobello MOC CAM MOC-00174 : Confirmation of 2,3,7,8-TCDF
- Corporate WI Publish to All COR WI-00010 : Corporate Procedure for Nonconformances
- Corporate WI Publish to All COR WI-00011 : Corporate Procedure for Corrective and Preventative Actions
- Corporate WI Publish to All COR WI-00012 : Definitions
- Corporate WI Publish to All COR WI-00018 : Determination of Estimation of Analytical Uncertainty of Measurement

- Corporate WI Publish to All COR WI-00040 : Corporate Procedure for Policy Deviation Forms
- Corporate WI Publish to All COR WI-00044 : Manual Integration of Chromatographic Peaks
- Corporate WI Publish to All COR WI-00049 : Continuing Calibration Verification (CCV) Acceptance Criteria
- Corporate WI Publish to All COR WI-00050 : Environmental Chemistry Method Validation
- Corporate WI Publish to All COR WI-00055 : Corporate Procedure for Control Charting
- Campobello WI CAM WI-00095 : Environmental Method Validation (NELAC + DOD requirements)
- Campobello WI CAM WI-00121 : Maxxam Lab QM Supplement to Meet Requirements of DoD QSM Version 4.2

Reason for Change

Date of Change July 4, 2007 **Version** 2
Section Changed 2.0, 3.6, 3.7, 8.10, 9.3
Change Made 2.0-clarified matrices
3.6-removed list of definitions
3.7-added reference to MU procedure
8.10-clarified control chart practice
9.3- clarified data validation practice

Date of Change August 7, 2007 **Version** 3
Section Changed Re-formatting entire document due to right side truncation when this SOP was printed
Change Made Tables 1-3 and Figure 1 were moved as attached files.
Added WHO 2005 TEFfor Dioxins and Dioxin-like Compounds.

Date of Change August 31, 2007 **Version** 4
Section Changed 3.1, 3.2.2, 4.1, 5.0, 6.2.1, 6.2.2, 6.2.3, 6.4, 6.4.1, 7.3, 7.7.4, 8.1, 8.2, 8.3, 8.7, 9.1, 9.4, 10.5, 10.6.2
Change Made Throughout the document (i.e., 3.1, 3.2.2, 6.2.3, 6.4, 6.4.1, 7.3, 7.7.4, 8.1, 8.2, 8.3, 8.7, 9.1, 10.6.2) corrected units from pg/mL tp pg/uL.
Section 4.0 added reference to PSEP 1997a,b, Ecology 2003. Added alternative method re: sample storage and holding time for soil/sludge and pulp samples
Section 5.0, removed first sentence since it was only refering to water samples. Added Temperature storage column for listed matrices. Changed "Biological" to "Tissue" in matrix column.
Section 6.2.2, added section for ODWS on determination of Drinking Water MDL, and referenced OMOE respective document.
The SOP has been removed from embedded to detached document due to difficulties in document formatting .
Section 9.1, for the non-detected 2,3,7,8-substituted congeneres added calculation methods for reporting TEQ
Section 9.4 and 10.5, updated sections to reflect current practice
Section 12.0, added Table 4 as 2005 WHO List
Minor corrections of typographical errors throughout the document

Date of Change August 21, 2008 **Version** 5
Section Changed 8.2, Table 4
Change Made Both sections corrected for typographical errors

Date of Change February 26, 2009 **Version** 6
Section Changed Header, 4.0
Change Made Header - reflect lab's current name
4.0 - changed to reflect current revision of EPA SW-846 8290A, Revision 1, February 2007.

Date of Change July 13, 2009 **Version** 7
Section Changed 7.3, Associated Documents
Change Made 7.3, Step 5, changed to: confirmation runs for 2,3,7,8-T4CDF are performed only if the primary result is greater than the RDL.
Added reference to CAM MOC-00174 in Associated Documents
9.1 corrected typographical error "quantification"

Date of Change June 1, 2010 **Version** 8
Section Changed 1.0, 3.2., 3.3, 3.4, 4.3, 8.5, 10.2, 10.6.1,
Change Made 1.0 updated to lab's current location
3.2+3.3 redefined correlation between MDL and detection limit, as well as Maxxam's RDL and LOQ, added performance of quarterly LOD and LOQ
3.4 updated to reflect current PT program
4.3 replaced with reference to QSI Associated Documents
8.5 added DoD requirements for method blank criteria & corrective actions re: DoD related projects
10.2 updated to reflect current practice re: use of COR WI-00040, Corporate Procedure for Policy Deviation Forms
10.6.1. updated storage of records offsite to reflect current practice

Date of Change September 6, 2010 **Version** 9
Section Changed 4.3, 6.1, 6.1.1, 7.3.4.1, 7.3.4.2, 8.3, 10.0
Change Made 4.3 Deleted test-codes that were not applicable
6.1 Removed solvents that were not applicable
6.1.1 Added nonane and removed nitogen from compressed gases list
7.3.4.1 Added optional solvents
7.3.4.2 Added OPRs and matrix spikes to analytical sequence table
8.3 Added action required if instrument malfunctions prior to injection of post CCV
10.0 Revised to reflect current practice

Date of Change December 7, 2010 **Version** 10
Section Changed 3.2, 6.2.1
Change Made 3.2; updated reference to CAM WI-00095
6.2.1; corrected typographical error in units from mL to uL.

Date of Change January 4, 2012 **Version** 11
Section Changed 6.4, 6.4.1, 7.4, 8.1, 8.2, 8.10,
Change Made Section 6.4 - updated instrumentation
Section 6.4.1 - updated capillary columns
Section 7.4 - revised RT criteria to -1 to +3
Section 8.1 - removed reference to CARB428
Section 8.2 - RSD criteria for labeled standards changed to <20%
Section 8.10 - included an additional analyte for control charting (23478-PeCDF)

Date of Change November 13, 2012 **Version** 12
Section Changed 3.4, 4.2, 7.3.1, 7.3.2, 7.3.4.1, 7.3.4.2, 7.4, 8.1, 8.2, 8.5, 8.10
Change Made 3.4 - updated to reflect CAM Wi-00095 for method validation and maintenance of method validation records
4.2 - Added modification to confirmation analysis
7.3.1 and 7.3.2 - Updated GC conditions
7.3.4.1 and 7.3.4.2 - Made solvents and MSPIKE optional
7.4 updated to reflect current practice, i.e: the signal to noise (S/N) for all monitored ions must be ≥2.5 and for PCDF identification, no peak having a S/N ≥ 2.5 may be found in the corresponding PCDPE channels
8.1 and 8.2 - Added = sign to < or > and changed column terminology
8.5 - Added additional method blank criteria for internal standard recovery exceedances
8.10 updated to reflect reference to COR WI-00055 for control charting procedure
Optional Field A Associated documents have been reviewed, and where required the CPro links were updated to reflect most current procedures in use by the HRMS laboratory

Approval Status Table

Approver Source **Role for Approvers** **Parallel-Everybody** Segment

Approver	Action	Date	Comment
Ewa Konieczna	Approve	November 13, 2012 12:45 PM GMT-5	
Owen Cosby	Approve	November 13, 2012 5:43 PM GMT-5	

DIOXINS AND FURANS BY HRGC HRMS IN WATER AND SOIL (based on EPA 8290A)

1.0 LOCATION:

This procedure is performed in the HRMS Prep Lab and the HRMS Instrument Laboratory.

2.0 PURPOSE:

This method is used to measure the concentration of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's), in water and soil samples.

NOTE: For the purpose of this procedure's clarity on matrices, use the following reference

Water Matrix - ground water, drinking waters, surface waters, wastewaters, etc.

Soil Matrix - solids, chemical materials, sludges, sediments and other solid wastes

Biota Matrix - biota (sample of a plant and/or animal)

2.1 Principle of the Method: PCDD's/DF's are extracted from solid samples with toluene and aqueous samples with methylene chloride. After extraction, the samples are cleaned up by passing through a series of columns that remove, by reaction and/or selective adsorption, the bulk of the organic matrix co-extracted with the PCDD's and PCDF's. The resulting fraction is concentrated to a known volume for analysis. Qualitative/quantitative analysis for PCDD's and PCDF's is performed using separation by Hi Resolution Capillary Gas Chromatography (HRGC) and measured by Hi Resolution Mass Spectrometry (HRMS). PCDD's/DF's are identified by comparing GC retention times and the ion abundance ratios of the m/z's with the corresponding values obtained for authentic standards.

The analyte concentration is determined using GC/MS and an isotope dilution technique. Quantitation is based on the use of internal standards and relative response factors (RRFs). Total PCDD's and PCDF's are reported as the sum of the individual isomers, corrected for internal standard recoveries. The toxic equivalence (TEQs) for the sample is the sum of the individual 2,3,7,8-Isomers found multiplied by its specific Toxic Equivalence Factor (TEF).

2.2 Nature of Samples: samples can be from many different sources including incinerator ashes, soils, sediments and effluents. The laboratory should be made aware of any past history involving the samples or the presence of potentially interfering substances at elevated levels (e.g. PCB). This can allow the preparation technician to take a smaller aliquot of sample so that internal standards are not diluted out during analysis.

2.3 Safety:

2.3.1 General Considerations: the toxicity or carcinogeneity of each compound or reagent used in this method has not been established precisely. Each compound should be treated as a potential health hazard and exposure should be reduced to the lowest possible level. On the basis of the available toxicological and physical properties of the PCDD's and PCDF's, these compounds should only be handled by highly trained personnel thoroughly familiar with handling and cautionary procedures, and who understand the associated risks. All work related to the analysis of PCDD's and PCDF's should be carried out within a specially designed laboratory. As a general guideline, PCDD's and PCDF's and samples suspected to contain these compounds should be handled using essentially the same techniques employed in handling radioactive or infectious materials.

2.3.2 Specific Warnings: the 2,3,7,8-tetrachlorodibenzo-p-dioxin isomer is acnegenic, carcinogenic, and teratogenic (laboratory animal studies). It is soluble in water to ~200 ppt and in organic solvents to 0.14%.

3.0 SCOPE:

This is a HRGC/HRMS method for the determination of PCDD's and PCDF's at low ppt (parts per trillion) to ppq (parts per quadrillion) levels in liquid and solid samples.

3.0.1 Chemical Abstracts No.

Analyte	Symbol	CAS No.
2,3,7,8-Tetrachlorodibenzo-p-dioxin	TCDD	1746-01-6
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	PeCDD	40321-76-4
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	HxCDD	39227-28-6
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	HxCDD	57653-85-7
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	HxCDD	19408-74-3
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	HpCDD	35822-46-9
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	OCDD	3268-87-9
2,3,7,8-Tetrachlorodibenzofuran	TCDF	51207-31-9
1,2,3,7,8-Pentachlorodibenzofuran	PeCDF	57117-41-6
2,3,4,7,8-Pentachlorodibenzofuran	PeCDF	57117-31-4
1,2,3,4,7,8-Hexachlorodibenzofuran	HxCDF	70648-26-9
1,2,3,6,7,8-Hexachlorodibenzofuran	HxCDF	57117-44-9
1,2,3,7,8,9-Hexachlorodibenzofuran	HxCDF	72918-21-9
2,3,4,6,7,8-Hexachlorodibenzofuran	HxCDF	60851-34-5
1,2,3,4,6,7,8-Heptachlorodibenzofuran	HpCDF	67562-39-4
1,2,3,4,7,8,9-Heptachlorodibenzofuran	HpCDF	55673-89-7
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	OCDF	39001-02-0

Note: Total TEQ is calculated as per Section 9.1.1.

Total Tetrachlorodibenzo-p-dioxin	TCDD	41903-57-5
Total Pentachlorodibenzo-p-dioxin	PeCDD	36088-22-9
Total Hexachlorodibenzo-p-dioxin	HxCDD	34465-46-8
Total Heptachlorodibenzo-p-dioxin	HpCDD	37871-00-4
Total Tetrachlorodibenzofuran	TCDF	55722-27-5
Total Pentachlorodibenzofuran	PeCDF	30402-15-4
Total Hexachlorodibenzofuran	HxCDF	55684-94-1
Total Heptachlorodibenzofuran	HpCDF	38998-75-3

3.1 **Linear Range:** the method is calibrated over the following linear ranges of calibration solutions.

Cl4 to Cl7: 1.0-500 pg/uL and Cl8: 5 to 1000 pg/uL

3.2 **Detection Limit:** Detection Limit is also referred to as Method Detection Limits (MDL): an MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. MDLs are determined by the procedure outlined in CAM WI-00095, Environmental Chemistry Method Development Revision and Validation

Target MDLs are verified annually by spiking water/soil replicates at the CS2-CS3 levels. These samples are carried through the full extraction and cleanup procedure. MDLs are determined by multiplying the standard deviation of the results by the Student's t-Value for the number of replicates used. If Target Limits are not achieved, the exercise is repeated spiking at a lower level. An MDL study is used to determine if the target limits

outlined in test methods have been achieved. These are maintained on file in the QSI MDL Module as well as at the instrument. To meet DOD requirements, these limits are then used to determine spiking levels for the Limit of Detection (LOD) verification. Each matrix is spiked two to three times the target limit (derived above) for a single analyte test or one to four times the detection limit for a multi-analyte test.

NOTE: As per CAM WI-00121, section D.1.2.1, Maxxam HRMS Lab schedules quarterly LOD verifications for each respective matric to meet DOD requirements.

Estimated Detection Limit (EDL): EDLs are sample specific and are calculated on a case specific basis for all levels of chlorination, tetra through octa, as well as for each 2,3,7,8-substituted isomers. If a signal produced is not at least 2.5 times the average background level at the expected retention time for specific isomers, the area response for the noise is calculated as follows:

$$2.5 \times \text{peak intensity of background noise} \times \frac{\text{area of internal standard}}{\text{height of internal standard}}$$

This is done for either the quantitation ion or the confirmation ion. Using theoretical ratios for the specific degree of chlorination an area for the second ion is generated. These areas are then totaled and applied to the same calculation scheme as for "positive" hits. (see Section 9). EMPCs (Estimated Maximum Possible Concentrations) are calculated whenever peaks are detected that meet all criteria except for ratios. The area in this case is recalculated (factored up or down) to meet the classical ratio and the result is flagged as an EMPC (NDR, not detected because of ratios, for Canadian Method).

NOTE: Maxxam HRMS lab schedules quarterly LOD verifications. They are analyzed with the next batch of samples for respective matrix.

3.3 Reporting Detection Limit (RDL): Reporting Detection Limit is also referred to as Limit of Quantitation (LOQ), equivalent to the Low Level Standard.

NOTE: As per CAM WI-00121, section D.1.2.1, Maxxam HRMS lab schedules quarterly LOQ verifications for each respective matrix to meet DOD requirements.

3.4 Other Method Validation: further method performance is evaluated/monitored by the participation in the Non Potable Water and Solid Waste Performance Testing Programs from Resource Technology Corporation (RTC). Results of these ongoing studies are maintained in the CPro database for method validation and the respective lab. Refer to CAM WI-00095 for Method Validation procedure.

3.5 Interferences: interferents co-extracted from the sample material will vary considerably with the matrix and the diversity of the site being sampled. PCDD's and PCDF's are often associated with other chlorinated organics that may potentially interfere with the analysis. These include polychlorinated biphenyls, polychlorinated methoxy biphenyls, polychlorinated hydroxy diphenyl ethers, polychlorinated benzylphenyl ethers, polychlorinated diphenyl ethers, polychlorinated naphthalenes, polychlorinated xanthenes, polynuclear aromatics, and pesticides.

Often the compounds responsible for interferences may be present at concentration levels several orders of magnitude higher than any PCDD's and PCDF's that may be present. Cleanup procedures can be used to reduce or eliminate these interferences to the maximum extent practicable in order to ensure reliable quantitation of PCDD's and PCDF's at trace levels. Despite rigorous cleanup procedures, the possibility of matrix interference will still exist. If detection limits are seriously elevated by the excessive background, the sample extract will have to be re-processed using alternative cleanup techniques.

3.6 Definitions: Refer to COR WI-00012 Corporate Definitions

3.7 Measurement Uncertainty: defines an interval about a sample result that would be expected to contain a large fraction of the distribution of values that would occur through repeated analysis of similar samples using the same methodology. Uncertainty is expressed as the standard deviation of the mean of a set of data (Blank Spikes/Laboratory Control Samples). Laboratory blunders or human errors are not incorporated into the calculations. Refer to COR WI-00018, Determination of Estimation of Analytical Uncertainty of Measurement.

The reported Expanded Uncertainty of an analyte is specific to the laboratory method used and incorporates laboratory procedures; physical measurements, (volume, temperature and mass), environmental variation, reagent and standard purity, sample preparation procedures (if applicable), personnel and instrumental parameters.

The most significant factors affecting the uncertainty of a measurement arise from the field-sampling program. They involve field site sample homogeneity; sampling technique; cleanliness of sampling equipment/containers; cross contamination of samples; environmental conditions; subsampling techniques; preservation techniques; sample storage; time to submit to laboratory. These variations are not incorporated into Maxxam's uncertainty calculations.

Maxxam uses a coverage factor "k" (multiplier of the combined standard uncertainty) to obtain an Expanded Uncertainty. Maxxam reports to a confidence level of 95% (k=2).

Maxxam does not correct sample data for bias or recoveries (except surrogate recoveries in Isotope Dilution methods). The final decision on the acceptability and application of the reported data is the responsibility of the client.

4.0 REFERENCES:

U. S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, SW-846 8290A, Revision 1, February 2007

4.1 Other Information Sources:

- U. S. Environmental Protection Agency, Tetra through Octa-chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B, October 1994.
- Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples, Section 3A [required for cleaning glass components of the sampling train].
- For further information contact Gary McAlister or Roger Shigehara, Emission Measurement Branch (MD-19), Technical Support Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, USA 27711, telephone (919)-541-1062.

4.2 Modifications and/or Improvements from Referenced Methods: Maxxam meets or exceeds all requirements of the referenced methods. For the two column confirmation analysis, Maxxam monitors only one descriptor (for tetras), not three (for tetras, pentas, hexas) as per Section 11.9.8.2 of Method 8290A.

4.3 Analytical Test Codes:

Waters:	**Analysis:**
DF8290-W	Method 8290 2378-substituted Isomers and PCDD/DF congeners (Tetra to Octa Homologue Groups) in water samples
DF8290S-LC	Method 8290 2378-substituted Isomers and PCDD/DF congeners (Tetra to Octa Homologue Groups) in TCLP leachate samples

Solids:	**Analysis:**
DF8290-S	Method 8290 2378-substituted Isomers and PCDD/DF congeners (Tetra to Octa Homologue Groups) in solid samples
DF8290-SB	Method 8290 2,3,7,8-substituted isomers and PCDD/DF congeners (Tetra to Octa Homologue Groups) in swab samples

Other test codes may be created as necessary

5.0 SAMPLE HANDLING AND PRESERVATION:

During transit, the samples should be packed in rigid-body coolers in an upright position and kept chilled at all times. Due to the fragile nature of the containers, the samples should be well wrapped with protective packaging during shipment from the field site to the laboratory. Samples that exceed the hold time will be flagged on the Certificate of Analysis. Different hold times may be imposed by other regulating agencies or as determined by client specific projects. Project specific and regulatory requirements for preservation method and reporting criteria (required detection limit, dry or wet weight basis) must be examined and made clear prior to sample analysis. All containers should have Teflon liners in the caps.

Matrix	**Container**	**Min. Vol.**	**Time to Extract**	**Time to Analysis**	**Temperature Storage**
Waters	4 x 1L amber glass	800 ml	30 days	45 days	4°C ±2°C
Soils/Sludge	100 ml amber glass	2 x 5 gram	30 days	45 days	4°C ±2°C
Pulp	100 ml amber glass	2 x 15 gram	30 days	45 days	4°C ±2°C
Tissue	100 ml amber glass	2 x 20 gram	30 days	45 days	< -10°C

6.0 APPARATUS AND MATERIALS:

6.1 Reagent Preparation: all reagent preparation information, Lot Nos., supplier, are documented in the Reagent Preparation Logbook kept in the sample preparation laboratory. Equivalent quality reagents and standards may be purchased from other suppliers as appropriate.

6.1.1 Solvents: nonane is purchased from Aldrich, Distilled in Glass quality or better and transferred to a 1L amber glass dispensette. This is stored at ambient temperature for up to 2 years.

- RODI Water: reverse osmosis deionized water produced in house
- Compressed Gases: UHP Grade helium. Air is provided by an on-site compressor.

6.2 Standard Preparations: all standards preparations, Lot Nos., supplier information, pertinent dates are documented by the analyst in the Standard Preparation Log Book located in the instrumentation laboratory. Stock standards are stored as per manufacturer's directions. Once prepared, the standards are transferred to amber glass vials with teflon-lined caps and refrigerated at 2-6 °C. They are equilibrated to room temperature and are then sonicated prior to use. Intermediate and Working level standards are stored for up to 2 years. Alternatively, commercially prepared "ready to inject" Calibration Standard mixes may be used.

6.2.1 Calibration Standards: refer to Appendix: Table 3 for the volumes of the stock standards to use for preparing Calibration Standards. Current Suppliers and Lot Numbers are in the Standards Prep Logbook in the Instrument Lab.

Intermediate Calibration Standards: add the volumes of stocks to 660 uL of nonane in a 2 ml vial

Component	Stock Conc. (ng/uL)	Final Conc. (ng/uL)	Vol. Added (uL)
2,3,7,8-T4CDD	50	1	20
2,3,7,8-T4CDF	50	1	20
P5-H7CDD/CDF	25	2.5	100
1,2,3,4,6,7,8,9-O8CDD	50	5	100
1,2,3,4,6,7,8,9-O8CDF	50	5	100

Initial Calibration Verification Standard (ICV): purchased as an injection ready standard from a second source supplier. The Standards Prep Logbook lists current information on the supplier and Lot No. This standard contains the following analytes at the indicated concentrations.

Native Analytes:	**Conc. (pg/ul)**	**Internal Standards:**	**Conc. (pg/ul)**
2,3,7,8-T4CDD	10	2,3,7,8-T4CDD$^{13}C_{12}$	50
2,3,7,8-T4CDF	10	2,3,7,8-T4CDF$^{13}C_{12}$	50
1,2,3,7,8-P5CDD	25	1,2,3,7,8-P5CDD$^{13}C_{12}$	50
1,2,3,7,8-P5CDF	25	1,2,3,7,8-P5CDF$^{13}C_{12}$	50
2,3,4,7,8-P5CDF	25	1,2,3,6,7,8-H6CDD$^{13}C_{12}$	125
1,2,3,4,7,8-H6CDD	25	1,2,3,4,7,8-H6CDF$^{13}C_{12}$	125
1,2,3,6,7,8-H6CDD	25	1,2,3,4,6,7,8-H7CDD$^{13}C_{12}$	125
1,2,3,7,8,9-H6CDD	25	1,2,3,4,6,7,8-H7CDF$^{13}C_{12}$	125
1,2,3,4,7,8-H6CDF	25	O8CDD$^{13}C_{12}$	250
1,2,3,6,7,8-H6CDF	25		
2,3,4,6,7,8-H6CDF	25	**Recovery Standards:**	**Conc. (pg/ul)**
1,2,3,7,8,9-H6CDF	25	1,2,3,4-T4CDD$^{13}C_{12}$	50
1,2,3,4,6,7,8-H7CDD	25	1,2,3,7,8,9-H6CDD$^{13}C_{12}$	125
1,2,3,4,6,7,8-H7CDF	25		
1,2,3,4,7,8,9-H7CDF	25		
O8CDD	50		
O8CDF	50		

6.2.2 Method Spiking Solution (Internal Standard): a 10 ml nonane working level internal standard solution, is prepared once per year or as required containing isotopically labeled PCDD's and PCDF's stock solutions. The volume of stock standards used is recorded in the Standard Preparation Log Book, located in the Instrument laboratory. Manufacturer Certified Stock standards are purchased from Cambridge Isotope Laboratories, Woburn, Massachusetts USA or Wellington Labs (Chemsyn Science Labs) in Guelph, Ontario, Canada.

Component	**Stock Conc. (ng/uL)**	**Final Conc. (pg/uL)**	**Vol. Added (uL)**
2,3,7,8-T4CDD$^{13}C_{12}$	50	100	20
1,2,3,7,8-P5CDD$^{13}C_{12}$	50	100	20
1,2,3,6,7,8-H6CDD$^{13}C_{12}$	50	250	50
1,2,3,4,6,7,8-H7CDD$^{13}C_{12}$	50	250	50
1,2,3,4,6,7,8,9-O8CDD$^{13}C_{12}$	50	500	100
2,3,7,8-T4CDF$^{13}C_{12}$	50	100	20
1,2,3,7,8-P5CDF$^{13}C_{12}$	50	100	20
1,2,3,4,7,8-H6CDF$^{13}C_{12}$	50	250	50
1,2,3,4,6,7,8-H7CDF$^{13}C_{12}$	50	250	50

6.2.3 Recovery Standard (Injection Std.): prepare a 10 ml final volume, nonane working level solution, once per year or as needed. Concentrations may vary with suppliers and with the same supplier. Volumes of stock standard used for the current standards are listed in the Standard Prep Book. The following are used for 50 ng/uL stocks.

Component	**Stock Conc. (ng/uL)**	**Final Conc. (pg/uL)**	**Vol. Added (uL)**
1,2,3,4-T4CDD$^{13}C_{12}$	50	50	10
1,2,3,7,8,9-H6CDD$^{13}C_{12}$	50	50	10

6.3 Apparatus: autosampler vials; assorted gas-tight micro syringes; assorted screw-cap amber vials with teflon-lined caps

6.3.1 Glassware Quality Control: all extraction glassware is engraved with a specific serial number. Glassware used for processing samples is tracked using this number. All glassware is subjected to a proven, rigorous cleaning procedure after which it is acceptable for reuse. The analysis of Method Blanks confirms the acceptability of this procedure.

- Soxhlet apparatus that were exposed to samples resulting in highly-coloured extracts are soaked in a soap solution (Extran) overnight
- after soaking they are rinsed thoroughly with successive rinses of RODI water and acetone
- all Soxhlets are then cycled with toluene overnight
- Rotovap glassware is rinsed thoroughly with appropriate solvents after each use

6.4 Instrumentation: High Resolution GCs coupled to High Resolution Mass Spectrometers

HR GC: **Associated HR MS:**

HP6890 Plus	(S/N US00021197)	Micromass Autospec Ultima	(S/N M278)
HP6890	(S/N US000034029)	Micromass Autospec Ultima	(S/N M384)
HP6890	(S/N US00029754)	Micromass Autospec Ultima	(S/N M230)
HP6890D	(S/N US00030341)	Micromass Autospec Ultima	(S/N M449)
HP6890N	(S/N US10131086)	Micromass Autospec Ultima	(S/N M536)
HP6890A Plus	(S/N US00038736)	Micromass Autospec Ultima	(S/N M526)

6.4.1 Gas Chromatographs: gas chromatographs consist of the following components

- Oven: must maintain a temp. ±1°C and perform programmed increases in temp. at rates of 3 °C/min
- Temperature Gauge: to monitor column oven, detector, & exhaust temperature ±1°C
- Gas Flow Metering System: to measure sample, fuel, combustion gas, & carrier gas flows
- Capillary Columns: the primary column is a fused silica column, Varian CP-Sil 8 CB, 60 m x 0.25 mm inside diameter (ID), or equivalent, and the confirmation column is a fused silica column, Restek, Rtx-Dioxin2, 60 m x 0.25 mm ID, or J&W DB225, 30m x 0.25mmID, or equivalent.

6.4.2 Mass Spectrometers: capable of routine operation at 1:10000 resolution with ±5ppm stability with a compatible data system capable of monitoring at least five groups of 25 ions

6.5 Miscellaneous Equipment: analytical balance capable of measuring within 0.1 mg

7.0 ANALYTICAL PROCEDURE:

7.1 Sample Extraction: refer to "BRL SOP-00407 for the Extraction of Liquid and Solid Samples for PCDD's and PCDF's."

7.2 Sample Clean Up and Fractionation: refer to "BRL SOP-00405 Clean Up of Sample Extracts for PCDD/DF Analysis."

7.3 Analysis: analyze the sample extract by HRGC/HRMS using the instrumental parameters in section 7.3.1 and 7.3.2.

Step 1 add 20 uL of Recovery Standard to the dry sample extract in the 1 mL Reacti-vial

Step 2 vortex for ~30 seconds and allow to equilibrate for at least 3 minutes

Step 3 transfer to an amber autosampler vial using a micropipettor

Step 4 seal with an aluminum teflon lined crimp cap

Step 5 inject 1 or 2 uL of the extract into the GC

Analyze the sample using a GC/MS with the instrument parameters given in Section 7.3.1 and 7.3.2. A 1-2 uL aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB-5 type capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra through octa). On a DB5 type column 2,3,7,8-T4CDF is not uniquely separated from 2,3,4,7-T4CDF and 1,2,3,9-T4CDF. Therefore, confirmatory runs for 2,3,7,8-T4CDF are performed only if the primary result is greater than the RDL. In either case the separation criteria in Figure 1 must be met and demonstrated.

7.3.1 Typical GC Operating Conditions (DB5 'type' 60 meter column): these are typical conditions and are optimized for each individual column to maximize performance.

- Injector: configured for capillary column, splitless, 290 °C
- Carrier Gas: helium at 1-2 ml/min
- Initial Temperature 150 °C for 2 minute
- 20 °C/minute to 200 °C
- 2.0 °C/min to 235 °C
- 8 °C/min to 310 °C
- hold at 310 °C for 7 minutes

7.3.2 Typical GC Operating Conditions (DB225/Rtx-Dioxin2 'type' column): these are typical conditions and are optimized for each individual column to maximize performance.

- Injector: configured for capillary column, splitless, 290 °C
- Carrier Gas: helium at 1-2 ml/min
- Initial Temperature 180 °C for 1 minute
- 45 °C/minute to 235 °C for 1 minute
- 3 °C/min to 250 °C for 10 minutes
- 50°C/min to 300 °C for 5 minutes

7.3.3 High Resolution Mass Spectrometer

- Resolution of 10,000 minimum
- Ionization Mode: Electron impact, 35-40 eV (optimize)
- Source Temperature: 290 °C (optimize)
- Monitoring mode: Selected ion recording - see Table 1 for a list of the ions to be monitored

7.3.4 Typical Run Sequence: at the beginning and the end of a run sequence, a hardcopy of the resolution check is printed out. The operator manually verifies that a minimum resolution of 1:10,000 has been achieved for each multi-group experiment (see the descriptor groups in see Table 1).

7.3.4.1 Initial Calibration: (process takes ~12 hours to perform)

- DB5 Window Performance Check
- Solvent
- Solvent (optional)
- CS1_8290
- CS2_8290
- CS3_8290
- CS4_8290
- CS5_8290
- Solvent (optional)
- NBS 1614
- Solvent (optional)
- CS3_8290 (second source check)
- Solvent (optional)

7.3.4.2 Typical Sample Analysis Sequence: (process takes ~12 hours to perform). At the beginning and the end of a run sequence a hardcopy of the resolution check is printed out. The operator manually verifies that a minimum resolution of 1:10,000 has been achieved for each multi group experiment, see the descriptor groups in Table 1. After this verification is complete the run can proceed as follows:

- DB5 Window Performance Check
- Solvent (optional)
- CS3_8290
- OPR
- OPR Dup (if available)
- Matrix Spike (if available)
- Matrix Spike Dup (if available)
- Solvent
- Solvent (optional)
- Method Blank
- Sample 1
- Sample 2
- Sample 3
- Sample 4
- Sample 5
- Sample 6
- Sample 7
- Sample 8
- Solvent (optional)
- CS3_8290 (post analysis calibration verification)
- Method Spike (optional, not used in any calculations, serves only as an aid to determine the source of potential problems for internal and matrix recoveries).

7.4 Identification Criteria: the following identification criteria shall be used for characterization of PCDD's and PCDF's.

- the integrated ion-abundance ratio shall be within ±15 percent of the theoretical value. Table 2 gives acceptable ion abundance ratio ranges for identification of chlorine-containing compounds

- analyte retention time must be within –1 to +3 seconds for the corresponding labeled internal, surrogate or alternate standard.

- the monitored ions shown in Table 1 for a given analyte shall reach their maximum within 2 seconds of each other

- the identification of specific isomers that do not have corresponding labeled standards is done by comparing the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e. within 0.005 RRT units), to the comparable RRT's found in the continuing calibration

- the signal to noise (S/N) for all monitored ions must be ≥2.5

- confirmation of 2,3,7,8-T4CDF shall satisfy all of the above criteria

- for PCDF identification, no peak having a S/N ≥ 2.5 may be found in the corresponding PCDPE channels

7.5 Quantification: the peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the 2,3,7,8-T4CDD$^{13}C_{12}$ is used to calculate the concentrations of all other tetra chlorinated dioxin isomers.

Recoveries of the tetra- and penta- internal standards are calculated using the 1,2,3,4-T4CDD$^{13}C_{12}$. Recoveries of the hexa through octa internal standards are calculated using the 1,2,3,7,8,9-H6CDD$^{13}C_{12}$.

7.6 Maintenance: emergency maintenance is performed by either Maxxam staff or the manufacturer's Service Engineer. Preventative maintenance is performed annually through a service contract.

7.7 Troubleshooting and Common Problems: the analyst may perform the following checks if he/she is capable. Otherwise call a Manufacturer's Service Engineer. Check for the following conditions:

- system is fully powered on and is in the Operate mode
- vacuum is in acceptable range, i.e. 10-6 mbar or better, if not check for leaks
- filament is "ON" and the trap is regulating
- source and transfer line heaters are at the proper operating temperature, the source temperature affects the fragmentation of the sample
- GC in good working order, adequate supply of carrier gas with respect to oven heater and temperature regulation
- Injector system is clean with a properly installed column, liner and septum. Leaks and contamination may cause performance problems
- capillary column Helium head pressure is adjusted to proper setting, i.e. ~25 psi for a 60 m x 0.25 mm ID column
- autosampler syringe is in good condition, not leaking nor plugged
- data system is running and is controlling and communicating with the instrument

7.7.1 Loss of Beam: may be caused by any of the following

- a defective source, collector or alpha slit may be obstructing the beam
- the isolation valve may not be completely open, check the pneumatic valve
- check the compressed air tank line pressure
- broken or blocked PFK jet or capillary line, replace if necessary

7.7.2 Loss of Filament Current, Trap Current and Electron Energy: may be caused by any of the following

- remove the source, check for short circuits, dirty or defective parts. Clean or replace if needed
- check the filament alignment in the source when replacing it
- if the filament comes on and there is no trap current, this could indicate that a trap contact problem has occurred
- check the electrical contacts and the alignment of the source magnets

7.7.3 Loss of Magnet: may be caused by any of the following

- high voltage breaker switch tripped due to a power interruption or surge
- high voltage breaker switch tripped due to a loss of the cooling water supply. When cooling water supply is lost or is too warm the magnet unit and the diffusion pumps overheat. The heat sinks on the power supply board cause the power to shut down and may trip the breaker on the power distribution panel on the front of the instrument. These must all be reset before the magnet can be turned back on

7.7.4 Loss of High Voltage: may be caused by any of the following

- an electronic fault and may be brought on by a discharge of a dirty lens or ceramics or arcing on the flight tube
- these regions must be cleaned to restore voltages and to re-establish control of the beam electronics and SI0S interface will also have to be reset to restore communications and control of the beam control and source control PCBs.

8.0 QUALITY CONTROL:

8.1 Column Separation and Performance Check: inject 1 uL of the DB5 Window Performance Mix, which documents resolution between 2,3,7,8-T4CDD and other T4CDD isomers for DB5. Resolution is acceptable if the result of the following equation:

$$\frac{\text{Height of valley between 2,3,7,8-T4CDD and the closest eluting peak}}{\text{Height of 2,3,7,8-T4CDD peak}}$$

Result must be ≤ 25% for DB-5 (2,3,7,8-T4CDD) or ≤ 25% for DB-225 (2,3,7,8-T4CDF)

See Figure 1. Sample analysis is not started until the above performance criterion is achieved.

8.2 Initial Calibration: calibrate the GC/MS system using the set of five standards (Table 3). These working level standards are used for a period of up to 2 years. If available, an "injection ready" standard from a second source supplier and an NBS 1614 standard reference material is also run as part of the Initial Calibration. Instrument parameters are adjusted and standards are analyzed until the following QC criteria are achieved.

- relative standard deviation (RSD) of the mean response factor for each unlabeled analytes must be ≤ 20%
- RSD of the mean response factor for each of the labeled standards must be ≤ 20%
- S/N ratio for the GC signal present in every selected ion current profile shall be ≥10 for both labeled and unlabeled analytes
- the ion abundance ratios shall be within the control limits in Table 2
- absolute retention time of 13C12-1,2,3,4-TCDD shall exceed 25.0 minutes on a DB5 type column and 15.0 minutes on the DB225 type column.
- 2nd Source standard should be ≤ 50% for both labeled / unlabeled analytes.

8.3 Continuing Calibration Verification: inject 1 uL of solution CS3 (see Table 3). At the beginning of each 12 hour sequence, calculate the relative response factors (RRFs) for each compound and compare each of them to the corresponding mean RRF obtained during the initial multi-point calibration. The following requirements must be met before sample analysis can begin.

- the measured %RSD of the RRF for the labeled analytes for the daily run must be ≤ 30%
- the measured %RSD of the RRF for the unlabeled analytes for the daily run must be ≤ 20%
- the ion abundance ratios must be within the limits given in Table 2

The CS3 standard is analyzed at the end of the run sequence. The %RSD of the RRFs are again compared to the initial calibration and must satisfy the above criteria to validate the analytical run.

NOTE: if the sample analysis sequence was unable to be completed due to instrument failure, immediately run a CS3 continuing calibration standard to validate the sample data. If this fails to meet criteria, all samples **must** be re-injected.

8.4 **Internal Standards**: are added to all samples and QC samples.

Recoveries must be 40-135% for the tetra through octa-chlorinated compounds

8.4.1 Corrective Actions: if the above criterion is not achieved

- the data will still be acceptable provided that the signal is equal to or greater than ten times the noise level
- this will be flagged in the Case Narrative section of the final report
- the sample may be re-extracted if nothing can be found to explain the low or high recoveries and no obvious interference is causing the problem.

8.5 **Method Blanks:** a method blank is run in every batch, and a minimum of one for every 20 samples. For any 2,3,7,8-substituted chlorinated dibenzo-p-dioxin or chlorinated dibenzofuran , the method blank must be less than the minimum levels (less than the CS1) as documented in EPA Method 8290.

NOTE : A low or high internal standard percent recovery for the method blank does not require discarding the analytical data as per Section 9.7 of EPA Method 8290A

<20 pg of T4CDD/DF

<50 pg of P5/H6/H7CDD/DF

<100 pg O8CDD/DF

NOTE: for DoD samples, the method blank will be considered to be contaminated if:

- The concentration of any target analyte in the blank exceeds 1/2 the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater);
- The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or
- The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives

8.5.1 Corrective Actions: if the above criteria are not met then

- investigate possible source of contamination by checking at a minimum: Instrument Spike Standard Solutions, Recovery Standards, proofing of glassware, proofing of solvent and absorbents used in clean-up
- all of the samples must be re-prepared and reanalyzed
- if sufficient sample is not available then any positive sample data must be flagged as possibly contaminated to the level found in the Method Blank

8.6 **Blank Matrix Spike**: must be prepared and analyzed at a frequency of 1 Blank Spike for every batch of samples up to a maximum batch size of 20 samples. Calculate the recovery as:

$$\text{Spike Recovery (\%)} = \frac{\text{Spiked Blank Result}}{\text{Spike Added}} \times 100$$

Native analyte recoveries must be 80-140%

Internal Standard recoveries must be 40-135%

8.6.1 Corrective Actions:

- check calculations and reanalyse if recoveries are outside of these limits
- if the blank spike is outside of limits but the matrix spike is acceptable then the blank spike may have been spiked incorrectly. Review the data with the Supervisor or Operation Manager. All data may be accepted but must be flagged as exceeding acceptance criteria
- if both the blank spike and the matrix spikes exceed their respective limits re-prepare and reanalyze the samples providing sufficient sample is available
- if sufficient sample is not available the data must be flagged in the Sample report remarks section in Maxxlims

8.7 Matrix Duplicate: must be prepared and analyzed using randomly selected samples, at a frequency of 1 matrix duplicate for every batch of samples up to a maximum batch size of 20 samples. The RPD is calculated as:

$$\% \text{ RPD} = \frac{\text{first sample result - duplicate sample result}}{\text{(first sample result + duplicate sample result)/2}} \times 100$$

RPD between duplicates should be ≤ 25%

8.7.1 Corrective Actions:

- check calculations for errors
- check solid samples for homogeneity, if not homogeneous, flag the data in Tester's Comments
- if the sample is homogeneous, re-prepare and reanalyze the sample

8.8 Matrix Spike/Matrix Spike Duplicate Recoveries: if sufficient sample is available, spike two separate aliquots of a sample in each batch of 20 samples or less with an appropriate level (2-5 times the sample concentration if possible) of native dioxin/furans and each of the 2,3,7,8-substituted congeners. Calculate the recoveries as follows:

$$\text{Matrix Spike Recovery (\%)} = \frac{\text{spiked sample result - sample result}}{\text{amount spike added}} \times 100$$

Recoveries of matrix spiked internal standards must be between 40-135%

Native analyte recoveries must be 80-140%

RPD between duplicates should be ≤ 20%

8.8.1 Corrective Actions:

- check calculations for errors
- if recovery calculations aren't possible (due to high sample concs.) flag the data in the Sample report remarks section in Maxxlims
- if the blank spike is acceptable then flag the data as a possible Matrix interference

- check solid samples for homogeneity, if not homogeneous, flag the data
- if the sample is homogeneous, re-prepare and reanalyze the sample
- if both the blank spike and the matrix spikes exceed their respective limits re-prepare and reanalyze the sample the sample if sufficient sample is available
- if sufficient sample is not available flag the data in Maxxlims.

8.9 Standard Reference Materials: NBS 1614 is analyzed with each initial calibration as a check on the accuracy of the calibration. The calculated value is plotted against the true value for the solution.

Each analyte must be within ± 20% of the true value

If not achieved, further investigation of standard ref. material and prepared calibration standard reliability is required.

8.10 Control Charts: Refer to COR WI-00055 Corporate Control Charting procedure for generating control charts via MaxLIMS and real time (i.e., plotted manually, each time the QC sample and/or standard is analyzed). Plot the blank spike recovery of 2,3,7,8-T4CDD and 2,3,4,7,8-P5CDF for both waters and soils on separate control charts. Update the chart immediately after the analysis of the QC point used or in the morning after an overnight run, prior to reporting of data. Monitor the chart for the development of trends on the chart. Take actions, if necessary, as defined in the SOP for Control Charting. If an "Out of Control" point is found, terminate the analysis and resolve the problem. Note the resolution directly on the chart or code the point to a reference in the analyst's workbook.

8.10.1 Possible Causes:

- deterioration of standard or reagents
- standard, QC sample or reagent preparation error
- standard contamination or evaporation
- improper sample introduction
- poor analyst technique or insufficient training
- deviation from SOP procedure
- imprecise measuring devices, i.e. pipettors, syringes

8.10.2 Corrective Actions: if "out of control points" are encountered

- check the other run QC, if acceptable report the data
- if not acceptable, reanalyze the QC samples and if acceptable, report the data
- if not acceptable, find and resolve the cause, re-extract and reanalyze the samples
- if insufficient sample exists report the data, flagged as "out of statistical control"
- if hold times will be exceeded upon re-extraction and reanalysis, flag the data
- if no reason can be found, report the data as "out of statistical control"

Note the resolution on the Control Chart or reference it to the Analyst's Workbook.

8.11 Additional QC: in addition to the QC samples listed above, blind replicates, audit and performance evaluation samples may be submitted. These samples may have specific instructions that must be followed, however, analysis is to proceed as for any other sample. Any USACE project has an Analytical Data Review Checklist, documented in the QA Manual, completed and submitted with the final data report.

9.0 DATA ANALYSIS:

9.1 Calculations: the internal standard method is used to quantify PCDD's/PCDF's. It relies upon consistent linearity of MS response over time and over the calibration range represented by the standard solutions defined in Table 3. This internal standard method is easily integrated into an automated routine for data quantification. Internal standard quantification is based on the use of Relative Response Factors (RRF). For native standards, the RRF is the ratio of analyte response factor to the response factor of the corresponding labeled surrogate (internal standard). These RRFs remain unchanged over the range of concentration for which MS response is linear. Using these RRFs, along with native and surrogate responses from the sample run, recovery-corrected concentrations of PCDD's/PCDF's are calculated directly. Internal standard recoveries are calculated separately and reported. They reflect the overall data quality.

Relative response factors for the native standard (RRFn) and for the Internal standard (RRFs) are calculated using the following equations:

$$RRFn = \frac{Ac * Csc}{Asc * Cc} \quad \text{and} \quad RRFs = \frac{Asc * Crs}{Ars * Csc}$$

Where:

RRFn = relative response factor, Native Standard to Internal Standard

RRFs = relative response factor, Internal Standard to Recovery Standard

Ac = quantification ion (single or both ions) peak area for Native Standard

Asc = quantification ion (single or both ions) peak area for the appropriate Internal Standard

Ars = quantification ion (single or both ions) peak area for 1,2,3,4-T4CDD13C12 or 1,2,3,7,8,9-H6CDD13C12

Cc = concentration of the Native Standard (pg/uL)

Csc = concentration of the appropriate Internal Standard (pg/ uL)

Crs = concentration of 1,2,3,4-T4CDD13C12 or 1,2,3,7,8,9- H6CDD13C12 (pg/ uL

Using the RRFs, sample PCDD's/PCDF concentrations (C) and internal std. recoveries (%R) are calculated as follows:

$$C(X) = \frac{\sum_{k=1}^{n} Ak \bullet Qss}{Ass \bullet RRFn} / Ws \text{ or } Vs \quad \text{and} \quad \%R(X) = \frac{Ass * Qrs * 100}{Ars * Qss * RRFs}$$

Where:

C(X) = recovery-corrected quantity of analyte X (pg/g for solids, pg/L in liquids)

Ak = quantification ion (single or both ions) peak area for the "kth" homologous isomer of analyte X (n=1 for isomer-specific analysis)

Qss = amount of internal standard X added to the sample (pg)

Ass = quantification ion (single or both ions) peak area for internal standard X in extract

%R(X) = percent recovery of internal standard X

Qrs = amount of 1,2,3,4-T4CDD13C12 (recovery std for T4 and P5-CDD/CDF) or 1,2,3,7,8,9-H6CDD13C12 (recovery std for H6, H7-CDD/CDF and O8CDD/DF) in sample extract (pg)

Ars = quantification ion (single or both ions) peak area for 1,2,3,4-T4CDD13C12 or 1,2,3,7,8,9-H6CDD13C12 in sample extract

Ws = weight of dry sample in grams

Vs = volume of sample in L

For homologues represented by more than one isomer in the calibration standards, the "homologue-average" RRF is used to quantify all target analytes that are not 2,3,7,8-substituted congeners.

9.1.1 Toxic Equivalence Determination: Polychlorinated dibenzo-para-dioxins (PCDD's) and Polychlorinated dibenzofurans (PCDF's) are known to exist as widespread environmental contaminants and to be toxic in nature. The 2,3,7,8-substituted congeners have been assigned Toxicity Factors by NATO (NATO-CCMS, 1988), with 2,3,7,8-TCDD, the most toxic, given a value of 1. International Toxicity Equivalency Factors (ITEFs) are shown below.

Toxic Equivalence (TEQ) is determined by multiplying the concentration of each detected 2,3,7,8-substituted congener by its repective TEF. Individual and Total TEQ are determined as follows using I-TEFs from the table shown below.

Individual TEQ = (congener conc. found) * (congener specific TEF)

Total TEQ = Sum of Individual TEQs

International Toxicity Equivalency Factors (I-TEF)

Congener of Concern	**I-TEF**
2,3,7,8-TCDD	1
1,2,3,7,8-P5CDD	0.5
1,2,3,4,7,8-H6CDD	0.1
1,2,3,6,7,8-H6CDD	0.1
1,2,3,7,8,9-H6CDD	0.1
1,2,3,4,6,7,8-H7CDD	0.01
OCDD	0.001
2,3,7,8-TCDF	0.1
2,3,4,7,8-P5CDF	0.5
1,2,3,7,8-P5CDF	0.05
1,2,3,4,7,8-H6CDF	0.1
1,2,3,6,7,8-H6CDF	0.1

2,3,4,6,7,8-H6CDF	0.1
1,2,3,7,8,9-H6CDF	0.1
1,2,3,4,6,7,8-H7CDF	0.01
1,2,3,4,7,8,9-H7CDF	0.01
OCDF	0.001

For the 2,3,7,8-substituted congeners that are non-detectable, the following TEQ calculation methods can be used:

- 2,3,7,8-substituted congener TEF x DL
- 2,3,7,8-substituted congener TEF x ½ DL
- 2,3,7,8-substituted congener TEF x 0 DL

Proper selection of the calculation method for TEQ determination of non-detectable PCDD's and PCDF's are based on a client specific requirements.

9.2 Data Transfer: data is processed using a custom application macro developed internally. A spreadsheet is generated which incorporates weights, dilution factors, splits, internal standard amounts added, recovery standard amounts added, toxic equivalence and estimated detection limits. The result file, once completed by authorized personnel is electronically transferred to MaxxLIMS using the super-interface upload macro.

9.3 Data Validation: Refer to BRL WI-00011 Review and Validation of Analytical Data and corresponding Data Review Checklist (BRL FCD-00002) to perform a primary and a secondary analytical data review and validation prior to issuance of the Certificate of Analysis. If the data and report are acceptable the Certificate of Analysis is signed by the Project Manager and sent to the client.

9.4 Data Storage: sample data is transferred to a separate computer system and backup monthly or as required.

10.0 DOCUMENTATION:

10.1 Tracking Sheet: before samples are prepared, a GC-MS sample tracking /work sheet is completed. This sheet includes details of the Job number, lab sample number, client sample ID, QC samples analyzed in the batch, spiking solutions used and their concentrations, preparation date and lot #, dates of analysis and cleanup, analyst's initials. A copy of the tracking /work sheet is maintained with analytical data

10.2 Instrument Logbook:

- Troubleshooting records with full descriptions of the actions taken to resolve the problem. This is required for <u>all instances</u> in which there is an acceptance criteria that is not achieved. Alternatively these may also be recorded on a separate tracking sheet designed for the analysis.
- Record of Instrument Service by the Supplier with the associated paperwork

10.3 Method Deviation Records: instances may arise in which the standard operating procedure may not be applicable to the nature of the sample and may require modifications to the normal methodology. These deviations must be discussed with the Supervisor or Operation Manager prior to application. Approval must be obtained as per COR WI-00040 and documented using QSI module for Policy Deviation Form. These deviations must also be described in the comment section of MaxxLIMS.

10.3.1 Sample Deviation Records: these deviations must be recorded in MaxxLIMS Comments.

10.4 Maintenance Tracking: analysts maintain logbooks/tracking sheets to include the following minimum information

- record of Instrument Service by the Supplier with the associated paperwork
- records of all maintenance performed indicating the date performed and by who

10.5 Standard and Reagent Preparation Tracking: record all preparations of standards and reagents in the Standard Preparation and the Reagent Preparation Logbooks. All records must contain at a minimum the following information

- Supplier Identification and Lot Number
- Date of Preparation and Expiry
- Concentration, and name of Analyst who prepared the standard

10.6 Certificates of Analysis for Standards and Reagents: all preparations of standards is recorded in the Standard Preparation Logbook. These records will contain at a minimum the following information.

- Supplier information and Lot Number
- Date received
- Date of Preparation and Expiry
- Concentration, and name of Analyst who prepared the standard

10.7 Storage of Records:

10.7.1 Paper Records: raw and calculated data, including calibrations and QC results are stored chronologically in file folders in the laboratory. These files are archived on-site for a period of one year and then transferred to an off-site storage for 5 years, unless otherwise instructed.

10.7.2 Electronic Media: data entered into LIMS is backed up daily

11.0 WASTE MANAGEMENT:

All efforts are taken to prevent or reduce to a minimum the effect of waste disposal on the environment. All solvents are collected for shipment to a recycling facility. All recyclable plastic, glass and paper products are shipped to an appropriate recycling facility. The disposal of waste materials and samples are to carried out in accordance with protocols outlined in the SOP for the Preparation, Storage and Disposal of Reagents and Standards and the SOP for the Receipt, Handling and Disposal of Hazardous Wastes. All waste disposal will comply with the Ontario Ministry of the Environment and Energy's Sewer Guidelines and Regulation 558.

Specific Disposal Issues: contaminated sample extracts are collected and sent for disposal to an approved hazardous waste subcontractor. Excess contaminated samples are either returned to the client or submitted for disposal as noted.

12.0 APPENDIX:

Table 1: Exact Masses of the Ions Monitored by Hi-Res Mass Spectrometry

Table 2: Theoretical Ion Abundance Ratios and their Control Limits

Table 3: EPA 8290 Calibration Standards

Table 4: Summary of WHO 1998 and WHO 2005 TEF values

Figure 1: Acceptable Chromatographic Separation for 2,3,7,8-T4CDD and 2,3,7,8,-T4CDF

TABLE 1:

EXACT MASSES OF THE IONS MONITORED BY HI-RES MASS SPECTROMETRY

Descriptor No:	Accurate Mass	Ion Type	Analyte
1	303.9016	M	T_4CDF
$T_4CDF/T_4CDD/H_6CDPE$	305.8987	M+2	T_4CDF
	315.9419	M	T_4CDF-$^{13}C_{12}$
	317.9389	M+2	T_4CDF-$^{13}C_{12}$
	319.8965	M	T_4CDD
	321.8936	M+2	T_4CDD
	327.8847	M	T_4CDD-^{37}Cl
	331.9368	M	T_4CDD-$^{13}C_{12}$
	333.9339	M+2	T_4CDD-$^{13}C_{12}$
	375.8364	M+2	H_6CDPE
	292.9825	LOCK MASS	PFK
2	339.8597	M+2	P_5CDF
$P_5CDF/P_5CDD/H_7CDPE$	341.8568	M+4	P_5CDF
	351.9000	M+2	P_5CDF-$^{13}C_{12}$
	353.8970	M+4	P_5CDF-$^{13}C_{12}$
	355.8546	M+2	P_5CDD
	357.8517	M+4	P_5CDD
	367.8949	M+2	P_5CDD-$^{13}C_{12}$
	369.8919	M+4	P_5CDD-$^{13}C_{12}$
	409.7974	M+2	H_7CDPE
	354.9792	LOCK MASS	PFK
3	373.8207	M+2	H_6CDF
$H_6CDF/H_6CDD/O_8CDPE$	375.8178	M+4	H_6CDF
	383.8639	M	H_6CDF-$^{13}C_{12}$
	385.8610	M+2	H_6CDF-$^{13}C_{12}$
	389.8156	M+2	H_6CDD
	391.8127	M+4	H_6CDD
	401.8559	M+2	H_6CDD-$^{13}C_{12}$
	403.8530	M+4	H_6CDD-$^{13}C_{12}$
	445.7555	M+4	O_8CDPE
	392.9760	LOCK MASS	PFK
4	407.7818	M+2	H_7CDF
$H_7CDF/H_7CDD/NCDPE$	409.7788	M+4	H_7CDF
	417.8253	M	H_7CDF-$^{13}C_{12}$
	419.8220	M+2	H_7CDF-$^{13}C_{12}$
	423.7766	M+2	H_7CDD
	425.7737	M+4	H_7CDD
	435.8169	M+2	H_7CDD-$^{13}C_{12}$
	437.8140	M+4	H_7CDD-$^{13}C_{12}$
	479.7165	M+4	NCDPE
	430.9728	LOCK MASS	PFK
5	441.7428	M+2	O_8CDF
$O_8CDF/O_8CDD/DCDPE$	443.7398	M+4	O_8CDF
	457.7377	M+2	O_8CDD
	459.7348	M+4	O_8CDD
	469.7780	M+2	O_8CDD-$^{13}C_{12}$
	471.7750	M+4	O_8CDD-$^{13}C_{12}$
	513.6775	M+4	DCDPE
	442.9728	LOCK MASS	PFK

H = 1.007825
C = 12.000000
$^{13}C_{12}$ = 13.003355
F = 18.9964
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

TABLE 2:

THEORETICAL ION ABUNDANCE RATIOS AND THEIR CONTROL LIMITS

Number of Cl Atoms	Ion Type	Theoretical Ratio	Control Limits lower	Control Limits upper	
4	M/M+2	0.77	0.65	0.89	
5	M+2/M+4	1.55	1.32	1.78	
6	M+2/M+4	1.24	1.05	1.43	
6	M/M+2	0.51	0.43	0.59	for H_6CDF-$^{13}C_{12}$ only
7	M/M+2	0.44	0.37	0.51	for H_7CDF-$^{13}C_{12}$ only
7	M+2/M+4	1.04	0.88	1.20	
8	M+2/M+4	0.89	0.76	1.02	

TABLE 3: EPA 8290 Calibration Standards

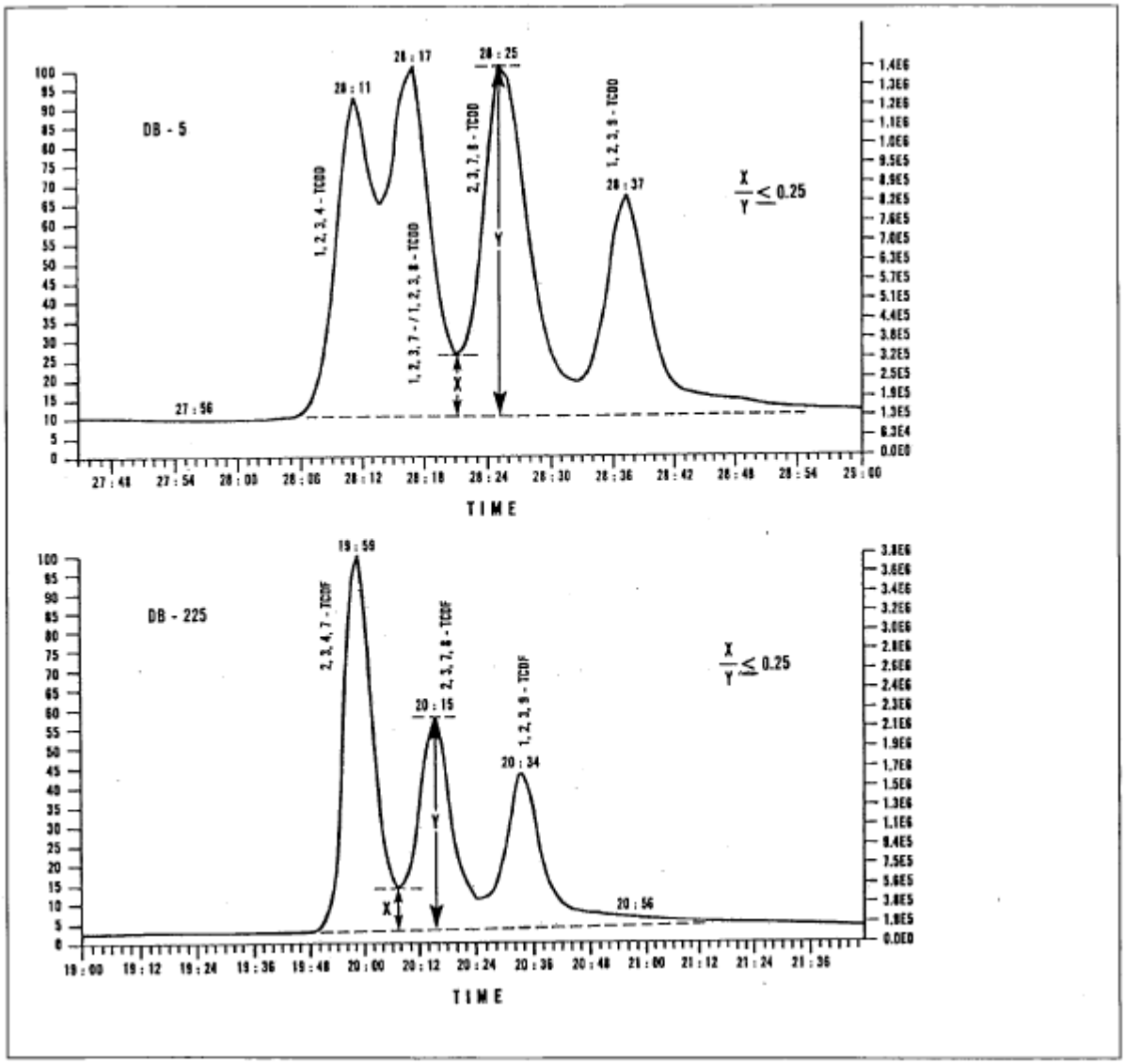
Component	Stock Conc. (ng/µl)	CS5		CS4		CS3		CS2		CS1	
		Conc. (pg/µl)	Vol. Req'd. (µl)	Conc. (pg/µl)	Vol. Req'd. (µl)	Conc. (pg/µl)	Vol. Req'd. (µl)	Conc. (pg/µl)	Vol. Req'd. (µl)	Conc. (pg/µl)	Vol. Req'd. (µl)
Native Analytes											
2,3,7,8-TCDD	50	200	40	50	10	10	100 µl of native Intermediate	2.5	25 µl of native Intermediate	1	10 µl of native Intermediate
2,3,7,8-TCDF	50	200	40	50	10	10		2.5		1	
P5-H7CDD/CDF	25	500	200	125	50	25		6.25		2.5	
1,2,3,4,6,7,8,9-O8CDF	50	1000	200	250	50	50		12.5		5	
1,2,3,4,6,7,8,9-O8CDD	50	1000	200	250	50	50		12.5		5	
Internal Standards											
2,3,7,8-T4CDD$^{13}C_{12}$	50	50	10	50	10	50	10	50	10	50	10
2,3,7,8-T4CDF$^{13}C_{12}$	50	50	10	50	10	50	10	50	10	50	10
1,2,3,7,8-P5CDD$^{13}C_{12}$	50	50	10	50	10	50	10	50	10	50	10
1,2,3,7,8-P5CDF$^{13}C_{12}$	50	50	10	50	10	50	10	50	10	50	10
1,2,3,6,7,8-H6CDD$^{13}C_{12}$	50	125	25	125	25	125	25	125	25	125	25
1,2,3,6,7,8-H6CDF$^{13}C_{12}$	50	125	25	125	25	125	25	125	25	125	25
1,2,3,4,6,7,8-H7CDD$^{13}C_{12}$	50	125	25	125	25	125	25	125	25	125	25
1,2,3,4,6,7,8-H7CDF$^{13}C_{12}$	50	125	25	125	25	125	25	125	25	125	25
1,2,3,4,6,7,8,9-O8CDD$^{13}C_{12}$	50	250	50	250	50	250	50	250	50	250	50
Recovery Standards											
1,2,3,4-T4CDD$^{13}C_{12}$	50	50	10	50	10	50	10	50	10	50	10
1,2,3,7,8,9-H6CDD$^{13}C_{12}$	50	125	25	125	25	125	25	125	25	125	25

Final Volume of all standards is 10 ml.

TABLE 4: Summary of WHO 1998 and WHO 2005 TEF values.

Compound	**WHO 1998 TEF**	**WHO 2005 TEF**
chlorinated dibenzo-p-dioxins		
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	**0.0003**
chlorinated dibenzofurans		
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	**0.03**
2,3,4,7,8-PeCDF	0.5	**0.3**
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,6,7,8,9-HpCDF	0.01	0.01
OCDF	0.0001	**0.0003**
non-ortho substituted PCBs		
3,3',4,4'-tetraCB (PCB 77)	0.0001	0.0001
3,4,4',5-tetraCB (PCB 81)	0.0001	**0.0003**
3,3',4,4',5-pentaCB (PCB 126)	0.1	0.1
3,3',4,4',5,5'-hexaCB (PCB 169)	0.01	**0.03**
mono-*ortho substituted PCBs*		
2,3,3',4,4'-pentaCB (PCB 105)	0.0001	**0.00003**
2,3,4,4',5-pentaCB (PCB 114)	0.0005	**0.00003**
2,3',4,4',5-pentaCB (PCB 118)	0.0001	**0.00003**
2',3,4,4',5-pentaCB (PCB 123)	0.0001	**0.00003**
2,3,3',4,4',5-hexaCB (PCB 156)	0.0005	**0.00003**
2,3,3',4,4',5'-hexaCB (PCB 157)	0.0005	**0.00003**
2,3',4,4',5,5'-hexaCB (PCB 167)	0.00001	**0.00003**
2,3,3',4,4',5,5'-heptaCB (PCB 189)	0.0001	**0.00003**

*Bold values indicate a change in TEF value.


DB - 5
1,2,3,4 - TCDD
1,2,3,7 - / 1,2,3,8 - TCDD
2,3,7,8 - TCDD
1,2,3,9 - TCDD
27 : 56
28 : 11
28 : 17
28 : 25
28 : 37
X
Y
X/Y ≤ 0.25
TIME
DB - 225
2,3,4,7 - TCDF
2,3,7,8 - TCDF
1,2,3,9 - TCDF
19 : 59
20 : 15
20 : 34
20 : 56
X
Y
X/Y ≤ 0.25
TIME

Ultra Trace Air Toxics SOP **BRL SOP-00407 / 7** **Ultra Trace Air Toxics**

Dioxin and Furan Extraction in Water and Soil Samples

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Change Categorization			
Ultra Trace Air Toxics Departments	Environmental HRMS		

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☑ **Update Completed Trainee Records**	

Insert Text
updated SOP as required BRL SOP00407_7

Associated Documents
Document Control Documents
Burlington SOP BRL SOP-00003 : GPC Cleanup
Burlington SOP BRL SOP-00405 : Dioxin and Furan Extracts Cleanup
Burlington SOP BRL SOP-00406 : Dioxins and Furans by HRGC HRMS in Water and Soil (EPA 8290)
Burlington SOP BRL SOP-00410 : Dioxins and Furans in Water and Soil by HRGC HRMS (EPA 1613)
Burlington SOP BRL SOP-00417 : Dioxins and Furans in Oil Samples
Burlington SOP BRL SOP-00402 : Dioxins and Furans by HRGC HRMS in Food Products and Biological Material
Burlington SOP BRL SOP-00424 : Extraction and Clean-up for Pine Needles
Burlington FCD BRL FCD-00015 : All Parameter Hi-Res Sample Tracking Sheet
Burlington FCD BRL FCD-00023 : Hi Res/ Low Res Sample Tracking Sheet
Corporate WI Publish to All COR WI-00012 : Definitions
Corporate WI Publish to All COR WI-00018 : Determination of Estimation of Analytical Uncertainty of Measurement
Corporate WI Publish to All COR WI-00040 : Corporate Procedure for Policy Deviation Forms
Corporate WI Publish to All COR WI-00050 : Environmental Chemistry Method Validation

Reason for Change

Date of Change August 30, 2007 **Version** 2
Section Changed 2, 7.4, 10.4, 10.5
Change Made Section 2, added clarification note on matrices
Section 7.4, changed sample drying time from minimum of 4 hr to 12hr; added oven temp. range to be 105 to 115 C
Sections 10.4 and 10.5 revised the steps to reflect current practice
Minor corrections of typographical errors troughout the document

Date of Change July 14, 2009 **Version** 3
Section Changed Header, 1.0, 4.0.1, 4.2, 7.3.1, 8.1-8.4, 10.1.2,
Change Made Header updated Maxxam's curent name
1.0, updated lab's current location
4.0.1, updated reference method 8290 to current revision
4.2, replaced SOP list with reference to Associated Documents
7.3.1, changed batch size from 14 to 20 samples
8.1-8.4, removed statements on Canadian protocol for QC frequencies (method blank, blank matrix spikes, matrix duplicates, MS/MSD, since they may vary. Additional or different frequency of QCs will be addessed on a project specific basis.
10.1.2, updated procedure to reflect current practice

Date of Change August 26, 2013 **Version** 4
Section Changed 4.1.1, 7.3, 7.6, Table 1
Change Made Section 4.1.1 and 4.1.2 Added use of tumbler as deviation from Ref. Method
Section 7.3 Added option of extended method of shaking by using tumbler for water samples and using conical funnel with Na2SO4 for filter the extract. Reogranised steps to reflect current flow of each step of sample extraction.
Section 7.6 Added to refer the seperate BRL SOP-00402 and BRL SOP-00424 that describe sample preparation to avoid duplication.
Table 1 removed DFCDN-TI, added DF-TI, DF-FD,DF-O
Optional Field A Associated documents have been reviewed, and where required the CPro links were updated to reflect most current procedures in use by the HRMS laboratory

Date of Change August 26, 2013 **Version** 5
Section Changed Header, 3.0, 8.3, 10.5.1, 10.5.2
Change Made Header, Removed "DRAFT - for review purpose only", (this was inadvertenly left after revision 4 was complete)
3.0, Changed to state for HRMS testing and added relevant reference method,EPA 1613B; removed reference to obsoleted procedure BRL SOP-00214
8.3, Corrected from " Matrix" to "Sample"
10.5.1, Removed last sencence to eliminate redundancy
10.5.2, Removed last bullet to reflrct current practice
All highlighted changes from rev 4 are carried into rev 5, due to immediate SOP correction
Optional Field A Associated documents have been reviewed, and where required the CPro links were updated to reflect most current procedures in use by the HRMS laboratory

Date of Change September 30, 2013 **Version** 6
Section Changed 7.4 step 7
Change Made Added information for extracting sample and keeping an archive
Optional Field A removed section about moisture as this is done by the processing lab
Optional Field B Added information about Method Spike

Date of Change March 11, 2014 **Version** 7
Section Changed 7.5 added
Change Made Section added for Fly Ash samples
Optional Field A Note: associated documents have been reviewed, and no changes to them are required.

Approval Status Table

Approver Source **Role for Approvers** **Parallel-Everybody** Segment

Approver	Action	Date	Comment
Betsy Cliffe	Approve	March 11, 2014 1:21 PM GMT-4	
Salima Haniff	Approve	March 5, 2014 5:41 PM GMT-5	

EXTRACTION OF POLYCHLORINATED DIBENZO-*P*-DIOXINS (PCDD's) AND POLYCHLORINATED DIBENZOFURANS (PCDF's) FROM WATER AND SOIL SAMPLES

1.0 LOCATION:

This procedure is performed in the HRMS Preparation Laboratory.

2.0 PURPOSE:

This method is used for the extraction of liquids and solids for the analysis of polychlorinated dibenzo-*p*-dioxins, (PCDD's), and polychlorinated dibenzofurans, (PCDF's). It is to be used for analysis by low and high resolution mass spectrometry.

NOTE: For the purpose of this procedure's clarity on matrices, use the following reference

Water Matrix - ground water, drinking waters, surface waters, wastewaters, etc.

Soil Matrix - solids, chemical materials, sludge, sediments and other solid wastes

2.1 Principle of the Method: PCDD's and PCDF's are extracted from solid samples with toluene and from aqueous samples with dichloromethane (DCM).

2.2 Nature of Samples: samples can be from many different sources including incinerator ashes, soils, sediments and effluents. Investigate for any information about the past history involving the samples or the presence of potentially interfering substances at elevated levels, (i.e. PCB). This information will allow the preparation technician to take a smaller aliquot of sample so that internal standards are not diluted out during analysis.

2.3 Safety:

2.3.1 General Considerations: each reagent, analyte and sample should be treated as a potential health hazard and exposure should be reduced to the lowest possible level. On the basis of the available toxicological and physical properties of the PCDD's and PCDF's, these compounds should only be handled by highly trained personnel thoroughly familiar with the handling and cautionary procedures, and who understand the associated risks. All work related to the analysis of PCDD's and PCDF's should be carried out within a specially designed laboratory. Safety glasses and protective lab clothing should be worn at all times. Refer to the appropriate MSDS for further information.

2.3.2 PCDD's and PCDF's: the 2,3,7,8-tetrachlorodibenzo-p-dioxin isomer has been found to be acnegenic, carcinogenic and teratogenic in laboratory animal studies. It is soluble in water to ~200 ppt and in organic solvents to 0.14 %. It is a solid at room temperature and has a relatively low vapour pressure. The physical properties of the 135 other tetra to octa chlorinated PCDD's/PCDF's have not been well established. It is presumed that the physical properties of these congeners are generally similar to those of the 2,3,7,8-TCDD isomer.

Laboratory ware, safety clothing, and other items contaminated with PCDD/PCDF in the course of analyses must be carefully secured and subjected to proper disposal. In the unlikely event that analytical staff experience skin contact with PCDD/PCDF or samples containing these, the contaminated area should be immediately and thoroughly scrubbed using mild soap and water. Personnel involved in any such accident should seek medical advice.

3.0 SCOPE:

This procedure is applicable to both solid and liquid matrices that are extracted for PCDD's and PCDF's by High Resolution Mass Spectrometry. It is based on EPA SW846 Method 8290A and EPA 1613B. However, client or regulatory requirements may dictate that a specific method be followed.

For precision, bias and detection limit information, refer to the CPro method validation module of relevant procedures for analysis: BRL SOP-00406, PCDD's/DF's in Liquid and Solid Samples (EPA 8290A) and BRL SOP-00410, PCDD/F in Liquid and Solids Samples by Isotope Dilution HiRes GC/MS (EPA 1613B).

3.1 Chemical Abstracts No.

Analyte	Symbol	CAS No.
2,3,7,8-Tetrachlorodibenzo-p-dioxin	TCDD	1746-01-6
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	PeCDD	40321-76-4
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	HxCDD	39227-28-6
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	HxCDD	57653-85-7
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	HxCDD	19408-74-3
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	HpCDD	35822-46-9
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	OCDD	3268-87-9
2,3,7,8-Tetrachlorodibenzofuran	TCDF	51207-31-9
1,2,3,7,8-Pentachlorodibenzofuran	PeCDF	57117-41-6
2,3,4,7,8-Pentachlorodibenzofuran	PeCDF	57117-31-4
1,2,3,4,7,8-Hexachlorodibenzofuran	HxCDF	70648-26-9
1,2,3,6,7,8-Hexachlorodibenzofuran	HxCDF	57117-44-9

1,2,3,7,8,9-Hexachlorodibenzofuran	HxCDF	72918-21-9
2,3,4,6,7,8-Hexachlorodibenzofuran	HxCDF	60851-34-5
1,2,3,4,6,7,8-Heptachlorodibenzofuran	HpCDF	67562-39-4
1,2,3,4,7,8,9-Heptachlorodibenzofuran	HpCDF	55673-89-7
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	OCDF	39001-02-0
Total Tetrachlorodibenzo-p-dioxin	TCDD	41903-57-5
Total Pentachlorodibenzo-p-dioxin	PeCDD	36088-22-9
Total Hexachlorodibenzo-p-dioxin	HxCDD	34465-46-8
Total Heptachlorodibenzo-p-dioxin	HpCDD	37871-00-4
Total Tetrachlorodibenzofuran	TCDF	55722-27-5
Total Pentachlorodibenzofuran	PeCDF	30402-15-4
Total Hexachlorodibenzofuran	HxCDF	55684-94-1
Total Heptachlorodibenzofuran	HpCDF	38998-75-3

3.2 Interferences: solvents, adsorbents, reagents, glassware and other sample processing hardware may yield artifacts or elevated baselines that may cause misinterpretation of the data. Proper cleaning of glassware is extremely important. Note that glassware may not only contaminate the samples, but may also remove the analytes of interest by adsorption on the glass surface. Method blanks must be analyzed in order to demonstrate that all laboratory materials are free from interferents under the conditions of the analysis. The use of high purity reagents and solvents helps to minimize interference problems.

The sensitivity of this method is dependent upon the level of interferences within a given matrix. Interferents co-extracted from the sample material will vary considerably with the matrix and the diversity of the site being sampled. PCDD's and PCDF's are often associated with other chlorinated organics, which may potentially interfere with the analysis. These include polychlorinated biphenyls, polychlorinated methoxybiphenyls, polychlorinated hydroxy diphenylethers, polychlorinated benzylphenyl ethers, polychlorinated diphenyl ethers, polychlorinated naphthalenes, polychlorinated xanthenes, polynuclear aromatics, and pesticides.

3.3 Definitions:

See COR WI-00012 Corporate Definitions

4.0 REFERENCES:

4.0.1 US EPA SW-846 8290A, Revision 1, February 2007

4.0.2 Environment Canada PCDD/PCDF in Pulp and Paper Mill Effluents (River Road Method), EPS 1/RM/19, February 1992

4.0.3 US EPA Method 1613, Tetra through Octa-chlorinated Dioxins and Furans by Isotope

Dilution, Rev. B, Oct. '94

4.1 Modifications and/or Improvements from Referenced Methods:

4.1.1 SW846 Method 8290A:

- in addition to regular glassware washing, Maxxam cleans Hi Res Soxhlet apparatus with a further 16-18 hour Soxhlet extraction using toluene
- Reference uses Snyder columns to concentrate extracts from aqueous samples, Maxxam uses rotary evaporators
- Maxxam air dries solid samples prior to extraction
- Maxxam uses either manual or tumbling at ~60-70rpm for shaking prior to separation by separatory funnel

4.1.2 EPA Method 1613:

- Maxxam air dries solid samples prior to extraction
- Maxxam uses either manual or tumbling at ~60-70rpm for shaking prior to separation by separatory funnel

4.1.3 Environment Canada River Road Method:

- None

4.2 Other Relevant SOPs – refer to Associated Documents of QSI Section for links provided

4.3 Extraction Test Codes:

Test codes may be created as needed

4.4 Analytical Test Codes: Other test codes may be created as needed.

Hi-Res Waters:	Analysis:
DFCDNPP-W	PCDD/PCDF by Environment Canada River Road protocol, EPS 1/RM/19
DFCDN-W / DFDW-W	PCDD/PCDF's by modified EPA Method 8290 protocol
DFATG24-W	PCDD/PCDF by OMOEE MISA protocol
DF1613-W	PCDD/PCDF by EPA Method 1613 protocol
DF8290-W	PCDD/PCDF by EPA Method 8290 protocol

DFHRMS-LC	PCDD/PCDF in leachates by modified EPA 8290 protocol
DFT4CDD-W	2,3,7,8-TCDD by EPA Method 1613 protocol
Hi-Res Soils:	**Analysis:**
DFCDN-S	PCDD/PCDF by modified EPA Method 8290 protocol
DF1613-S	PCDD/PCDF by EPA Method 1613 protocol
DF8290-S	PCDD/PCDF by EPA Method 8290 protocol
Hi-Res Tissues:	**Analysis:**
DFW-TI	PCDD/DF in tissue by EPA Method 1613 protocol
DF-PT	PCDD/DF in plant tissue by EPA Method 1613 protocol
Hi-Res Swabs:	**Analysis:**
DF8290-SB	PCDD/DF in Swabs by EPA Method 8290 protocol
Lo-Res Waters:	**Analysis:**
DF8280-W	PCDD/PCDF by EPA Method 8280 Protocol
Lo-Res Soils:	**Analysis:**
DF8280-S	PCDD/PCDF by EPA Method 8280 Protocol

4.5 Regulations/Agencies Supported

- Canadian Environmental Protection Act, River Road Protocol for Pulp and Paper Mill Effluent
- this method also applies to a variety of regulatory agencies and methods i.e. US EPA RCRA

5.0 SAMPLE HANDLING AND PRESERVATION

All samples should be stored at 2-6 °C during shipment. Samples should be stored at 2-6°C until the point of extraction. During transit, the samples should be packed in rigid-body coolers in an upright position. Due to the fragile nature of the containers, the samples should be well wrapped with

protective packaging during shipment from the field site to the laboratory. Samples that exceed the hold time will be flagged on the Certificate of Analysis. Different hold times may be imposed by other regulating agencies or as determined by client specific projects. Project specific and regulatory requirements for preservation method and reporting criteria, (required detection limit, dry or wet weight basis), must be examined and made clear prior to sample analysis.

Matrix	Container	Min. Vol.	Time to Extract	Time to Analysis
Waters	4x1 L amber glass	800 ml	30 days	45 days
Soils/Sludge	100 ml amber glass	2x5 gram	30 days	45 days
Pulp	100 ml amber glass	2x15 gram	30 days	45 days
Biological	100 ml amber glass	2x20 gram	30 days	45 days

6.0 APPARATUS AND MATERIALS

6.1 Apparatus (includes Labware and Equipment): 1L and 2 L glass separatory funnels; 500 ml flat bottomed flasks; Soxhlet apparatus; 90 mm Buchner funnels; 1L vacuum flasks; graduated cylinders; disposable Pasteur pipettes; microsyringes; Allihn filters; glass wool: 8 micron; 35 ml borosilicate glass vials with closures, pre-rinsed with DCM (VWR Catalogue No. 66012-066); 1L amber glass bottles with teflon lined caps; 250 ml wide mouth jars with teflon-lined caps; 1 ml Reacti-vials, (Kimble 60700-1), pre-rinsed with DCM; Whatman 1.0 µm Acrodisc syringe filters; Buchi/Brinkman RF-121 Rotary evaporator, GPC System: Autovap As-2000 Sample Processing System, Autoprep 1000 Chromatograph, Autovap 1000-evaporation module. Other suitable suppliers may be used as appropriate. Equivalent labware and equipment may be purchased from other suppliers as available

Note: all glassware used for Hi-Res samples is kept separate from Lo-Res glassware. This includes flasks, Soxhlets, Allihn filters and microsyringes. Flasks and Soxhlets used for Lo-Res samples are not Soxhlet extracted with toluene (cleaned) prior to use.

6.1.1 Glassware: clean glassware as in BRL WI-00006 General Glassware Washing.

6.2 Reagents: information regarding the concentration, source, lot number, preparation date, expiry date and analyst responsible is written on the label of the bottle used to store the solutions. This information is also recorded in the reagent preparation logbooks. Equivalent reagents may be purchased from other suitable suppliers as available. Other volumes of a reagent solution may be prepared as necessary by modifying the amount of stock used appropriate to the final volume required.

6.2.1 **Nitrogen:** UHP from Linde

6.2.2 **RODI:** Reverse Osmosis Deionized Water, (RODI), >16MΩ purity, produced in house

6.2.3 **Solvents:** dichloromethane (DCM), toluene, hexane, benzene, cyclohexane, ethyl acetate, iso-octane are purchased from Caledon, Distilled in Glass quality, or equivalent. Store in its original container at ambient temperature for up to one (1) year.

6.2.4 **Anhydrous Sodium Sulfate:** granulated, reagent grade from Caledon, Cat. No. 8220-1 or equivalent. Store in its original container at ambient temperature for up to 1 year. Prior to use the Na_2SO_4 is rinsed with the same solvent used in for the extraction procedure.

6.2.5 **Sulfuric Acid (concentrated), H_2SO_4:** (Reagent grade), Baker or other suitable supplier. Store in its original container at ambient temperature for up to one (1) year.

6.2.6 **Hydrochloric Acid (concentrated), HCL:** (Reagent grade), Baker or other suitable supplier. Store in its original container at ambient temperature for up to one (1) year.

6.3 Standards: information regarding the concentration, source, lot number, preparation date, expiry date and analyst responsible is written on the label of the bottle used to store the solutions and in the Standard and Reagent Logbook. Equivalent standards may be purchased from other suitable suppliers as available. Other volumes of a standard may be prepared by modifying the amount of stock used appropriate to the final volume required.

6.3.1 Internal Standard and Matrix Spike Preparation: information regarding the labeled compounds and their concentration is specific to the type of analysis required. Details of Internal and Surrogate Standards and Blank and Matrix Spike preparation are found in the analytical SOP that is being followed for analysis. Also Method Blank preparation and frequency. For the purposes of extraction, Table 1 at the end of this SOP lists the amount and type of spike required for analytical testcodes. Amounts and types may change based on the sample matrix or client requirements. All standards preparations, Lot No's., supplier information, and pertinent dates are documented by the analyst in the Standard Preparation Log Book located in the instrumentation laboratory.

SPIKES MUST BE WITNESSED BY A SECOND STAFF MEMBER FAMILIAR WITH THE PROCEDURE

Both the person spiking the solution and the witness must sign off the tracking sheet.

7.0 ANALYTICAL PROCEDURE

7.0.1 **Sample ID Check:**

Step 1 check that the MAXXAM laboratory label and the original container label have identical Client Ids

Step 2 initial the preparation/extraction sheet in the appropriate box verifying that this check has been done

In most cases, the following procedures for sample extractions and clean ups are followed. However, clients will occasionally submit or require a specific method to be followed. Aqueous samples with solids > 1.0% require filtration and separate analysis of the solids. For any batch where at least one sample requires filtration additional QA/QC samples (method blank, LCS) will be processed in the same manner.

7.1 **Glassware:** clean glassware as in BRL WI-00006 General Glassware Washing. Ensure the appropriate glassware is used for the type of analysis to be done. (Lo-Res vs Hi-Res)

7.2 **Method Spike:** prepare a method spike with each batch of samples extracted. Spike a clean Reacti-vial with the same volume of internal standards and spikes that are used for the extraction. Reduce in volume to dryness with a gentle stream of nitrogen with the samples in the batch.

7.3 **Preparation of Liquid Samples**

Extraction of samples can be processed by either procedures outlined in 7.3.1 or 7.3.2.

7.3.1 **Extended liquid-liquid Extraction:** prior to any liquid extractions, use empty 1L amber bottles (rinse with DCM about 5 ml two times for QC, add Rodi water to each bottle ~800ml. For all samples, make volume according to the bottle size about ~800 ml to ~900 ml each **(volume may vary according to the size of the sample bottle).**

Step 1 **Samples Not Requiring Filtration (<1% Solids):** for each sample perform the following:

Step 2 Samples that have no visible suspended materials do not require filtration.

Step 3 Mark the position of the meniscus on the bottle to allow the initial volume determination (Note: for River Road protocol weigh the bottles)

Step 4 Use 900ml of RODI water for the method blank and 900ml for the blank spike. Note: prepare one of each for every batch of 20 samples, or less, depending on the client's requirements

Step 5 Add the internal standard as described in Sections 7.3.2.1

Step 6 Spike the blank and matrix spikes as described in Sections 7.3.2.3

Step 7 Add 100ml of DCM to the sample bottle and shake vigorously for ~1 minute, relieve the pressure and check for leak from cap if any leak change the cap

Step 8 Put all samples in the Tumbler @ ~ 60 – 70 RPM for an hour

Step 9 Prepare all glassware for the set during the time of tumbling

Step 10 Cleaned glassware must be thoroughly rinsed as follows: separatory funnels are first rinsed with 100-150 ml of DCM, i.e. shake for ~2 minutes and then proceed with the DCM rinses as follows:

Step 11 Rinse separatory funnels 3x with ~100-150 ml DCM, shaking for ~2 minutes each time

Step 12 Rinse flasks 3x times with DCM

Step 13 Prepare Allihn filters by rinsing with DCM fill the Allihn filter ~1/3 to 1/2 full with

anhydrous Na_2SO_4 or use a conical funnel containing 10-20 grams of Na2SO4

Step 14 Rinse with 50-100 ml of DCM

Step 15 Label flasks and separatory funnels with sample number

Step 16 After one hour tumbling put all samples in labeled Sep. Funnel

Step 17 Allow the layers to stand for ~10 minutes to achieve separation

Step 18 If necessary break up any emulsions as per Section 7.3.3

Step 19 Drain the DCM through a pre-rinsed Allihn filter or conical funnel into a 500 ml flat bottom flask

Step 20 Put all samples back in the sample bottles, add 50 ml DCM in bottles and put in the tumbler for half an hour ,extract the aqueous phase one more with further 50ml aliquots of DCM and half hour in tumbler

Step 21 Apply vacuum to the funnel to collect the remaining DCM

Step 22 Add 3-5 ml of iso-octane and rotary evaporate the extract to ~2 ml. Note: transfer samples directly from the flask to the first clean up column if no splits are required

Step 23 Measure the sample volume by filling the sample bottle with water to the mark and pour into a 1000 ml graduated cylinder. Record the volume on the tracking sheet.

Step 24 Proceed to Section 7.8

7.3.2 **Manual Shaking: P**rior to any liquid extractions, cleaned glassware must be thoroughly rinsed as follows

- Rinse separatory funnels 3x with ~100-150 ml DCM, shaking for ~2 minutes each time
- Rinse flasks 3x times with DCM
- Prepare Allihn filters by rinsing with DCM fill the Allihn filter ~1/3 to 1/2 full with anhydrous Na_2SO_4 or use a funnel containing 10-20 grams of Na2SO4
- Rinse with 50-100 ml of DCM
- Label flasks and separatory funnels with sample number

Samples Not Requiring Filtration (<1% Solids): for each sample perform the following. Samples that have no visible suspended materials do not require filtration.

Step 1 mark the position of the meniscus on the bottle to allow the initial volume determination (Note: for River Road protocol weigh the bottles)

Step 2 use 1L of RODI water for the method blank and 1L for the blank spike. Note: prepare one of each for every batch of 20 samples, or less, depending on the client's requirements

Step 3 pour the sample into a 2L separatory funnel

Step 4 add the internal standard as described in Sections 7.3.2.1

Step 5 spike the blank and matrix spikes as described in Sections 7.3.2.3

Step 6 add 50 ml of DCM to the sample bottle and shake vigorously for ~1 minute

Step 7 add the DCM to the separatory funnel

Step 8 repeat this process two more times
Step 9 shake the separatory funnel vigorously for at least 4-5 minutes, with occasional venting
Step 10 allow the layers to stand for ~10 minutes to achieve separation
Step 11 if necessary break up any emulsions as per Section 7.3.3
Step 12 drain the DCM through a pre-rinsed Allihn filter or conical funnel into a 500 ml flat bottom flask
Step 13 extract the aqueous phase twice more with further 100 ml aliquots of DCM
Step 14 filter each through the same Allihn filter
Step 15 rinse the Allihn filter or conical funnel with ~10-15 ml of DCM
Step 16 apply vacuum to the funnel to collect the remaining DCM
Step 17 add 3-5 ml of iso-octane and rotary evaporate the extract to ~2 ml. Note: transfer samples directly from the flask to the first clean up column if no splits are required
Step 18 measure the sample volume by filling the sample bottle with water to the mark and pour into a 1000 ml graduated cylinder. Record the volume on the tracking sheet.
Step 19 proceed to Section 7.8

7.3.2.1 Internal Standard Spiking Water Samples:

Step 1 use the syringe dedicated for spiking the Internal Standard
Step 2 prior to spiking, rinse the syringe several times with acetone
Step 3 a dilution of the appropriate internal standard is prepared, on a daily basis, by transferring using the dedicated syringe, the volume as follows into a 25 mL volumetric flask:

Method:	**Volume Int. Std.**	**Final volume With Acetone**
EPA 23 & EPA 1613B	500 µL	25 mL
EPA 8290A	250 µL	25 mL
River Road EPS 1/RM/19	250 µL	25 mL

Note: depending on sample batch size, a different final volume of Daily Working Internal Standard, may be prepared by modifying the amount of relevant internal standard used appropriate to the final volume required.

Step 4 rinse the dedicated internal syringe thoroughly with acetone after use
Step 5 using a vortex mixer, thoroughly mix this solution prior to use
Step 6 using a syringe, transfer 1.0 mL of this Daily Working Internal Standard, to the method blank, the blank spike, samples, duplicates or matrix spikes

7.3.2.2 **Internal Standard Spiking Soil Samples:**

Step 1 use the syringe dedicated for spiking the Internal Standard
Step 2 prior to spiking, rinse the syringe several times with acetone
Step 3 use this syringe to add the appropriate amount of the relevant Internal Standard as

per Appendix Table 1, to the method blank, the blank spike, samples, duplicates and matrix spikes

Step 4 rinse the syringe thoroughly with acetone after use

Note: do not use syringes intended for matrix spikes when spiking internal standards. In addition, there are separate syringes for Low Res spiking solutions, which are kept in separate boxes labeled "for Low Res use only".

SPIKES MUST BE WITNESSED BY A SECOND STAFF MEMBER FAMILIAR WITH THE PROCEDURE
Both the person spiking the solution and the witness must sign off the tracking sheet

7.3.2.3 **Blank and Sample Matrix Spikes:**

Step 1 use the syringe dedicated for matrix spiking

Step 2 rinse the syringe several times with acetone

Step 3 spike the blank spike and matrix spike samples with the native spike mixture, (see Appendix Table 1, for volumes used)

Step 4 rinse the syringe with acetone after use

Note: do not use syringes intended for internal standards when spiking matrix spikes. There are separate syringes for Low Res spiking solutions.

SPIKES MUST BE WITNESSED BY A SECOND STAFF MEMBER FAMILIAR WITH THE PROCEDURE
Both the person spiking the solution and the witness must sign off the tracking sheet

7.3.3 **Samples Requiring Filtration (Solids >1%):** filter these samples prior to extraction

Step 1 samples that have visible suspended solids require filtration

Step 2 mark the position of the meniscus on the bottle to allow the initial volume determination

Note: for River Road (EPS 1/RM/19) protocol obtain the weight of the sample by recording the weight of the sample plus the bottle and then the empty bottle after the sample has been removed

Step 3 use 1L of RODI water for each of the method blank and blank spike. Note: prepare these for every batch of 20 samples, or less, depending on the client's requirements

Step 4 spike the sample bottles with the internal standard as described in Sections 7.3.2.1

Step 5 spike the blank and matrix spikes as described in Sections 7.3.2.3

Step 6 shake the bottle several times over the course of an hour, allow the internal standard to equilibrate within the sample matrix

7.3.3.1 **Extraction of Water Portion of Sample:**

Step 1 rinse a pre-washed 1 L vacuum flask 3x with DCM

Step 2 rinse a 90 mm Buchner funnel 3x with DCM

Step 3 pre-weigh an 11 cm Gelman glass fiber filter and record the weight on tracking sheet

Step 4 dry the filter overnight at room temp., record final weight prior to Soxhlet extraction
Step 5 place the filter into the bottom of the funnel
Step 6 carefully pour the sample into the funnel with the vacuum applied
Step 7 rinse the bottle with minimal RODI, ensure particulates are transferred, if required
Step 8 keep sample bottle for extraction
Step 9 continue suction until the flow stops completely
Step 10 carefully transfer the filter to a Petri dish, allow to dry overnight at room temperature
Step 11 transfer the contents of the flask to the clean, labeled separatory funnel
Step 12 rinse the flask and the funnel with DCM and add to the separatory funnel
Step 13 add 30 ml of DCM to the sample bottle and shake vigorously for ~2 minutes
Step 14 add to the separatory funnel or keep in the bottle for extended liquid-liquid extraction
Step 15 repeat this process twice more
Step 16 Proceed to the section 7.3.1 (Samples Not Requiring Filtration Step 2).

7.3.3.2 **Extraction of the Solids Portion of the Water Sample:**

Step 1 prepare a Soxhlet apparatus with the filter according to Section 7.5, steps 1-5
Step 2 the filter may be Soxhlet extracted using the extraction flask from the water portion
Step 3 add ~250-300 ml toluene to the flask and proceed as in Section 7.5, step 7
Step 4 a second clean flask may be used instead and both extracts combined prior to cleanup

7.3.4 **Emulsions:** emulsions covering >1/3 of the organic layer must be broken up. The following techniques may help to break up the emulsified layer

Step 1 use a glass rod to break up the emulsion or
Step 2 drain the organic layer into a 250 ml wide mouth clear glass jar, well-rinsed with DCM, and centrifuge the sample for ~5 minutes at 3000 rpm
Step 3 if the emulsion still exists add ~2 drops of conc. H_2SO_4 and shake gently, (use caution!), then re-centrifuge the layer
Step 4 carefully pour the jar's contents back to the separatory funnel, allow the layers to separate
Step 5 drain the organic phase through the Allihn filter into the flask
Step 6 rinse the jar with 50 ml of DCM and add to the separatory funnel
Step 7 add another 50 ml of DCM to the separatory funnel and continue the extraction
Step 8 if this cycle has to be repeated each time, the final rinse of the jar should be added to the separatory funnel before it is drained

7.4 **Preparation of Solid Samples:**

Step 1 thoroughly rinse all glassware, flasks and Soxhlet apparatus 3x with toluene
Step 2 for method blanks and blank spikes, use a glass rod and place ~5 cm of glass wool in the

bottom of the Soxhlet, ensure that it is covering the hole in the side

Step 3 add ~5 cm anhydrous Na_2SO_4 into the Soxhlet, ensuring none gets through the glass wool

Step 4 rinse the Na_2SO_4 with toluene and discard the toluene to waste

Step 5 label the flasks and Soxhlet apparatus

Step 6 add enough, ~250-300 ml, toluene to the flask so that the sample will cycle and not go dry

Step 7 accurately weigh 2-10 g of each sample, (analyst experience may help in the estimate of this weight or the client may have specific MDL requirements that need to be met). Alternately ~20g of each sample is accurately weighed and double spiked – once the extraction is compete (minimum of 16 hour soxhlet) the extract is accurately split and one portion is used for cleanup and the other is kept as an archive.

Step 8 record weights on the work sheet including QC (use Ottawa Sand for Blank and Blank Spike)

Step 9 carefully add each sample to a Soxhlet and cover with ~1.5cm of anhydrous Na_2SO_4

Step 10 spike the sample with the internal standard, see Section 7.3.2.2

Step 11 spike the blank spike and matrix spikes, see Section 7.3.2.3

Step 12 rinse the inside of the Soxhlet with toluene

Step 13 place the Soxhlet apparatus on a burner and wrap the flasks with aluminum foil

Step 14 turn on the condenser water supply, set the burners on “high” and extract for 16-18 hrs

Step 15 cool and remove from the burners

Step 16 quantitatively transfer the toluene left in the Soxhlet condenser area to the 500 ml flask

Step 17 rinse the Soxhlet apparatus several times with toluene and collect in the flask

Step 18 rotary evaporate the extract to ~2 ml

Step 19 proceed to Section 7.8

7.5 **Preparation of Fly Ash**

Caution: Because of the tendency of fly ash to “fly”, all handling steps should be performed in a hood in order to minimize contamination.

Step 1 Weigh about 4g of fly ash to 2 decimal places onto a glass fiber filter placed in a glass funnel [~4g sample size will be double spiked and ½ of the extract will be cleaned up]

Step 2 Add approx. 20mL of 2 M HCL to run through the sample and allow it to sit for 30 minutes

Step 3 After 30 minutes rinse the filter with approx. 200mL of RODI water and set the sample in the filter to air dry – the RODI rinse water is collected and extracted 3 times with 20mL DCM and the combined DCM extract is added to the toluene extract after soxhlet extraction.

Step 4 Once the filter and sample are dry place the sample and filter paper into a soxhlet

Step 5 spike the sample with the internal standard, see Section 7.3.2.2

Step 6 spike the blank spike and matrix spikes, see Section 7.3.2.3

Step 7 rinse the inside of the Soxhlet with toluene

Step 8 place the Soxhlet apparatus on a burner and wrap the flasks with aluminum foil

Step 9 turn on the condenser water supply, set the burners on "high" and extract for 16-18 hrs

Step 10 cool and remove from the burners

Step 11 quantitatively transfer the toluene left in the Soxhlet condenser area to the 500 ml flask

Step 12 rinse the Soxhlet apparatus several times with toluene and collect in the flask

Step 13 rotary evaporate the extract to a known volume

Step 14 All ash sample extracts require an sulfuric acid extraction before proceeding with the cleanup – information on this and the cleanup procedure is found in BRL SOP-00405

7.6 **Preparation of Biota (Grasses, Pine Needles, Soybeans, Corn, etc):**

Step 1 **7.6.1 Soxhlet Extraction for Biota:**

- See BRL SOP-00402 for prep of Biota / Food Samples
- See BRL SOP-00424 for prep of Pine Needles

7.7 **GPC Procedure:** See BRL SOP-00003, Clean Up of Extracts Using Gel Permeation Chromatography for GPC calibration and procedure.

7.8 **Cleanup and Fractionation Procedure (Liquids and Solids):** see BRL SOP-00405 "SOP for the Clean Up of Sample Extracts For PCDD and PCDF Analysis.

8.0 QUALITY CONTROL:

8.1 **Method Spike**: a method spike is prepared with each batch of samples. The method spike consists of all the spiking solutions added to the blank spike.

8.2 **Method Blanks:** a method blank of RODI water is processed with each batch of water samples and a method blank of Na_2SO_4 for each batch of solid samples. The frequency to be 1 blank prepared for every 20 samples unless regulations, contracts or the relevant analysis SOP require or allow a different frequency; with at least 1 blank prepared for each batch of samples of the same matrix prepared together for every batch containing 1 or more samples. See relevant analysis SOP for acceptance criteria and corrective actions.

8.3 **Blank Matrix Spikes, (Reference Sample/LCS):** an aliquot equal to, or as close as possible to that used for the method blank is spiked with the relevant matrix spiking solution. The blank matrix spike is extracted along with samples in the same batch. A blank matrix spike is analyzed once every 20 samples unless regulations, contracts or the relevant analysis SOP require or allow a different frequency. A spiked method blank is processed from the start of sample preparation. See the relevant analysis SOP for acceptance criteria and corrective actions.

8.3 **Sample Duplicate:** a randomly selected separate portion of a sample is extracted along with samples in the same batch. A matrix duplicate is analyzed once every 20 samples unless regulations, contracts or the relevant analysis SOP require or allow a different frequency. A matrix duplicate is processed from the start of sample preparation. See the relevant analysis SOP for acceptance criteria and corrective actions.

Note: some protocols may require matrix spike and matrix spike duplicates within a batch to monitor precision. If this is being done duplicate analysis is not required. If there are positive results, duplicate analysis may be substituted for matrix spike duplicates

8.4 **Matrix Spike/Matrix Spike Duplicates (MS/MSD):** a matrix spike and matrix spike duplicate, as close as possible to that used for the sample, are spiked with the relevant matrix spiking solution. The sample matrix spike and matrix spike duplicate are extracted along with samples in the same batch. A blank matrix spike and matrix spike duplicate are analyzed once every 20 samples unless regulations, contracts or the relevant analysis SOP require or allow a different frequency. A matrix spike and matrix spike duplicate are processed from the start of sample preparation. See the relevant analysis SOP for acceptance criteria and corrective actions.

Note: if insufficient sample is submitted by the client to perform a duplicate Matrix Spike sample, a Duplicate Blank Matrix Spike will be performed.

8.5 **Internal Standards:** see the relevant analysis SOP for calculation formulae, acceptance limits and corrective actions

8.6 **Control Charts:** control charts are maintained as detailed in the relevant analysis SOP

8.7 **Additional Quality Control:** in addition to the samples mentioned above, SRMs, blind replicates, audit and performance evaluation samples may be submitted or required by the relevant analysis SOP. These samples may have specific instructions that must be followed; however, analysis is to proceed as for any other sample.

9.0 DATA CALCULATIONS:

9.1 **Data Storage:** the original tracking/work sheets are stored in binders in the extraction lab. A photocopy accompanies the extracts to the instrument.

10.0 DOCUMENTATION

10.1 **Preparation/Extraction Tracking /Work Sheets:** A tracking /work sheet is completed for each batch of samples. It contains Job /sample specific information i.e.; Job number, extraction date, clean up date, , sample number, client name, client sample id, sample weight/volume, number of

splits, amount and type of spike added, witness signoff, solvent lots, reagent lots or preparation dates and any additional information pertaining to the extraction or cleanup. A photocopy accompanies the completed samples to the instrument and the original is kept in a binder in the HRMS Prep Lab.

10.1.1 **Sample Deviation Records:** Deviations must be recorded in the MaxLIMS report remarks area which is linked to the Job number / worksheet number. These entries appear on the Certificate of Analysis. Examples are as follows:

- analyzed past hold time
- sample is not homogeneous

10.1.2 **Method Deviation Records:** instances may arise in which the standard operating procedure may not be applicable to the nature of the sample and may require modifications to the normal methodology. These deviations must be discussed with the Supervisor or Operations Manager prior to application. Refer to COR WI-00040, Corporate Procedure for Policy Deviation to determine if deviation is deemed appropriate; record the procedure in the CPro Policy Deviation Form and submit to the Supervisor or Operations Manager for approval. Deviation must be approved prior to its implementation. These deviations must also be described in the MaxLIMS Job report remarks section. This information is retrieved by the project manager and is included in the final report sent to the client.

10.2 **Maintenance Tracking:** analysts maintain separate logbooks or specific tracking sheets in which they include the following minimum information

- record of Instrument Service by the Supplier with the associated paperwork
- records of all maintenance performed indicating the date performed and by who

10.3 **Standard and Reagent Preparation Tracking:** record all preparations of standards and reagents in the Standard Preparation and the Reagent Preparation Logbooks. All records must contain at a minimum the following information

- Supplier Identification and Lot Number
- Date of Preparation and Expiry
- Concentration and name of Analyst who prepared the standard

10.4 **Certificates of Analysis for Standards and Reagents:** certificate of analyses are kept for all solutions utilized in this SOP. These records will contain at a minimum the following information.

- supplier information and Lot Number
- date received

10.5 **Storage of Records:**

10.5.1 **Paper Records:**

- raw and calculated data, including calibrations and QC results are stored chronologically in folders in the laboratory as space permits. These files are archived to the warehouse for long term storage (i.e., 5-year retention time).

10.5.2 **Electronic Media:**

- data entered into LIMS is backed up daily by IT

11.0 WASTE MANAGEMENT:

All efforts are taken to prevent or reduce to a minimum the effect of waste disposal on the environment. All solvents are collected for shipment to a recycling facility. All recyclable plastic, glass and paper products are shipped to an appropriate recycling facility. The disposal of waste materials and samples are to be carried out in accordance with protocols outlined in the SOP for the Preparation, Storage and Disposal of Reagents and Standards and the SOP for the Receipt, Handling and Disposal of Hazardous Wastes. All waste disposals will comply with the Ontario Ministry of the Environment Sewer Guidelines and Regulation 558.

11.1 **Specific Disposal Issues:** contaminated sample extracts are collected and sent for disposal to an approved hazardous waste subcontractor. Excess contaminated samples are either returned to the client or submitted for disposal as noted.

12.0 APPENDIX

- Table 1: Internal Standard and Matrix Spike Amounts for Liquid and Solid Samples

TABLE 1:
INTERNAL STANDARD AND MATRIX SPIKE AMOUNTS
FOR LIQUID AND SOLID SAMPLES

Testcode	**Internal Standard**	**Matrix (Native) Spike**	**Cleanup Alternate Standard**
Waters			
DFCDNPP-W	As per 7.3.1.1, River Road Internal Standard	20 µl River Road Matrix Spike	
DFCDN-W DFHRMS-LC	As per 7.3.1.1, EPA 23 Internal Standard	5 µl EPA 23 Matrix Spike	
DFATG24-W	As per 7.3.1.1, EPA 23 Internal Standard	5 µl EPA 23 Matrix Spike	
DF1613-W DFDW-W DFT4CDD-W	As per 7.3.1.1, EPA 1613 Method Spike	5 µl EPA 'PAR' Spike Solution	5 µL Alt. Std. (Clean-up)
DF8290-W -	As per 7.3.1.1, Region 4 / 8290 Internal Standard	20 µl Region 4 /8290 Matrix Spike	
DF8280-W	50 µl Lo-Res PCDD/F Spike Solution	10 µl EPA 23 Matrix Spike	

Solids			
DFCDN-S DF-FD DF-O	20 µl EPA 23 Internal Standard	5 µl EPA 23 Matrix Spike	
DF1613-S DF-TI	20 µl EPA 1613 Method Spike	5 µl EPA 'PAR' Spike Solution	5 µL Alt. Std. (Clean-up)
DF8290-S	25 µl Region 4 / 8290 Internal S Standard	50 µl Region 4 / 8290 Matrix Spike	
DF8280-S	50 µl Lo-Res PCDD/F Spike Solution	10 µl EPA 23 Matrix Spike	

APPENDIX B

ENVIRONMENTAL PROTECTION PLAN

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APPENDIX B
FINAL
ENVIRONMENTAL PROTECTION PLAN

South Shore Area
Former Mare Island Naval Shipyard
Vallejo, California
July 2015

Base Realignment and Closure
Program Management Office West
1455 Frazee Road, Suite 900
San Diego, California 92108

CONTRACT NO. N62473-12-C-4812

DCN: NRS-4812-0000-0009

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ABBREVIATIONS AND ACRONYMS

APP	Accident Prevention Plan
CDFW	California Department of Fish and Wildlife
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CIH	Certified Industrial Hygienist
CWA	Clean Water Act
DOT	United States Department of Transportation
EPA	Environmental Protection Agency
EPP	Environmental Protection Plan
IR	Installation Restoration
MINS	Mare Island Naval Shipyard
Navy	United States Department of the Navy
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NOREAS	NOREAS, Inc.
NPDES	National Pollution Discharge Elimination System
NTCRA	Non-Time Critical Removal Action
OSHA	Occupational Safety and Health Administration
PM	project manager
PMA	Production Manufacturing Area
RI	Remedial Investigation
ROICC	Resident Officer in Charge of Construction
RPM	Remedial Project Manager
SMHM	Salt Marsh Harvest Mouse
SSA	South Shore Area
SSHO	Site Safety and Health Officer
SSHP	Site Safety and Health Plan
SWPPP	Storm Water Pollution Prevention Plan
USFWS	United States Fish and Wildlife Service
WEAP	Worker Environmental Awareness Program
WMP	Waste Management Plan

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1.0 INTRODUCTION

This Environmental Protection Plan (EPP) complements the on-going efforts by the United States Department of the Navy (Navy) to perform Remedial Investigations (RI) at the South Shore Area (SSA) of the former Mare Island Naval Shipyard (MINS), Vallejo, California (Figure 1-1). The SSA is located on the southern portion of Mare Island (Figure 1-2) between the former Western Magazine Area and the Production Manufacturing Area (PMA). Activities associated with the subject investigation of SSA will hereafter be referred to as the Project (Project). The Project is being performed as part of the Navy's Environmental Restoration Program and Munitions Response Program in compliance with the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the National Oil and Hazardous Substances Pollution Contingency Plan (NCP). CERCLA and the NCP establish a comprehensive, statutory framework for identifying, investigating, and remediating the SSA.

This EPP presents information regarding the environmental management program for the SSA of the Former MINS, Vallejo, California. The purpose is to detail the means of compliance with environmental regulatory requirements for the RI at the SSA. The document will also help ensure that activities associated with the environmental management program are conducted in a systematic and well-documented manner. The EPP includes environmental compliance procedures and regulatory, procedural, and training requirements associated with conducting the RI field activities.

Due to the potential for protected wildlife species to be present at the SSA, biological minimization and avoidance are also detailed in this document. NOREAS, Inc. (NOREAS) will provide biological education training, biological monitoring, and appropriate avoidance and minimization measures.

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2.0 PROJECT RESOURCES AND KEY CONTACTS

2.1 PROJECT RESOURCES

As stated previously, the SSA is located on the southern portion of MINS between the former Western Magazine Area and the PMA. The area was created in several stages between 1930 and 1950 utilizing material, consisting primarily of rock and soil, taken from the upland areas of Mare Island. That material was placed over the clays and silts that had been deposited at the edge of Mare Island through natural and by engineered accretion involving the deposition of river silt, tidal action, and the construction of dikes. The area was used for storage of general shipyard items as well as for the storage and handling of ammunition. Experience and historical evidence suggest that a wide variety of buried explosive ordnance items may be present in the SSA including propellants, small arms ammunition, fuzes, primers, and minor to medium caliber gun ammunition with high explosive projectiles.

MINS includes 1,364 acres consisting of wetlands, tidelands, and dredge sediment ponds. Habitats within MINS include disturbed uplands, seasonal and tidally-influenced wetlands, tidal mudflats, exposed shoreline and open tidal waters. The study area for this project consists of approximately 38 acres located at the southern end of MINS (Figure 1-2).

Wetland habitats within the SSA consist of tidal areas that support coastal salt marsh vegetation, which rotationally provide open water, mudflat and pickleweed marsh habitat. This EPP was developed to ensure that project team members comply with applicable laws and regulations. Protocols and measures are provided throughout this document to allow some latitude within the law to deal with biological issues on a case-by-case basis. It is important for each member of the team to understand that his/her actions and behavior in the field are critical for keeping the project in compliance and avoiding unnecessary delays or work shutdowns.

For the purposes of this EPP, the “study area” has been defined as the project’s physical ground disturbance footprint (Disturbance Footprint). The study area also includes a 100-foot buffer, staging areas, lay-down areas, and temporary-use lands needed for environmental investigations and clean up at the SSA. The study area is approximately 38 acres and it is located on the Benicia and Mare Island United States Geological Survey 7.5-minute quadrangle maps; Mt. Diablo Meridian Township 3 North, Range 4 West, Section 25 and an un-sectioned area (USGS 1999).

2.2 CONTRACTOR PERSONNEL

Project/Site Superintendent

Wendy Bryant, NOREAS - (949) 351-3378

Project Manager (PM)

Jeff Brenner, PG, NOREAS - (949) 467-9106

Project Engineer

Vitthal Hosangadi, PE, NOREAS - (949) 467-9099

Biological Resources

Lenny Malo, MS, NOREAS - (714) 458-5695

2.3 NAVY PERSONNEL

Remedial Project Manager (RPM)

Ms. Brooks Pauly, PE - (619) 532-0789

Resident Officer In Charge of Construction (ROICC)

Mr. Izzat Amadea - (510) 755-5876

3.0 FIELD ACTIVITIES AND RESOURCE PROTECTION

3.1 PLANNED FIELD ACTIVITIES

As part of the RI for the SSA, soil borings will be advanced to depths of approximately 20 feet below ground surface at a minimum of 46 planned locations for the purposes of collecting soil samples. In addition, seven groundwater monitoring wells will be installed at the SSA to obtain groundwater data for the RI. The planned soil boring and well locations are depicted on Figure 3.1. Equipment necessary to complete the soil boring and well installation activities will be limited to truck-mounted direct-push technology and hollow-stem auger drilling rigs.

During the RI field activities, a Final Status Survey (FSS) will also be conducted in one location at the SSA where a radium button was recovered during a munitions removal action in 1999 (RSRS and NOREAS 2014). As part of the FSS, a small area measuring 10 feet by 10 feet will be excavated by hand-digging or backhoe down to a depth of 4 feet below ground surface.

3.2 ENVIRONMENTAL RESOURCE PROTECTION

There is a potential for discrete portions of the SSA to be inhabited by threatened or endangered species, and remedial investigation activities will be conducted in a manner that minimizes impacts. Potentially disruptive activities planned as part of the field effort include drilling small diameter (2 to 8 inch diameter) soil borings to depths of approximately 20 feet below ground surface in several locations across the SSA. In addition, a 10 foot by 10 foot area will be excavated to a depth of 4 feet in one location at the SSA as part of a Final Status Survey (RSRS and NOREAS 2014). All soil boring, well installation, and excavation activities will be conducted in a manner that minimizes environmental impacts.

Biological monitoring will be conducted to ensure disturbances are minimized and that appropriate avoidance measures are implemented in the presence of federally or state fully protected, threatened or endangered species. Biological monitoring, including a detailed discussion of specific biological avoidance, minimization, and mitigation measures, is provided in Section 7.0.

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4.0 REGULATORY REQUIREMENTS

The specific environmental/regulatory requirements that are applicable to the RI at the SSA are described below.

4.1 HAZARDOUS WASTE MANAGEMENT

MINS has a United States Environmental Protection Agency (EPA) generator identification that will be used on the manifests that accompany each hazardous waste shipment.

4.2 AIR EMISSIONS

None of the planned investigation activities are anticipated to (1) result in air emissions that exceed national emissions standards for hazardous air pollutants or national or state ambient air quality standards; (2) require a Prevention of Significant Deterioration program; or (3) become subject to New Source Performance Standards.

4.3 STORM WATER POLLUTION PREVENTION PLAN

Based on the limited disturbance foot print of the activities planned under the RI (less than 1 acre total area), a National Pollutant Discharge Elimination System (NPDES) storm water construction permit or Storm Water Pollution Prevention Plan (SWPPP) is not required.

4.4 BASE APPROVALS

NOREAS will coordinate with the Navy contracted support project manager (PM), caretaker site office representative and Resident Officer in Charge of Construction (ROICC) to obtain necessary MINS approvals for the removal of impacted soil from the SSA. Required approvals may include, but are not limited to, underground utility clearance and selection of the analytical laboratory and off-site disposal facilities.

4.5 PLANT AND WILDLIFE PROTECTION

Due to the potential for discrete portions of the SSA to be inhabited by threatened or endangered species, remedial investigation activities will be conducted in a manner that minimizes impacts. NOREAS will provide biological education training, biological monitoring, and appropriate avoidance and minimization measures.

Natural and biological resources present at MINS are detailed in Section 6.0. Specific measures designed to minimize the potential for adverse impact to particular biological resources on or near the study area conducted are presented in Section 7.0.

4.6 WORKER HEALTH AND SAFETY

Field activities will be governed by the Accident Prevention Plan (APP)/Site Safety and Health Plan (SSHP), prepared for the RI activities by NOREAS. All activities will be performed in accordance with Occupational Safety and Health Administration (OSHA) requirements for worker safety. The APP/SSHP will provide requirements and guidelines that will be used in the field to protect the health and safety of workers. A Site Safety and Health Officer (SSHO) will provide full-time oversight of activities to ensure compliance with OSHA regulations and the APP/SSHP.

4.7 PERSONNEL TRAINING / CERTIFICATION REQUIREMENTS

NOREAS is responsible for ensuring proper training of its staff. All project personnel (subcontractors and contractors) will be trained according to the contractor compliance policies and procedures. Contractor personnel records will be verified along with the subcontractors' training records prior to beginning project activities.

project-specific training/certification records will be kept onsite until project completion. At project completion, the records will be filed within the project file.

4.8 INSPECTION AND AUDIT PROCEDURES

Site inspections and audits may occur during the remedial activities to ensure compliance with applicable state and federal regulations, as well as the APP/SSHP.

5.0 RELEASE PREVENTION, RESPONSE, AND REPORTING

Based on the limited scope of the field activities planned for this project (described in Section 3.1), the use and/or storage of hazardous materials is expected to be limited to the storage and/or handling of potentially contaminated soil and groundwater and use of motorized vehicles (drill rigs and support vehicles). This plan describes the general housekeeping practices and preventative measures that will be implemented during the field activities to protect adjacent land and surface waters from potentially contaminated or hazardous materials

5.1 SPILL PREVENTION

The primary activities that may result in a spill include vehicle fueling, management of decontamination waste, or dewatering activities. The spill prevention practices that will be implemented for the RI field activities include the following:

- **Fueling** – To minimize the potential for fuel spills during the field activities, all vehicles will be fueled at off-site locations prior to being brought on site. Refueling of the drill rigs or other vehicles on while on site will not be permitted. Fuels will not be stored on site.

- **Wastewater** – Wastewater from groundwater well purging and decontamination activities will be stored in temporary double-walled tanks or DOT-approved 55-gallon drums within a secondary containment area pending waste characterization and disposal. Therefore, any spills from the containers or tanks will be contained and will not be released to the surrounding areas.

- **Soil Cuttings** – Soil cutting from soil boring and well installation activities will be temporarily stored in DOT-approved 55-gallon drums within a secondary containment area pending waste characterization and disposal.

- **Good Housekeeping** – Good housekeeping practices will be implemented throughout the field activities. Garbage and waste materials or debris will be regularly picked up and properly disposed. Spill kits with the appropriate quantity and types of sorbent materials will be stored and maintained on each drill rig and in those work areas where there is a potential for a spill or release.

- **Inspections and Maintenance** – All equipment will be operated and maintained in accordance with the manufacturer's recommendations. Vehicles or other equipment found to be leaking will be repaired immediately or removed from the site.

- **Training** – All field personnel will be trained in hazard communication, spill prevention, spill response, and reporting requirements described in this EPP.

5.2 SPILL RESPONSE

In the event of a release of hazardous materials into the environment, NOREAS will take immediate action to contain or control the release or evacuate the area if the spill is significant or represents an immediate health threat. Spills, leaks, and fires at MINS SSA must be reported to the contracted support PM and ROICC. Absorbent pads, booms, shovels, and DOT-approved 55-gallon drums will be kept onsite to address the possibility of spills.

For the purposes of this project, spills are defined as non-emergency spills and emergency spill as described in the following subsections.

5.2.1 Non-Emergency Spills

A non-emergency spill is defined as the release of a known material or hazardous substance that does not pose an immediate threat to human health or the environment and can be cleaned up safely by the contractor. For a non-emergency spill:

1. Stop the source of the spill/release if safe to do so.
2. Contain the spill and keep it away from drains or waterways. Block off drains near the spill if there is a chance that the spill will reach them.
3. Don appropriate PPE and clean up the spill.
4. Handle all spill and waste material (including used PPE) in accordance with Waste Management Plan (included as Appendix C of this RI Work Plan).
5. Immediately notify the RPM and PM.

5.2.2 Emergency Spills

An emergency spill is defined as any release that poses an immediate or imminent threat to human health of the environment, any release to a waterway (including storm drains), and any release that does not meet the criteria for a non-emergency spill. For an emergency spill:

1. For an immediate or imminent threat to human health, immediately evacuate to a predetermined safe location and call emergency responders.
2. If others are in the area, warn and direct them to the predetermined safe location.
3. Immediately notify the RPM and PM.

5.3 SPILL / RELEASE REPORTING

The steps below outline the chain of communications that will be followed if a significant spill of any hazardous substance occurs. A significant spill is considered any spill over the reportable quantity, as determinable by federal and/or state regulations, as well as any spill below the reportable quantity that is not properly contained, and is released to the environment. In addition, spills of petroleum, which cause a sheen on water, must be reported.

1. Site personnel involved in the spill will immediately contact NOREAS Spill/Release Onsite Coordinator, Site Superintendent, or SSHO, who will notify the project manager (PM). At least one of the following two individuals will be onsite during all remedial activities:

   - SSHO: Bryan Economy

     Cell: (714) 914-0724

   - Onsite Coordinator and Site Superintendent: Wendy Bryant

     Cell: (949) 351-3378

   NOREAS SSHO or Site Superintendent will contact the contracted support PM and ROICC identified below:

   - RPM: Ms. Brooks Pauly, PE
     (619) 532-0789
   - ROICC: Mr. Izzat Amadea
     (510) 755-5876

2. If a release of a waste or hazardous substance, regardless of quantity, could threaten human health or the environment outside the facility, the PM will verify that the National Response Center ([800] 424-8802) and the local Emergency Response Coordinator (Fire Department) have been notified by the Navy. Releases will be reported and written follow-up emergency notices will be submitted under Superfund Amendments and Reauthorization Act Title II requirements.

3. In concert with the above actions, the following persons will be contacted by the PM or Site Superintendent:

   - NOREAS Regulatory Compliance: John Gleason
     Cell: (949) 981-3867
   - NOREAS Certified Industrial Hygienist (CIH): Dr. Maureen Sassoon, Ph.D., CIH
     Cell: (310) 544-2912

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6.0 BIOLOGICAL RESOURCES

6.1 RESOURCE EVALUATION

Numerous pedestrian-based field evaluations have historically been conducted and technical reports were prepared within the study area and on surrounding lands. Furthermore, resource specialists were consulted and available information from resource management plans and relevant documents were evaluated to determine the locations and types of biological resources that have the potential to exist within and adjacent to project limits (Figure 6-1 through Figure 6-3).

The primary data sources reviewed included, but were not limited to, the following:

- Final Environmental Protection Plan/Waste Management Plan for the Non-Time Critical Removal Action at the Production Manufacturing Area and the South Shore Area Former Mare Island Naval Shipyard Vallejo, California (Battelle 2012);
- Salt marsh harvest mouse and California clapper rail recovery plan (USFWS 1984);
- Critical Habitat Mapper and File Data (USFWS 2012b);
- National Wetland Inventory File Data (USFWS 2012c);
- California Natural Diversity Database maintained by the California Department of Fish and Wildlife (CDFW 2012);
- Conceptual Site Model Production Manufacturing Area And South Shore Area at Former Mare Island Naval Shipyard Vallejo, California (Weston 2008);
- California Native Plant Society Electronic Inventory (CNPS 2012);
- The Ecology of the Salt Marsh Harvest Mouse (Reithrodontomys raviventris) in a Diked Salt Marsh and Adjacent Grassland in Palo Alto, California (Johnson and Shellhammer 1988);
- Ecology of the salt marsh harvest mouse in San Pablo Bay (Bias 1994);
- Avocet Research Associates (Evens 2001); and
- Aerial Photographs (Microsoft Corporation 2012).

6.2 EXISTING NATURAL RESOURCES

The SSA is bounded by the Carquinez Strait shoreline to the south and the upland hills to the north, the PMA and Installation Restoration (IR) Site 05 to the northeast and west. The SSA is generally characterized by a relatively flat topography. The shoreline was extended during the early 1900s using upland fill to provide additional space for the manufacturing and processing of ordnance material. The growth of the SSA occurred in several stages between 1930 and 1947. Rock and soil taken from the upland hills area were used to expand the shoreline into the Carquinez Strait. The SSA currently contains buildings, structures, utilities and has metallic

debris both on and below the ground surface. A detailed description of the physical and geological features of the SSA is provided in the updated conceptual site model found in Appendix I of the Geophysical Investigation Report (Weston 2008).

6.2.1 Land Resources

The area comprising the SSA is currently not in use and remains the property of the Navy. The remaining manmade features on the site consist primarily of the buildings formerly used for the production and storage of munitions. The SSA is generally characterized by a relatively flat topography and consists of uplands, wetlands, and tidal mudflat areas located at the southern end of the former MINS.

6.2.2 Surface Waters and Groundwater

Apart from indications for shallow groundwater in the SSA, there is little information available with respect to the hydrologic conditions in this portion of MINS. Given the proximity to San Pablo Bay, it is expected that groundwater elevations, gradient, and flow are influenced by tidal fluctuations. Hydrologic data from the groundwater monitoring wells proposed for RI will be used to evaluate the hydrologic conditions at the SSA.

6.3 BIOLOGICAL RESOURCES WITH THE POTENTIAL TO OCCUR IN THE STUDY AREA

The SSA includes disturbed uplands comprised of asphalt, aggregate, and dirt roads. Ruderal plant communities make up the remainder of these uplands, consisting primarily of sweet anise (*Foeniculum vulgare*), bristly ox-tongue (*Picris echioides*), willow herb (*Epilobium* sp.), scotch broom (*Cytisus scoparius*), common winter cress (*Barbarea vulgaris*), Russian thistle (*Salsola tragus*), vetch (*Vicia* sp.), oats (Avena sp.), hare barley (*Hordeum murinum ssp. leporinum*), coyote bush (*Baccharis pilularis*) and similar upland plants. The ruderal community may be utilized by a variety of mammals including house mice, raccoons, opossums, jackrabbits, squirrels, skunks, and rats. Wetland habitats within the SSA consist of tidal areas that support coastal salt marsh vegetation, may rotationally provide open water, mudflat and pickleweed marsh habitat. The tidal marsh areas and surrounding lands on MINS may provide habitat for the following special-status species:

Mason's Lilaeopsis (*Lilaeopsis masonii*). Federal Listing Status: None; State Listing Status: Rare; CNPS List: 1B.1. This rhizomatous herb in the carrot family (Apiaceae) occurs in brackish, freshwater and occasionally coastal salt marshes and swamps, as well as in riparian scrub habitats from 1 to 32.8 ft. It is typically found in habitats readily inundated by waves or tidal influence. The blooming period extends from April through November. This species is endemic to California and extends over low elevation marshes and wetlands near Suisun Bay and Clifton Court Forebay in Alameda, Contra Costa, Marin, Napa, Sacramento, San Joaquin, and Solano counties. Occurrences of this species are highly limited and at serious risk. Mason's

lilaeopsis is locally common in Suisun Bay. This species often occurs on frequently disturbed substrate as ephemeral populations, and is threatened by erosion, channel stabilization, development, flood control projects, recreation, agriculture, shading due to marsh succession, and competition with non-native water hyacinth *Eichhornia crassipes*.

Several extant occurrences are documented on Mare Island including the southeast tip where Mare Island meets Carquinez Strait, just south of the Mare Island pipeline area and within the Mare Island Southern Escarpment (CNDDB, 2012).

A qualified biologist will visually inspect potential work areas for this species prior to the commencement of work. Should Mason's lilaeopsis be observed in the planned work area, the Navy will carefully consider input from the CDFW and other agencies when developing and implementing this field work.

Salt Marsh Harvest Mouse (*Reithrodontomys raviventris*). Federal Listing Status: Endangered; State Listing Status: Endangered and State Fully Protected Species. Although the salt marsh harvest mouse is federally endangered, critical habitat has not been formally designated for this species. Historically, the salt marsh harvest mouse had been found in the saline emergent wetlands of San Francisco Bay and its tributaries. At least 79 percent of all the tidal marshes around the Bay have been filled in or destroyed over the last 150 years; therefore, existing salt marsh harvest mouse populations in the more highly developed portions of the Bay Area are fragmented and small (Shellhammer, 1982). The highest core populations are found in salt marshes along San Pablo Bay, including Mare Island (CNDDB, 2012). Salt marsh harvest mice also occur in isolated non-tidal wetlands on Mare Island along the western shore of the Napa River, and within the extensive tidal marshes south of State Route 37 on the northwestern and western boundary of the Mare Island Naval Shipyard (CNDDB, 2012).

The salt marsh harvest mouse is dependent on thick perennial salt marsh cover, primarily pickleweed. Although salt marsh harvest mice primarily stay under the cover of pickleweed, they will use upland grassy areas, especially during times when the pickleweed is influenced by high tide (Shellhammer, 1982). The use of grasslands bordering marshes increased in the spring time when grasses sprout and provide increased cover. Mice typically will not move outside of cover, as Shellhammer (1977) found when studying the species in Santa Clara County; no movements were found between marshes separated by levee roads as little as 3 m wide. The salt marsh harvest mouse does not burrow in the ground, and likely does not use existing rodent burrows, and tidal action would preclude burrow use. Loosely organized nests of dry grasses are occasionally built on the ground surface and are probably rebuilt quickly after tidal events (Shellhammer, 1982). Numerous trapping efforts from the early 1970s and into the 1980s indicate that Mare Island has a relatively robust population. In the 1980s alone, more than 1000 mice were captured. Approximately 30 captures resulted from trapping efforts in the summer of 2000 in the south shore area (CNDDB, 2010). Trapping in the south shore in the early 1990s confirmed presence of the salt marsh harvest mouse within the project area. Bias and Morrison

(2006) trapped salt marsh harvest mice throughout Mare Island, resulting in 4,147 captures between the years 1989 and 1992.

Suisun Shrew (*Sorex ornatus sinuosus*). Federal Listing Status: None; State Listing Status: Species of special concern. The shrew occurs in the tidal marshes of the northern shores of San Pablo and Suisun bays, as far east as Grizzly Island and as far west as the mouth of Sonoma Creek (Rudd, 1955a). *Sorex o. sinuosus* is a small shrew, with total body length ranging 91-108 mm and a tail length ranging 35-48 mm (Rudd, 1955). It is a dark, nearly black shrew with a long nearly unicolored tail; it is considered the darkest subspecies of ornate shrew (Owen and Hoffmann, 1983). Weight is from 3.4-6.8 g for males and 3.3-6.7 g for females (Rudd, 1955b). Life span is typically 12 to 16 months (Owen and Hoffmann, 1983). The shrew typically occurs in tidal salt marsh habitats vegetated with *Salicornia virginica*, *Baccharis pilularis*, *Grindelia cuneifolia*, and *Distichlis spicata*. The species is most often trapped at marsh characterized with Salicornia, Baccharis and grasses within levee areas (Hadaway and Newman, 1971). Within a 24 hour period the Suisun shrew is active 24 percent of the time (Rust, 1978). Most activity was confined to the night, although there is some diurnal activity (Rust, 1978). Seasonal activity increases during the breeding peaks, one in spring and the other in fall (Johnston and Rudd, 1957; Rust, 1978). The CNDDB has two records of the Suisun shrew on Mare Island. Both detections occurring during trapping efforts for the salt marsh harvest mouse. One shrew was captured in September of 1987 in non-tidal areas and 16 adults were captured in May, June, and October of 1990 in the same general location.

California Clapper Rail (*Rallus longirostris obsoletus*). Federal Listing Status: Endangered; State Listing Status: Endangered and State Fully Protected Species. Formerly, this subspecies occurred from Humboldt Bay to Morro Bay. Currently it is found only in the San Francisco Bay and Suisun Bay Complexes. Since the mid-1800s, about 80 percent of San Francisco Bay's marshlands have been eliminated through filling, diking, or conversion to salt evaporation ponds (Eddleman and Conway, 1998). As a result, habitat for California clapper rails was destroyed, the population declined severely, and the species was listed as endangered. The California Clapper Rail is found only in saline and brackish emergent wetlands of San Francisco Bay and its tributaries. Clapper rails along the Pacific Coast prefer salt marshes and brackish marshes dominated by cordgrass (*Spartina foliosa*) and marsh gumplant (*Grindelia stricta*). In brackish marshes, they frequent areas supporting bulrushes (*Scirpus* sp.). These birds require shallow areas or mudflats for foraging, particularly channels with overhanging banks and vegetation (Eddleman and Conway, 1998). As a refuge from extreme high tides and as a supplementary foraging area, rails move to the upper marsh vegetation where it intergrades with peripheral upland vegetation. These birds have no requirement for fresh water (Eddleman and Conway, 1998).

San Pablo Song Sparrow (*Melospiza melodia samuelis*). Federal Listing Status: None; State Listing Status: Species of Special Concern (year round). The San Pablo song sparrow is a

medium-sized American sparrow. Adults have brown upperparts with dark streaks on the back and are white underneath with dark streaking and a dark brown spot in the middle of the breast. They have a brown cap and a long brown rounded tail. Their face is grey with a streak through the eye (Spautz and Nur, 2008). In the field, they are most easily confused with its congener the Lincoln's sparrow, and the savannah sparrow. The former can be recognized by its shorter, greyer tail and the differently-patterned head, the brown cheeks forming a clear-cut angular patch (Sibley, 2000). The Savannah Sparrow has a forked tail and yellowish flecks on the face when seen up close (Sibley, 2000). Preferred habitat is brushy areas and marshes, including salt marshes (Spautz and Nur, 2008). These birds forage on the ground, in shrubs or in very shallow water. They mainly eat insects and seeds, but birds in salt marshes may also eat small crustaceans. They nest either in a sheltered location on the ground or in trees or shrubs (Spautz and Nur, 2008).

Northern Harrier (*Circus cyaneus*). Federal Listing Status: None; State Listing Status: Species of Special Concern. The northern harrier is commonly found in open grasslands, agricultural areas, and marshes. Nests are built on the ground in areas where long grasses or marsh plants provide cover and protection. Harriers hunt for a variety of prey, including rodents, birds, frogs, reptiles, and insects by flying low and slow in a traversing manner utilizing both sight and sound to detect prey items. Northern harriers are fairly common within the marsh habitats on Mare Island.

White-tailed Kite (*Elanus leucurus*). Federal Listing Status: None; State Listing Status: Fully Protected Species. This species prefers habitats with low ground cover and variable tree growth. Kite nests are built near the tops of oaks, willows, or other dense broad-leafed deciduous trees in partially cleared or cultivated fields, grassy foothills, marsh, riparian, woodland, and savannah. Kites prey primarily on small rodents (especially the California vole), but also feed on birds, insects, reptiles, and amphibians. White-tailed kites are fairly common within the marsh habitats on Mare Island.

Osprey (*Pandion haliaetus*). Federal Listing Status: None; State Listing Status: Species of Special Concern. The Osprey is a diurnal, fish-eating bird of prey. It is a large raptor, reaching 24 in (60 cm) in length with a 6 ft (1.8 m) wingspan. It is brown on the upperparts and predominantly grayish on the head and under parts, with a black eye patch and wings. The Osprey tolerates a wide variety of habitats, nesting in any location near a body of water providing an adequate food supply. It is found on all continents except Antarctica although in South America it occurs only as a non-breeding migrant. The Osprey is considered a migrant in this part of the state. Ospreys occur on Mare Island during the nesting season.

California Black Rail (*Laterallus jamaicensis coturniculus*). Federal Listing Status: Species of Management Concern; State Listing Status: Threatened and State Fully Protected Species. The California black rail is a small (12 to 15 cm), secretive, marsh-associated species (Eddleman and Conway, 1998). They are black to gray in color with a small black bill, sides and back speckled

with white, and a nape of deep chestnut brown. Difficult to observe, rails are usually identified by their call. The breeding season begins as early as February with pair formation and extends through approximately early to mid-June. Egg laying peaks around May 1 (Eddleman and Conway, 1998). The species is generally known as a medium-distance migrant that winters in Mexico and Central America; however, recently discovered inland populations in California are thought to be year-round residents.

The majority of California Black Rails (>90 percent) are found in the tidal salt marshes of the northern San Francisco Bay region, primarily in San Pablo and Suisun. Smaller populations occur in San Francisco Bay, the Outer Coast of Marin County, freshwater marshes in the foothills of the Sierra Nevada, and in the Colorado River Area. The California Black Rail has been documented in the salt marshes of Mare Island. Loss of more than 80 percent of historic tidal marsh habitat, as well as habitat fragmentation and degradation, have directly and indirectly impacted this and other tidal marsh breeding species. Although there are a few historic records of Black Rail presence and abundance in the Bay, recent survey efforts indicated that the species is absent from some marshes in the northern Bay region and that population sizes may be low enough to cause concern. Due to its small population sizes, it has been listed as a State of California Threatened Species and a Federal Species of Management Concern.

Salt Marsh Common Yellowthroat (*Geothlypis trichas sinuosa*). Federal Listing Status: None; State Listing Status: Species of Special Concern. The common yellowthroat breeds broadly from southeastern Alaska across Canada south through the United States (very local in the southwest) into northern Baja California and the Pacific slope and central high¬lands of Mexico (Guzy and Ritchison, 1999). Birds are resident in the very southern United States and in the Mexican breeding range, but northern breeders retreat to winter south to Panama and the Caribbean. In North America, the highest breeding densities are mainly in the states of the upper Midwest and Northeast and in adjacent Canada (Sauer et al., 2005). In California, the species breeds throughout much of the state, except in the higher mountains and most of the southern deserts, and retreats from much of the north in winter (Grinnell and Miller, 1944).

For the San Francisco Bay area as a whole, about 60% of yellowthroats occupy brackish marsh, 20% riparian woodland/swamp, 10% freshwater marsh, 5% salt marsh, and 5% upland. The yellowthroat occupies the ecotone between moist and upland situations; thus, the proximity of various habitat types appears to enhance overall habitat suitability. The last recorded observation of a salt marsh common yellowthroat on Mare Island was in 1998.

7.0 BIOLOGICAL AVOIDANCE, MINIMIZATION, AND MITIGATION MEASURES

As-needed biological monitoring support activities will be provided throughout the duration of the RI field activities and will include lay-down areas, staging areas, access roads, and any other locales subject to physical disturbance . Biological monitors will work closely with field staff, and other interested parties, to ensure that the project environmental-compliance requirements are satisfied.

The biological monitors are an integral part of the team and will also work closely with investigation staff to answer questions and provide direction when appropriate. Resource specialists who have expertise in mammalogy, ornithology, and botany will be available to assess specific concerns and will provide required monitoring and reporting functions to ensure protection of biological resources during project activities.

A summary of the specific biological avoidance, minimization, and mitigation procedures that will be implemented during the RI field work is provided in the subsections that follow.

7.1 BIOLOGICAL RESOURCE EDUCATION PROGRAM

A U.S. Navy contracted biologist (approved by the USFWS and CDFW) will conduct a Biological Resource Education Program briefing to all contractor and subcontractor personnel prior to entry to the project area. The biologist will have experience with knowledge regarding the salt marsh harvest mouse, rails, rare plants, and birds protected by the Migratory Bird Treaty Act (MBTA). This briefing will review sensitive biological resources (e.g., salt marsh harvest mouse, jurisdictional wetlands, etc.) within the work area and will identify all protection measures to be implemented to comply with the applicable State and Federal ARARs. New employees will attend a briefing by the biological monitor prior to participating in work activities.

7.2 OPERATIONS, EQUIPMENT, AND PERSONNEL

Soil boring and well installation activities will be conducted when the non-tidal seasonal wetlands are dry. In addition, work within or adjacent to wetland habitat will not be conducted within two hours before and after extreme high tides (6.5 ft above mean lower low water), as measured at the Golden Gate Bridge. Drill rigs and support vehicles will be confined to the access routes, designated staging areas and designated intrusive investigation areas. Upland routes covered with pavement, bare ground, or non-native vegetation will be utilized as access routes to and from the intrusive investigations, to the maximum extent practicable. The equipment decontamination area will be located in the designated upland staging area away from any wetlands habitat.

7.3 BIOLOGICAL MONITOR

A qualified biological monitor, approved by the USFWS and CDFW, will be present onsite to monitor for salt marsh harvest mice (and rails, rare plants, and birds protected by the MBTA) during all work activities in potential habitat areas. The biological monitor also will periodically observe work within the adjacent upland areas. The biological monitor will have the authority to stop work if deemed necessary for any reason to protect salt marsh harvest mice (or any other State or Federal "Threatened or Endangered" or "Fully Protected" species, including rails, rare plants, and birds protected by the MBTA).

If breeding clapper rails are determined to be present, activities will not occur within 700 feet of an identified calling center. If the intervening distance across a major slough channel or across a substantial barrier between the clapper rail calling center and any activity area is greater than 200 feet, then it may proceed at that location within the breeding season.

Prior to the initiation of work each day within potential habitat, the biological monitor will thoroughly inspect the work area and adjacent habitat areas to determine if SMHM (or rails, rare plants, or birds protected by the MBTA) are present in these areas and will remain onsite throughout the day while work activities are occurring in habitat areas. If a mouse of any species (or a rail, or rare plant species) is observed in the work area (i.e., in the immediate vicinity of an intrusive investigation), then work in the area of the observed species will not be initiated.

If a mouse or rail is observed, work will be stopped immediately by the biological monitor until the mouse (or rail) leaves the intrusive investigation area of its own volition and the USFWS and CDFW are notified. The USFWS and CDFW will also be notified if a rare plant species is observed. If the mouse or rail does not leave the intrusive investigation area, work would not be reinitiated until the USFWS and CDFW are contacted and have made a decision on how to proceed with work activities. The biological monitor would direct the contractor on how to proceed accordingly.

If a rare plant species is observed in the work area, the USFWS and CDFW-OSPR will be notified and the Navy will coordinate appropriate avoidance and mitigation measures with these agencies. The location of the rare plant species will be noted in the daily biological monitoring report and reports will be submitted to the USFWS and DTSC for forwarding to the CDFW-OSPR.

7.4 PICKLEWEED REMOVAL

If necessary, coastal salt marsh wetlands vegetation will be removed under the supervision of a qualified biologist who will evaluate the areas for SMHM, rails, rare plants, and birds protected by the MBTA prior to vegetation removal. For any work that requires vegetation removal, a qualified biologist will visually inspect for rare plants that may be present, during the time of year when the species are evident and identifiable, and prior to the start of field activities.

Inspections for Mason's lilaeopsis, California seablite, and Contra Costa goldfields will be performed in June 2015, and an additional visual inspection will be conducted in early July 2015, prior to the field activities, to overlap the blooming periods of the California seablite.

Vegetation removal may begin when no mice are observed. If vegetation removal is in the 50 ft buffer zone, it will start at the edge farthest from the salt marsh and work its way towards the salt marsh. This method of removal provides cover for SMHM and allows SMHM to move towards the salt marsh on its own volition as vegetation is being removed. Coastal salt marsh wetlands and any vegetation which needs to be removed for anomaly investigation within a 50 ft buffer around the coastal salt marsh wetlands will be removed using non-motorized (mechanized tools are acceptable) hand tools only. A biological monitor will be present during removal of vegetation within 50 feet of coastal salt marsh wetlands. Non-handheld equipment will be limited to the areas where the vegetation has been cut.

The portions of the coastal salt marsh wetlands within the project area that are temporarily affected by the proposed action will be restored to coastal salt marsh wetlands habitat for the SMHM. These areas will be restored by backfilling the excavated areas and recontouring the excavated areas to elevations that provide hydrologic conditions sufficient to support re-establishment of coastal salt marsh wetlands.

7.5 SILT FENCE INSTALLATION AND MAINTENANCE

Intrusive investigations in coastal salt marsh wetlands will be conducted after hand clearance of vegetation. If machinery is required in the wetlands, hand clearance of vegetation will be conducted and silt fencing will be installed around the area to be accessed by the machinery. Excavations in the 50 ft buffer area around the wetlands will be conducted using motorized equipment after vegetation is cleared using non-motorized equipment starting from the edge farthest from the wetlands to give SMHM opportunity to move toward the wetlands as vegetation is being removed. The qualified biological monitor shall observe the excavation and have the authority to stop work if protected species are observed.

When used, the fencing will be trenched into the ground and backfilled to prevent salt marsh harvest mice from moving underneath the fencing. All silt fencing will be installed with stakes facing towards the work site and away from the habitat. The final design and proposed location of the fencing will be reviewed and approved by the USFWS and CDFW prior to being installed. The biological monitor will have the ability to make field adjustments to the location of the fencing depending on site-specific habitat conditions.

The biological monitor will monitor silt fencing periodically during the work day to ensure that it remains an effective barrier to prevent entry of SMHM into work areas. Maintenance of the fencing will be conducted as needed throughout the work period, including the habitat restoration work. Any necessary repairs to the fencing will be completed within 24 hours of the initial

observance of the damage. Work will not continue until the fences are repaired and the site is inspected by a qualified biologist to ensure that SMHM have not entered the work area.

7.6 MONITORING DURING PROTECTED SPECIES NESTING SEASON

The proposed activities are not response or remedial actions but rather a field sampling effort. There will be no staging, storage or stockpile areas. The field investigation consists of collecting samples at individual locations and the onsite biologist will visually inspect for nesting birds prior to work. The field crew will not return to that sampling area after the samples have been collected and therefore multiple inspections of the sampling locations will not be required. The Navy will have a biologist onsite to conduct inspections on a daily basis during work in potential habitat areas.

If site work is conducted between the dates of February 1 and September 15, a visual inspection for protected nesting birds will be conducted by a qualified biologist for all staging and storage areas, transportation routes, work areas, and soil stockpile areas within a reasonable time prior to commencement of any project activities. If work is already occurring within the area when protected nesting season starts, a protected species nesting visual inspection will not be required. If work is stopped for more than a reasonable time as determined by the qualified biologist during the protected species nesting season, staging and storage areas, work areas, and soil stockpile areas will be reassessed before a return to work activities. The site biological monitor will inspect the work area and natural habitats occurring within a reasonable distance of the work area to identify active nests of protected species. If no active nests of protected species are found, no further mitigation will be conducted.

If protected nesting birds are found during visual inspections, the location will be noted, appropriate avoidance and mitigation measures will be recommended by the qualified biologist, and the daily report will be submitted to the USFWS and CDFW. If vegetation containing protected nesting birds must be removed during nesting season (February 1-September 15) as a result of project implementation, the Navy will coordinate with both the USFWS and CDFW to assess appropriate avoidance or mitigation measures.

If a qualified biologist in coordination with the USFWS and CDFW determines the project activity will not be likely to adversely affect the active nest, the project may proceed. The qualified biologist will monitor the activity of the protected nesting birds (including rails or birds protected by the MBTA) during work activities. If the birds behave normally, the biologist will monitor them twice per week to ensure the status has not changed. If the birds change their behavior as a result of work activities, the biologist will continue to monitor the birds as work is modified until the birds act normally. The biologist will then monitor the birds twice per week to ensure the status has not changed.

8.0 DOCUMENTATION AND RECORDS RETENTION

Documentation of regulatory compliance issues and records retention will be conducted in accordance with the NOREAS' compliance procedures for documentation and records retention and the Environmental Restoration Program Manual (Navy 2006).

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9.0 WORKER ENVIRONMENTAL AWARENESS (WEAP) CERTIFICATE OF COMPLETION

Date: _____ Instructor(s): _____

Initial

- ***I have attended the WEAP Training and understand the information.*** ☐
- ***I understand that failure to abide by the procedures outlined in this document may have an adverse effect on the Project.*** ☐
- ***I understand that it is illegal to knowingly disturb or destroy common or special-status plant and animal species, and that major enforcement actions will result for violating any applicable state or federal laws, ordinances, and regulations detailed within this WEAP.*** ☐

PLEASE NOTE: By signing below, I acknowledge that I have attended the WEAP Training for the project and I agree to comply with all the environmental requirements presented.

			FOR OFFICE USE ONLY
Name (print)	**Name (signature)**	**Company**	**Employee identification number**

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10.0 UPDATING THE EPP

This EPP will be updated as needed to reflect changing site conditions or if changes in applicable regulations occur.

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FIGURES

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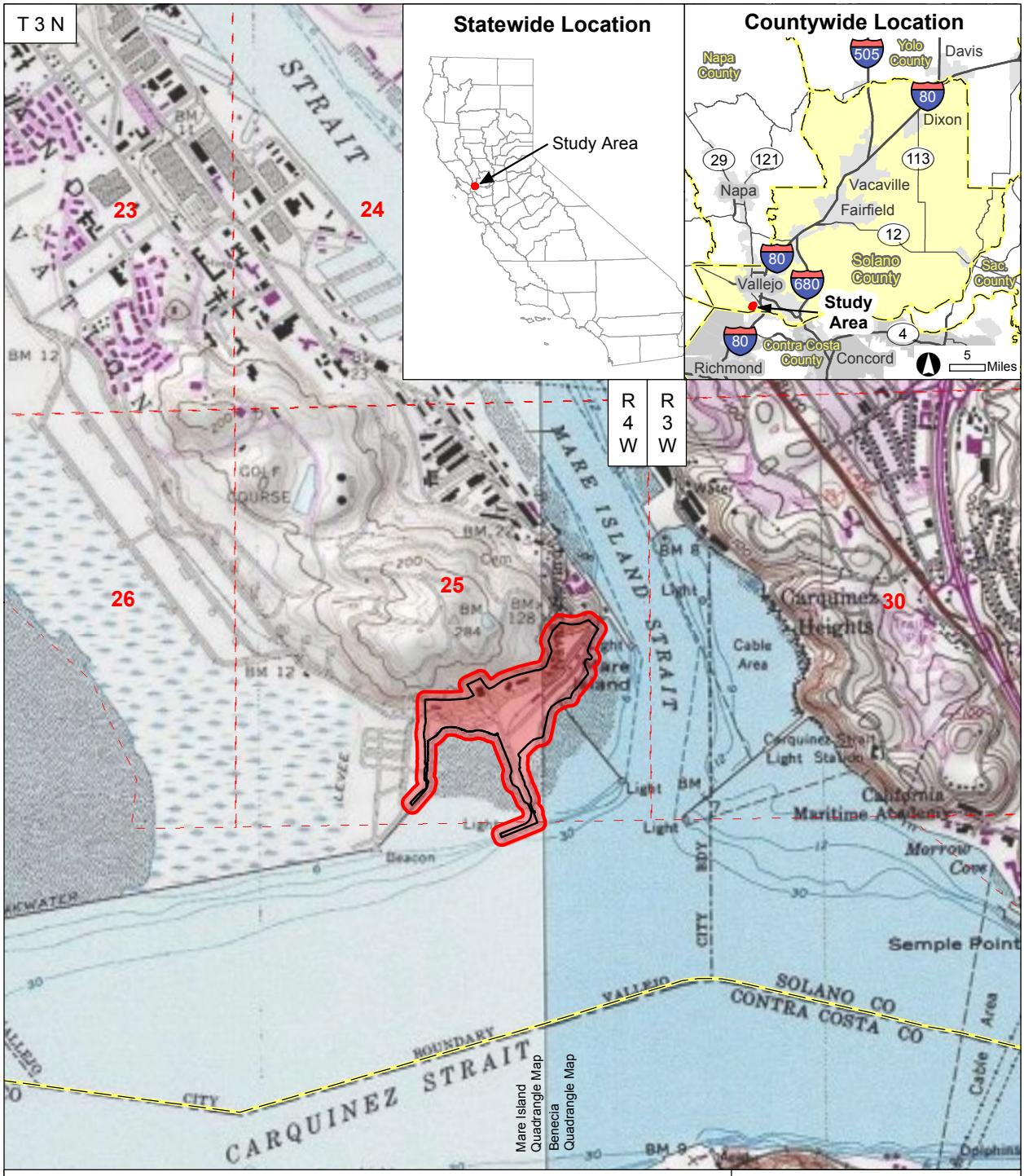

Project Site Boundary

Study Area

Section Boundary

County Boundary

Urban Area (inset)

Interstate or US Highway (inset)

Water Body

0 1,000 2,000 Feet

1 inch = 2,000 feet

Data Sources:
- ESRI StreetMap North America 2012
- ESRI US Topo Maps accessed Apr 2014
- US Geological Survey, CalFire 1999

Map Prepared: 4-16-14

Prepared by:

NOREAS Environmental Engineering and Science

The Study Area is located on the Benicia and Mare Island USGS 7.5-minute quadrangle maps; Mt. Diablo Meridian Township 3 North, Range 4 West, Section 25 and an unsectioned portion of the Carquinez Straight.

Mare Island SSA

Figure 1-1. Regional Location

Project Site Boundary (37.7 acres)

Study Area Boundary (65.3 acres which includes a100-ft buffer and the Project Site)

0 500 1,000 Feet

1 inch = 1,000 feet

Data Source:
- US Department of Agriculture, National Agriculture Imagery Program (NAIP), photo dated 5-20-12

Map Prepared: 4-16-14

Prepared by:

NOREAS
Environmental Engineering and Science

Mare Island SSA

Figure 1-2. Site Vicinity

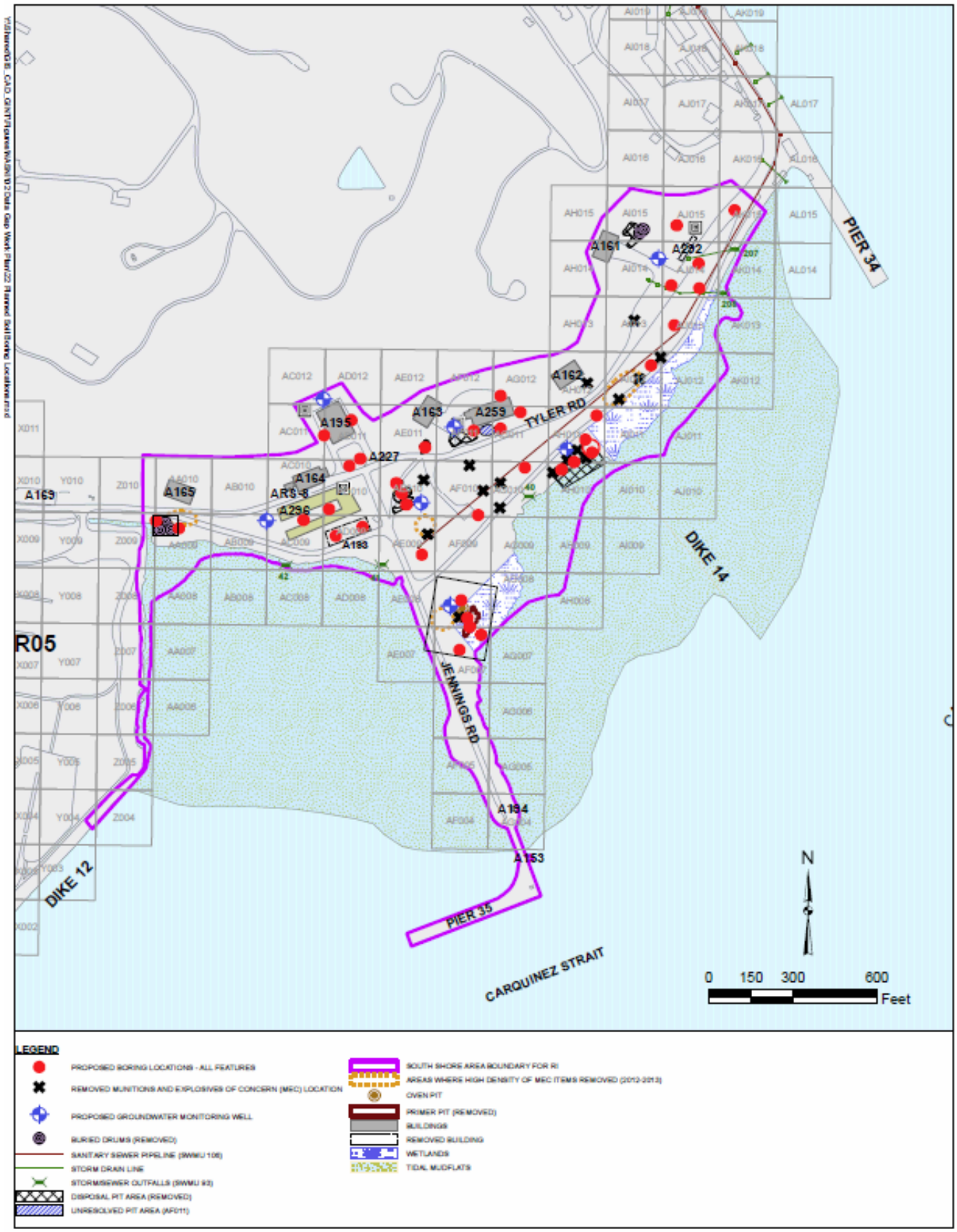

Figure 3-1. Planned Soil and Groundwater Sampling Locations

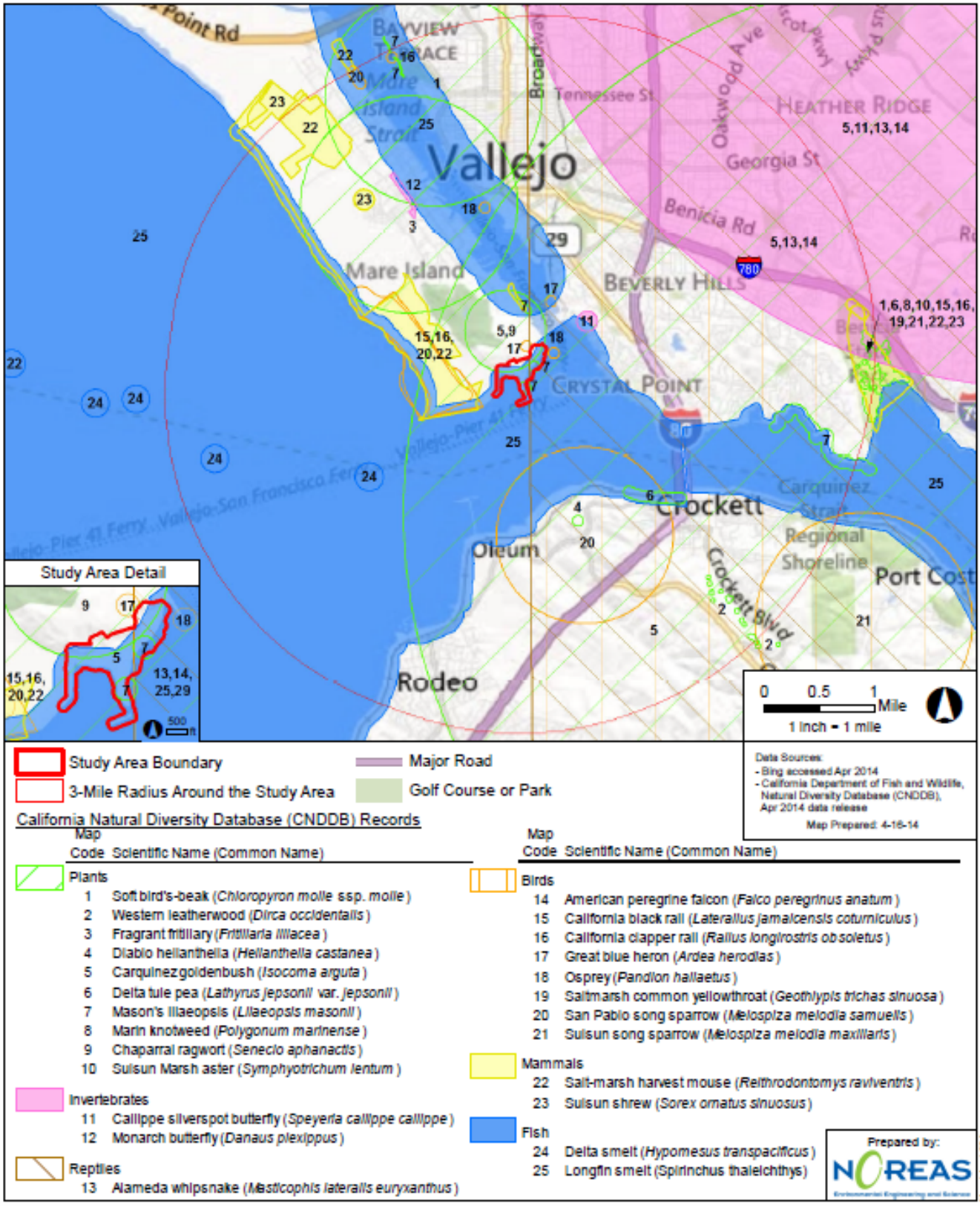

Figure 6-1 . Literature Review

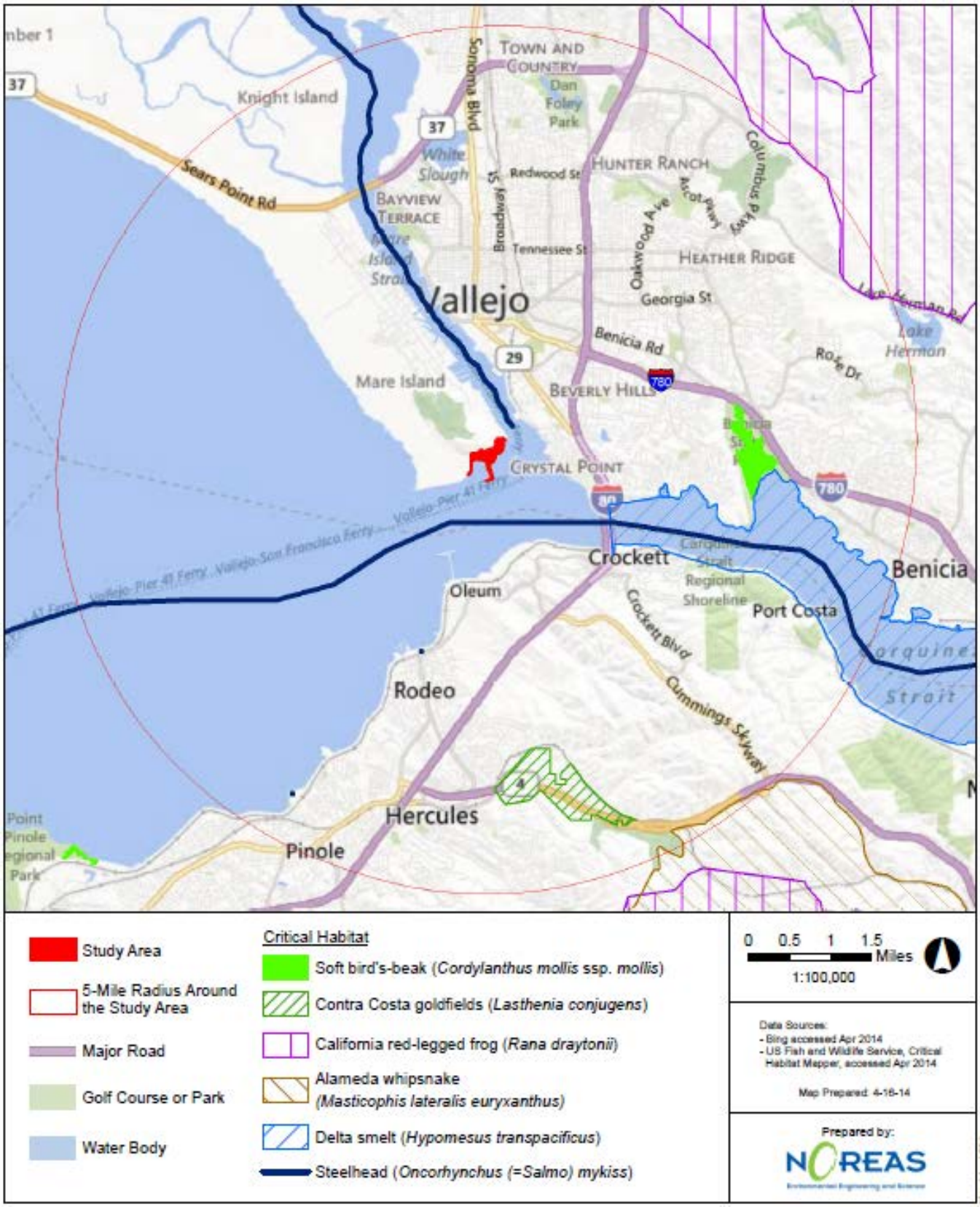

Figure 6-2. Critical Habitat

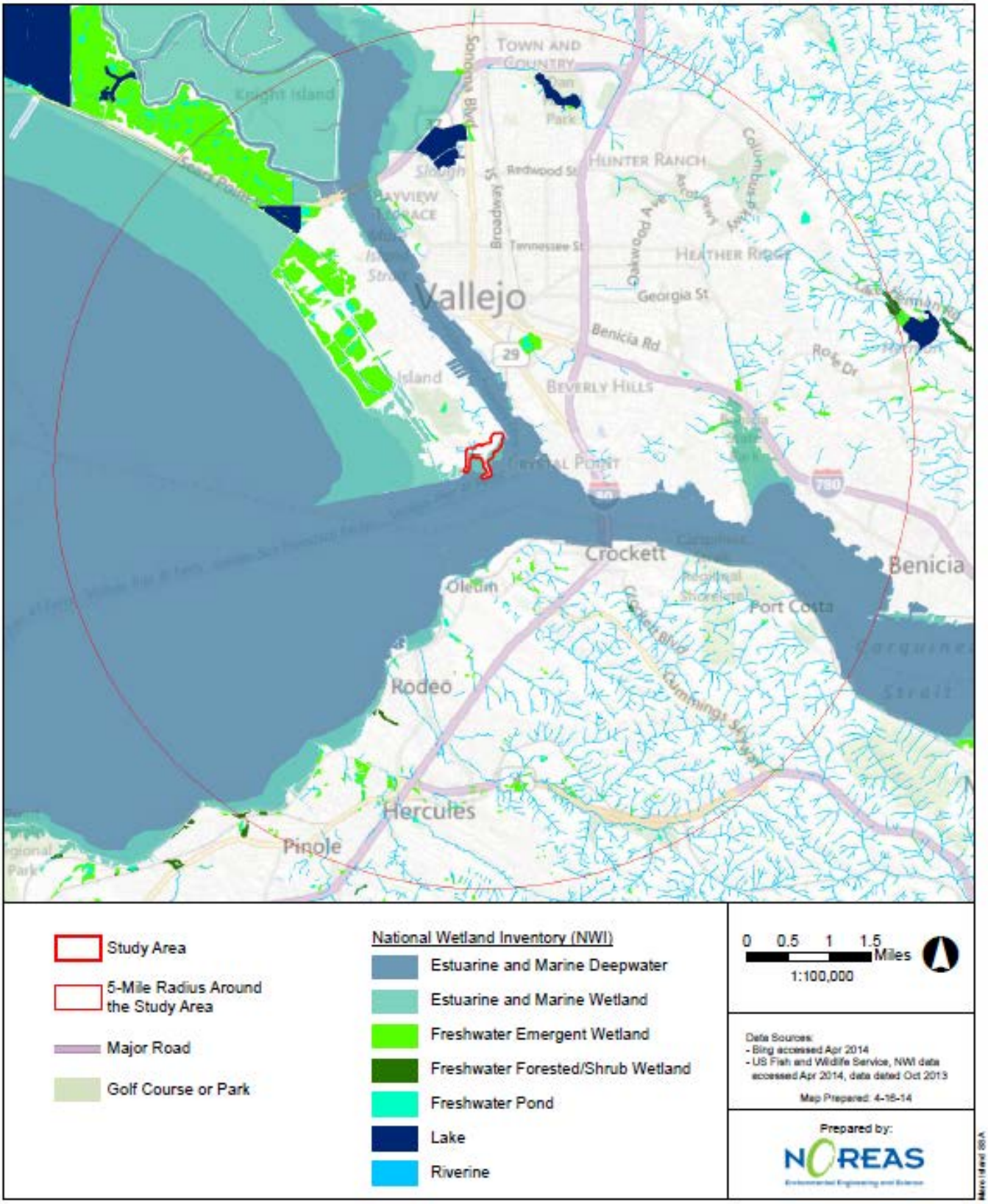

Figure 6-3. National Wetland Inventory

APPENDIX C

WASTE MANAGEMENT PLAN

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APPENDIX C
WASTE MANAGEMENT PLAN

South Shore Area
Former Mare Island Naval Shipyard
Vallejo, California
July 2015

Base Realignment and Closure
Program Management Office West
1455 Frazee Road, Suite 900
San Diego, California 92108

CONTRACT NO. N62473-12-C-4812

DCN: NRS-4812-0000-0009

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Table 2-2 California Hazardous Waste Characteristics

Table 2-3 Waste Management Summary Requirements

ABBREVIATIONS AND ACRONYMS

APP/SSHP	Accident Prevention Plan/Site Safety and Health Plan
CCR	California Code of Regulations
CFR	Code of Federal Regulations
DOT	United States Department of Transportation
DTSC	State of California Department of Toxic Substance Control
ID	identification
LDR	Land Disposal Restriction
NRC	National Response Center
PCB	polychlorinated biphenyl
PPE	personal protective equipment
RCRA	Resource Conservation and Recovery Act
RMMP	Radiological Materials Management Plan
RI	Remedial investigation
SVOC	semi-volatile organic compound
SSA	South Shore Area
STLC	Soluble Threshold Limits Concentrations
TCLP	Toxicity Characteristic Leaching Procedure
TSDF	treatment, storage, and disposal facility
TTLC	Total Threshold Limits Concentration
UHC	Underlying Hazardous Constituents
USEPA	U.S. Environmental Protection Agency
VOC	volatile organic compound
WET	California waste extraction test

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1.0 WASTE MANAGEMENT PLAN

This waste management plan describes the waste management requirements and procedures that will be implemented during the project. This plan will be modified, as necessary, to address changing conditions that would necessitate activity-specific waste management or disposal requirements.

Consistent with Resource Conservation and Recovery Act (RCRA) and State of California waste management regulations, contaminated environmental media such as soil and water must be managed as waste as long as they are contaminated, or as long as they contain waste. Accordingly, throughout this document, the requirements and procedures applicable to waste also apply to environmental media.

1.1 EXPECTED WASTE STREAMS

Waste streams generated during the Remedial Investigation (RI) at the South Shore Area (SSA) include:

- Soils and soil cuttings contaminated with volatile organic compounds (VOCs) and/or, semi-volatile organic compounds (SVOCs), munitions constituents, metals, petroleum hydrocarbons, dioxins/furans, polychlorinated biphenyls (PCBs), radium-226.
  - Soil cuttings
  - Decontamination solids
- Debris
  - Uncontaminated debris such as daily trash, asphalt, and concrete
  - Personal protective equipment (PPE), used sampling equipment, and liners
- Liquids potentially contaminated with VOCs, SVOCs, petroleum hydrocarbons, PCBs, metals, and dioxins/furans
  - Decontamination water
  - Purged groundwater

Soils contaminated with the various organic constituents will be disposed of based on waste characterization requirements and results. Soil containing metals exceeding the applicable toxicity characteristic thresholds using the U.S. Environmental Protection Agency (USEPA) Toxicity Characteristic Leaching Procedure (TCLP) method will be managed as RCRA hazardous waste. Soil with metals exceeding the Total Threshold Limits Concentrations (TTLC) or Soluble Threshold Limits Concentrations (STLC) will be managed as non-RCRA hazardous waste (California hazardous waste). Soils containing radium-226 will be handled and managed under the Radiological Materials Management Plan (RMMP) prepared under separate cover.

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2.0 WASTE MANAGEMENT FOR HAZARDOUS AND NONHAZARDOUS WASTES

The various waste streams generated during the remedial action must be managed, accumulated, and classified for proper transportation and disposal.

2.1 WASTE CLASSIFICATION

Waste classification determinations will be made using process knowledge and laboratory analyses in compliance with 40 Code of Federal Regulations (CFR) Part 261 Subpart C, as well as 22 California Code of Regulations (CCR) Division 4.5 Chapter 11. In general, wastes will undergo totals analysis, 96-hour aquatic toxicity test, and TCLP analysis as described in the UFP-SAP (Appendix B). Characterization results will first be compared with 40 CFR 261 Subpart C then with 22 CCR Division 4.5 Chapter 11, TTLC.

2.1.1 RCRA Hazardous Waste

Waste is considered RCRA hazardous if it exhibits one or more of the hazardous characteristics listed in Table 2-1, and will be assigned a "D0XX" waste code. The characteristic waste codes are described below. RCRA hazardous waste analytical results must then be compared to the Land Disposal Restriction (LDR) criteria (40 CFR 268.7) to determine if treatment is required prior to landfill disposal.

2.1.2 Non-RCRA or California Hazardous Waste

Waste is considered non-RCRA hazardous and California hazardous if it exhibits one or more of the characteristics listed in Table 2-2. Additional criteria with regard to non-RCRA hazardous waste are found in 22 CCR 66261.24(a)(3-8). California hazardous waste codes are not assigned based on substances and concentrations, but as described in 22 CCR Chapter 11, Appendix XII. In general, totals analysis is completed prior to the California waste extraction test (WET) to determine if a waste is non-RCRA hazardous as compared to the TTLC. If totals results exceed the TTLC, the waste may be analyzed using the WET and compared to the STLC, or simply considered non-RCRA hazardous waste.

2.1.3 Nonhazardous Waste

Nonhazardous waste materials, those below all RCRA and California criteria described above, will be transported and disposed at a permitted Class 2 or Class 3 nonhazardous landfill. It is expected that the soil cuttings, purged groundwater, and decontamination will be classified nonhazardous.

2.2 WASTE ACCUMULATION AND STORAGE

Table 2-3 summarizes the waste management requirements. Hazardous wastes will be segregated from nonhazardous wastes. Additionally, incompatible hazardous wastes (e.g., flammable and corrosive wastes) will be segregate Wastes of the same matrix, contamination, and source may be aggregated to facilitate accumulation and disposal. It is assumed for the purposes of this project that all explosive waste has been removed and will not be generated during this remedial investigation.

Wastes will be staged in a designated laydown area adjacent to the SSA. All containers will be inspected on arrival at the site for signs of disrepair or contamination, and to verify that the containers are empty and clean. If a container does not arrive in good condition, is contaminated, or is not empty, it will be immediately rejected and documented. Existing damage (dings, significant paint scratches, broken wheels, etc.), if not significant enough to result in rejection, shall be documented upon arrival of the containers using photographs and written documentation.

Good housekeeping practices will be conducted at the waste staging area.

2.2.1 Drums and Small Containers

The following guidelines relate to drums and other containers:

- Drums will be inspected and inventoried upon arrival onsite for signs of contamination and/or deterioration.
- Drums and small containers will be transported to the designated staging area on wood pallets and will be secured together with nonmetallic banding.
- Adequate aisle space (e.g., 30 inches) will be provided for containers such as 55 gallon drums to allow the unobstructed movement of personnel and equipment. A row of drums should be no more than two drums wide.
- Each drum will be provided with its own label; labels will be visible for inspection purposes.
- Drums will remain closed (i.e., the lid and/or bung must be on and securely tightened) except when removing or adding waste to the drum.
- Drums will be disposed of with the contents.
- Drums containing liquids or hazardous waste will be provided with secondary containment.

2.2.2 Large Portable Containers (Portable Tanks)

- Portable tanks will be inspected upon arrival onsite for signs of deterioration and contamination. Any tank arriving onsite with contents or in poor condition will be rejected. Existing damage (dings, significant paint scratches, broken wheels, etc.), if

not significant enough to result in rejection, shall be documented upon arrival using photographs and written documentation.

- Portable tanks will be provided with covers and secondary containment.
- Only non-stationary (i.e., portable) tanks such as a cargo tank or other wheeled tank, capable of being moved when full, will be used to accumulate hazardous waste. These portable tanks are regulated as hazardous waste containers.
- Portable tanks shall not be hard plumbed or permanently attached to the ground or other structures.
- Portable tanks will remain closed except when removing or adding waste. Covers will be properly secured when waste is not being added or remove
- Each portable tank will be provided with its own label; labels will be readily visible.

2.2.3 Roll-Off Boxes

- Roll-off boxes will be inspected upon arrival onsite. Any roll-off containers arriving with contents, residual contamination, or deterioration will be rejected. Existing damage (dings, significant paint scratches, broken wheels, etc.), if not significant enough to result in rejection, shall be documented upon arrival of the box using photographs and written documentation.
- Roll-off boxes will be provided with covers and disposable liners.
- When not in use and at the end of each workday, the covers will be properly secure
- Old labels will be removed and each box will be provided with its own label; labels will be readily visible.
- Roll-off containers will be inspected by the transporter after removal of the liner, and decontaminated in the event of evidence of liner failure.

2.2.4 Waste Storage Time Limits

Non-RCRA and RCRA hazardous wastes will be removed from the site within 90 days from date of generation. Other wastes will be removed from the site as soon as possible. The date of generation is the day that a waste is first placed in a container (i.e., drum, roll-off box, or portable tank).

2.2.5 Container Labeling

The labeling of waste containers will be in accordance with 22 CCR, Division 4.5 Chapter 12; and 49 CFR Part 172, 173, and 178. Labels will include the type of waste, location from which the waste was generated, and accumulation start date. Containers, roll-off boxes, and portable tanks used to store/accumulate waste (including soil and groundwater) will include one of the following labels.

"Analysis Pending" or "Waste Material"—Temporary or handwritten label until analytical results are received and reviewed. This label will include generator information, type and location of waste, and the accumulation start date.

"Hazardous Waste"—Preprinted hazardous waste labels with the following information:

- Accumulation start date
- Generator name
- USEPA identification (ID) number
- Waste codes
- Description of waste, including hazardous properties and physical state
- United States Department of Transportation (DOT) proper shipping name
- Prior to transport, the manifest number must be added

"Nonhazardous Waste"—Preprinted labels with the following information:

- Accumulation start date
- Generator name
- USEPA ID number
- Waste-specific information

The appropriate DOT hazard class label will be placed on the container prior to loading onto the transport vehicle.

2.3 WASTE ACCUMULATION AREAS

NOREAS will implement the following hazardous waste storage area requirements for waste stored onsite:

- A sign with the legend, "Hazardous Waste Area-Unauthorized Personnel Keep Out" (written in English and Spanish), along with 24-hour emergency contact phone numbers, will be posted at the designated waste accumulation area sufficient quantity to be seen from any approach. The signs will be legible from a distance of at least 25 feet.
- Aisle space will be maintained to allow for the unobstructed movement of personnel, fire protection equipment, spill control equipment, and decontamination equipment to any area of facility operation in an emergency, unless aisle space is not needed for any of these purposes.
- The following emergency equipment will be located or available to personnel during active waste management activities at each accumulation area.

1. A device, such as a telephone or a hand-held two-way radio, capable of summoning emergency assistance will be available.
2. Portable fire extinguishers, fire control equipment, spill control equipment, and decontamination equipment will be available.
3. Water at adequate volume and pressure to supply water hose streams, or foam-producing equipment, or water spray systems will be available.
4. A spill response kit for minor spills will be available. The kit will include a shovel, absorbent pads and/or "kitty litter," and a collection container.

2.4 2.4 INSPECTIONS

Waste accumulation and equipment storage containers and areas will be inspected weekly for malfunctions, deterioration, discharges, and leaks that could result in a release.

- Containers, portable tanks, and roll-off containers will be inspected for leaks, signs of corrosion, or signs of general deterioration, proper labeling, and length of accumulation time.
- All areas will be inspected to ensure that good housekeeping practices are maintained

Any deficiencies observed or noted during inspection will be corrected immediately, and corrective measures documented. Appropriate measures may include transfer of waste from leaking container to new container, or replacement of liner or cover. Copies of inspection reports and corrective measures will be maintained onsite, and available for review.

2.5 EMPLOYEE TRAINING

Field staff that will manage hazardous or potentially hazardous waste will comply with 22 CCR 66265.16 through the following actions:

- OSHA 1910.120 Hazardous Waste and Emergency Operations (HAZWOPER) training
- On-the-job training that includes, at a minimum:
  1. Site-specific health and safety plan review – requires each site worker and guest to review and sign the plan
  2. Activity hazard analysis and daily "tailgate" meetings
  3. Project-specific Work Plan review (e.g., this waste management plan)
- Additionally, only staff with DOT hazardous material training (49 CFR 172.704) will perform activities associated with transportation of hazardous waste.

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3.0 PRE-DISPOSAL DOCUMENTATION

3.1 WASTE PROFILE

Waste characterization information will be documented on a waste profile form provided by the designated off-site treatment, disposal, or recycling facility as part of the waste acceptance process. The profile will be reviewed by a regulatory specialist, approved, and signed by the generator (Navy). NOREAS will not sign transportation and disposal documentation. Signed profile(s) will then be submitted to the off-site facility for acceptance.

The profile typically requires that the following information be included (though it may not be limited to only this information):

- Generator information including name, address, contact, and phone number
- Site name including street/mailing address
- Process generating waste
- Source of contamination
- Historical use for area
- Physical state of waste (e.g., solid, liquid, etc.)
- DOT proper shipping name
- Applicable hazardous waste codes and, if characteristically hazardous, associated Underlying Hazardous Constituents (UHCs)

A copy of the approved waste profile or approval letter/e-mail will be received prior to scheduling off-site transportation of the waste.

3.2 LAND DISPOSAL RESTRICTIONS

If a waste is determined to be hazardous, the waste characterization data will be reviewed to identify whether the waste meets the LDR criteria, as required under RCRA (40 CFR 268.7). Specifically, a generator of hazardous wastes must determine if the waste must be treated prior to land disposal (i.e., meets the LDR treatment standards listed in 40 CFR 268.40, 268.45, or 268.48). This determination is then documented on one of two forms:

LDR Notification—Notifies the receiving treatment, storage, and disposal facility (TSDF) that the waste does not meet the applicable LDR treatment standards. This is the more common of the forms, and will be submitted to the off-site treatment/disposal facility; or

LDR Certification—Certifies to the receiving TSDF that the waste meets the applicable LDR treatment standards. This form is applicable for wastes treated onsite to LDR standards, or for listed wastes that already meet a numerical treatment standard.

In general, the off-site hazardous waste TSDF will assist or supply this form for the generator. In complying with the LDR generator requirements for hazardous waste, the following information will be required:

1. Determine the appropriate waste codes that apply to the wastes.
2. Determine which constituents to analyze – i.e., constituents associated with a waste code.
3. For characteristic hazardous wastes, the UHCs must also be identified. The UHCs are any of the 200+ constituents identified in 40 CFR 268.48 (except fluoride, selenium, sulfides, vanadium, and zinc) that can reasonably be expected to be present at the point of generation at a concentration above the constituent-specific universal treatment standard (also specified in 40 CFR 268.40).

The generator (Navy) will sign, and a copy of this form will be included with each load of waste removed from the site along with the manifest.

3.3 SHIPPING DOCUMENTATION AND WASTE MANIFESTS

Prior to off-site disposal of any waste, manifests, LDRs, etc., will be provided by the disposal facility and reviewed by the regulatory specialist and Navy for errors. Only Navy personnel have the authority to sign disposal documents including the profile, waste manifest, LDR, and certain other documents as required by the disposal facility.

Every load of waste material will be manifested with either a nonhazardous or hazardous waste manifest, as appropriate, prior to leaving the site. At a minimum, the manifest form will include the following information:

- Generator information including name, address, contact, phone number, and USEPA ID number
- Transporter information including name, address, contact, phone number, and USEPA ID number
- Designated facility information including name, address, phone number, and USEPA ID number
- Site name including street/mailing address
- DOT proper shipping name (e.g., hazardous waste solid, Not Otherwise Specified (N.O.S.), 9, UN 3077, PG III [D008])
- Type and number of containers

- Quantity of waste (volumetric estimate)
- Waste codes (RCRA and California)
- Task order or job number
- Profile number
- 24-hour emergency phone number

The Navy and the transporter must sign the manifest prior to the load of waste leaving the site. If waste is hazardous, an LDR certification also will be required to accompany the manifest during transportation to the disposal facility. A copy of the “generator’s initial copy” signed by the generator and transporter will be sent to the State of California Department of Toxic Substance Control (DTSC) within 30 days of waste pickup by the Navy.

If any signed hazardous waste manifest from the designated facility is not received within 35 days, the generator must contact the transporter or the designated facility to determine the status of the waste. If the signed hazardous waste manifest has not been received within 45 days, the generator must submit an "Exception Report" to DTSC, as required under 22 CCR 66262.42.

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4.0 WASTE TRANSPORTATION

Requirements under 49 CFR 171 to 178 will apply to all off-site shipments of hazardous materials. The information contained in this section is provided as a general guide. Requirements specific to each hazardous material will be determined in the field. It is the responsibility of a DOT-trained individual to ensure that the requirements of 49 CFR 171 to 178 are met.

4.1 SHIPPING NAME

Material that exhibits one of the nine DOT hazard class characteristics (for example, explosive, flammable, poisonous, or combustible) is regulated under DOT rules for the transportation of hazardous material. If material is suspected to be hazardous, it will be shipped under the suspected hazard class.

Each shipment of a suspected hazardous material will be properly named using the Hazardous Materials Table in 49 CFR 172.101. All determinations will be made by DOT trained personnel.

4.2 PACKAGING, MARKING, AND LABELING

Appropriate packaging must be provided for all wastes as described in 49 CFR. The shipping name, hazard class, ID number, technical names (if applicable), USEPA markings and waste code numbers, and consignee/consignor designations will be marked on packages for shipment (49 CFR 172.301). Once a waste is characterized, reference will be made to the Hazardous Materials Table in 49 CFR 172.101 to determine the appropriate marking and label.

4.3 PLACARDS

Appropriate placards will be determined by DOT-trained personnel. Specific placard descriptions are listed in 49 CFR 172.521. If a placard is required, it will be affixed on each side and each end of the vehicle. The generator (or representative) is responsible for providing the placards if the driver does not have them.

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5.0 TRANSPORTER REQUIREMENTS

Each transportation vehicle and load of waste will be inspected before leaving the site and documented. NOREAS will verify that the driver has the appropriate class of driver's license with appropriate endorsements for the class of vehicle being driven before loading waste onto the vehicle. The quantities of waste leaving the site will be recorded on a transportation and disposal log. A contractor licensed for commercial transportation will transport nonhazardous wastes. In the event that wastes are hazardous, the transporter must be registered with DTSC as a hazardous waste hauler, have a USEPA ID number, and must comply with transportation requirements outlined in 49 CFR 171 to 179 (DOT) and 22 CCR Division 4.5 Chapter 13 (Hazardous Waste Transportation).

The transporter will be responsible for weighing loads at the project site as well as the certified scale at the disposal facility. For each load of material, weight measurements will be obtained for each full and empty container and dump truck. Disposal quantities will be based on the difference of weight measurements between the full and empty container or dump truck. Weights will be recorded on the waste manifest and weight ticket by the disposal facility.

The transporter will observe the following practices when hauling and transporting wastes off-site:

- Minimize impacts to general public traffic.
- Repair road damage caused by construction and/or hauling traffic.
- Line and cover trucks/trailers used for hauling hazardous or regulated waste to prevent spills or releases.
- Decontaminate vehicles prior to reuse, and after hauling contaminated waste.
- Ensure seals on trucks transporting liquids are in good condition.
- Do not combine wastes or materials from other projects with wastes generated during this project.

All personnel involved in off-site disposal activities will follow safety and spill response procedures outlined in the Accident Prevention Plan/Site Safety and Health Plan (APP/SSHP) (Appendix E).

5.1 SPILL REPORTING

In the event of a spill or release of waste, the transporter must immediately notify NOREAS. The following information about the spill will be reported and recorded:

- Type of material (for example, soil, sludge, or water) and contaminant

- Location
- Estimated volume
- Media affected (for example, spilled on concrete pad or soil)
- Time of spill/release
- Final disposition of spilled material

The transporter also will report any spill or release of hazardous waste, as required by 49 CFR 171.15, to the National Response Center (NRC) at (800) 424-8802 or (202) 267-2675.

The transporter will further report in writing, as required by 49 CFR 171.16, to the Director, Office of Hazardous Materials Regulations, Materials Transportation Bureau, Department of Transportation, Washington, C. 20590.

For any spill of hazardous wastewater from a bulk shipment (for example, tanker), the transporter will immediately notify the NRC—(800) 424-8802 or (202) 267-2675—as required in 22 CCR 66263.30.

5.2 SPILL RESPONSE

The transporter will clean up any spill or release of waste (including soil or water) that occurs during transportation, or take such action as may be required or approved by federal, state, or local officials. Spilled waste will be immediately cleaned up, including soils on the outside of the trucks, the truck and/or container, or road surface. Where appropriate, the spilled material will be returned to the original waste container. In any case, the spilled material will be properly contained and dispose

5.3 HAZARDOUS MATERIAL SECURITY PLAN

If it is determined that DOT hazardous materials requiring placard notifications will be generated onsite, a DOT Hazardous Material Security Plan will be prepared as a stand-alone document. The Hazardous Material Security Plan will be prepared in accordance with 49 CFR 172, Subpart H, and will guide the management for security purposes of hazardous materials prior to shipment. Site personnel responsible for hazardous material security will receive both general awareness and plan-specific training. This training will be documented in the project file.

6.0 WASTE DISPOSAL

Hazardous and nonhazardous wastes will be transported off-site for appropriate recycling or disposal. Used PPE will generally be managed and disposed of along with contaminated soil. Other waste streams requiring off site disposal will be sampled and analyzed, as necessary, to ensure that it is properly characterized and profiled and meets the waste acceptance criteria and packaging requirements for the TSDF prior to transport.

Hazardous waste and non-RCRA hazardous wastes will be disposed only at a hazardous waste disposal facility that has been prequalified by NOREAS and is permitted for the disposal of the particular type of hazardous waste generate Wastes from this project must be sent to RCRA Subtitle C or RCRA Subtitle D facilities that meet the requirements of 40 CFR, Part 300.440 (CERCLA Off-Site Rule). The following regional facilities are provided for informational purposes.

6.1 CLASS I FACILITIES (RCRA SUBTITLE C FACILITY; RCRA HAZARDOUS AND NON-RCRA HAZARDOUS WASTES)

- Buttonwillow, Lokern, California (managed by Clean Harbors) – approximate distance is 265 miles from the field site
- Kettleman Hills, Kettleman City, California (managed by Waste Management) – approximate distance is 215 miles
- US Ecology, Beatty, Nevada (managed by American Ecology) – approximate distance is 500 miles

6.2 CLASS II FACILITIES (RCRA SUBTITLE D FACILITY; NONHAZARDOUS WASTES)

- Forward Landfill, Stockton, California (managed by Allied Waste) – approximate distance is 65 miles
- Altamont Landfill, Livermore, California (managed by Waste Management); approximate distance is 50 miles
- Keller Canyon Landfill, Pittsburgh, California (managed by Allied Waste) – approximate distance is 25 miles
- La Paz County Landfill, Parker, Arizona (Managed by Allied Waste) – approximate distance is 600 miles

6.3 CLASS II/III FACILITIES

- Antelope Valley Landfill, Palmdale, California (managed by Waste Management) – approximate distance is 375 miles

- Lancaster Landfill and Hauling, Lancaster, California (managed by Waste Management) – approximate distance is 365 miles
- Simi Valley Landfill, Simi Valley, California (managed by Waste Management) – approximate distance is 380 miles
- Azusa Land Reclamation/TRS (Thermal Remediation Services), Azusa, California (managed by Waste Management) – approximate distance is 400 miles

6.4 CLASS III FACILITIES

- Allied Waste Services San Diego, San Diego, California (managed by Allied Waste) – approximate distance is 500 miles

7.0 DOCUMENTATION AND RECORD KEEPING

Wastes will be inventoried the day of generation at the site using the Transportation and Disposal Log. Wastes will be tracked from day of generation through final disposal using this log. All pages of the field data record log will be signed and dated by the Site Supervisor. In addition, the following information will be recorded in the log:

- Description of waste-generating activities
- Location of waste generation (including depth, if applicable)
- Matrix, waste classification, and volume of waste
- Date and time of generation
- Description of any waste sampling
- Name of person recording information
- Name of field manager at time of generation
- Transporter name
- Disposal facility name

A carbon copy of the initial manifest form for each load will be retained onsite and attached to the Daily Report. All required transportation manifests will be prepared and/or approved by NOREAS and signed by a Navy representative.

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8.0 CHANGES TO THE WASTE MANAGEMENT PLAN

The waste management plan will be updated as changes in site activities or conditions, or changes in applicable regulations occur. Revisions to the waste management plan will be reviewed and approved by the Navy.

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TABLES

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TABLE 2-1
RCRA Hazardous Waste Characteristics

Waste Code	Characteristic	Regulatory Citation (40 CFR)	Criteria (Units are mg/L)			
D001	Ignitability	261.21	Liquid with flashpoint <140°F, etc. (see regulatory text)			
D002	Corrosivity	261.22	pH ≤2 or ≥12.5, able to dissolve metals or burn skin			
D003	Reactivity	261.23	Capable of rapid chemical reaction, detonation, explosion, or generation of toxic fumes			
D004 - D043	Toxicity: Waste contains specific contaminant in leachate extracted from waste using TCLP (SW-846 Method 1311)	261.24	D004-Arsenic ----------	5.0	D023-o-Cresol ----------	200
			D005-Barium----------	100	D024-m-Cresol ----------	200
			D006-Cadmium----------	1.0	D025-p-Cresol ----------	200
			D007-Chromium----------	5.0	D026-Cresol ----------	200
			D008-Lead----------	5.0	D027-1,4Dichlorobenzene -	7.5
			D009-Mercury----------	0.2	D028-1,2 Dichloroethane --	0.5
			D010-Selenium----------	1.0	D029-1,1Dichloroethylene -	0.7
			D011-Silver----------	5.0	D030-2,4Dinitrotoluene -----	0.13
			D012-Endrin ----------	0.02.0	D031-Heptachlor ----------	0.008
			D013-Lindane ----------	10	D032-Hexachlorobenzene -	0.13
			D014-Methoxychlor -----	0.5	D033-Hexachlorobutadiene	0.5
			D015-Toxaphene --------	10	D034-Hexachloroethane	3.0
			D016-2,4-D ----------	1.0	D035-Methyl ethyl ketone --	200
			D017-2,4,5-TP(Silvex) -	0.5	D036-Nitrobenzene ------	2.0
			D018-benzene ----------	0.5	D037-Pentachlorophenol	100
			D019-carbon tetrachloride	0.3	D038-Pyridine ----------	5.0
			D020-Chlordane ---------	100	D039-Tetrachloroethylene -	0.7
			D021-Chlorobenzene --	6.0	D040-Trichloroethylene -	0.5
			D022-Chloroform --------		D041-2,4,5-Trichlorophenol	400
					D042-2,4,6-Trichlorophenol	2.0
					D043-Vinyl chloride ------	0.2

TABLE 2-2
California Hazardous Waste Characteristics

Substance	STLC (mg/L)	TTLC (wet weight; mg/kg)
Antimony and/or antimony compounds	15	500
Arsenic and/or arsenic compounds	5	500
Asbestos		1.0 (as percent)
Barium/barium compounds (not barite)	100	10,000
Beryllium and/or beryllium compounds	0.75	75
Cadmium and/or cadmium compounds	1	100
Chromium (VI) compounds	5	500
Cobalt and/or cobalt compounds	80	80,000
Copper and/or copper compounds	25	2,500
Fluoride salts	180	18,000
Lead and/or lead compounds	5	1,000
Mercury and/or mercury compounds	0.2	20
Molybdenum and/or molybdenum compounds	350	3,500
Nickel and/or nickel compounds	20	2,000
Selenium and/or selenium compounds	1	100
Silver and/or silver compounds	5	500
Thallium and/or thallium compounds	7	700
Vanadium and/or vanadium compounds	24	2,400
Zinc and/or zinc compounds	250	5,000
Aldrin	0.14	1.4
Chlordane	0.25	2.5
DDT, DDE, DDD	0.1	1.0
2,4-Dichlorophenoxyacetic acid	10	100
Dieldrin	0.8	8.0
Dioxin (2,3,7,8-TCDD)	0.001	0.01
Endrin	0.02	0.2
Heptachlor	0.47	4.7
Kepone	2.1	21

TABLE 2-2
California Hazardous Waste Characteristics

Substance	STLC (mg/L)	TTLC (wet weight; mg/kg)
Lead compounds, organic	--	13
Lindane	0.4	4
Methoxychlor	10	100
Mirex	2.1	21
Pentachlorophenol	1.7	17
PCBs	5.0	50
Toxaphene	0.5	5
Trichloroethylene	204	2,040
2,4,5-Trichlorophenoxypropionic acid	1	10

DDT – dichlorodiphenyltrichloroethene
DDE – dichlorodiphenyldichloroethene
DDD – dichlorodiphenyldichloroethane
2,3,7,8-TCDD – 2,3,7,8-tetrachlorodibenzo-p-dioxin

TABLE 2-3
Waste Management Summary Requirements

Waste Types	Characterization Requirements	Containment Requirements	Accumulation Requirements	Transportation Requirements	Disposal Requirements
Contaminated Soil	Stockpiled soil will be sampled in accordance with the UFP-SAP, unless the disposal facility requires a different suite of analysis based on generator knowledge. Samples will be analyzed for total potential contaminants including: VOCs, SVOCs including PAHs, TPH, PCBs, explosives, and total CAM metals analysis including total chromium, herbicides, with STLC or TCLP extractions, as needed.	Contain in maximum 1,500-cy-stockpiles with underlying 20-mil liners.	Excavated soil will be stockpiled on liners and will have appropriate erosion, wind, and stormwater run-on and runoff controls. Stockpiles will be identified as hazardous or nonhazardous waste. If hazardous, the stockpiles will be managed in accordance with the staging pile requirements of 40 CFR Section 264.554. Stockpiles will be covered at the end of each day and when not being actively managed. In addition, stormwater BMPs will be employed.	If material is a hazardous waste, a hazardous waste manifest must be completed, and waste will be transported as a DOT hazardous material. Must use a Cal-EPA permitted transporter. Must also have LDR certifications as necessary. Hazardous and nonhazardous waste manifests to be signed by the Navy. Individuals involved in overseeing or shipping hazardous materials must meet DOT and waste management training requirements.	The waste will be containerized and sent off-site for disposal at an appropriate Class I or II (or out of state Class III) facility, depending on waste classification results.
Construction Debris (clay balls, rock, concrete, asphalt, and oversized material)	Unless the disposal facility requires a different suite of analysis based on generator knowledge, the material will be sampled to determine appropriate management and disposal procedures. Samples will be analyzed for total potential contaminants including: VOCs, SVOCs including PAHs, TPH, PCBs, explosives, total metals analysis including total chromium, and herbicides, with STLC or TCLP, as needed. Debris not having contact with waste or contaminated soil may be characterized as a nonhazardous solid waste.	Hazardous and nonhazardous debris stored in rolloff bins or covered stockpiles.	Decontaminated debris (debris that meets the debris treatment standard and is not contaminated with a listed waste) and nonhazardous debris may be stored in nonhazardous solid waste roll-offs. Hazardous debris that cannot be decontaminated and does not meet the debris treatment standards will be stored in containers and/or bins and will be marked as follows: "HAZARDOUS WASTE" and include the accumulation date, composition and physical state of the waste, hazardous properties, and name and address of generator. Containers and/or bins will be sealed/ covered when not being loaded/unloaded. Containers will be elevated to prevent contact with any ponded precipitation and/or liquids. Wet soil will be placed into secondary containment. Soils must be drained of free liquids prior to shipment.	No special transporter requirements for debris determined to be nonhazardous. Contracted solid waste management company to collect material. If material is a hazardous waste, a hazardous waste manifest must be developed and waste will be transported as a DOT hazardous material. Must use a Cal-EPA permitted transporter. Must also have LDR certifications as necessary. Hazardous and nonhazardous waste manifests to be signed by the Navy. Individuals involved in overseeing or shipping hazardous materials must meet DOT and waste management training requirements.	Nonhazardous debris that does not contain any CERCLA hazardous substances may be disposed of at a Class III facility. Nonhazardous debris containing CERCLA hazardous substances or hazardous debris must be disposed of at a prequalified, Class I or II (or out of state Class III) CERCLA off-site rule facility, depending on characterization.
Wastewater (decontamination water and collected stormwater)	Unless the disposal facility requires a different suite of analysis based on generator knowledge, the material will be sampled to determine appropriate management and disposal procedures. Samples will be run for potential contaminants including VOCs, SVOCs including PAHs, TPH, PCBs, explosives, dioxins/furans, and metals analysis including total chromium.	DOT-approved 55-gallon (bunghole-type) metal drums (1A1) or aboveground tank.	90-day storage limit applies to tanks and containers containing hazardous waste. Containers and tanks will be marked as "HAZARDOUS WASTE" and include the accumulation start date. Containers and tanks will be sealed when not being filled/unloaded. Containers will be elevated to prevent contact with any ponded precipitation and/or liquids. Store in pre-designated hazardous waste storage areas with secondary containment. Storage areas will be inspected weekly.	If material is a hazardous waste, a hazardous waste manifest must be developed and waste will be transported as a DOT hazardous material. Must use a Cal-EPA permitted transporter. Must also have LDR certifications as necessary. Hazardous and nonhazardous waste manifests to be signed by the Navy. Individuals involved in overseeing or shipping hazardous materials must meet DOT and waste management training requirements.	The wastewater will be containerized and sent off-site for disposal at an appropriate disposal facility, depending on waste classification results.
Uncontaminated waste (trash, inert construction debris, calibration canisters, clean polyethylene liners, etc.)	Materials generated during the remedial action project and not contaminated with any CERCLA hazardous substances may be characterized as a nonhazardous solid waste.	Waste to be stored in nonhazardous roll-offs or stockpiles.	Nonhazardous waste to be stored separate from hazardous waste and labeled accordingly to prevent commingling of hazardous and nonhazardous wastes.	No special transporter requirements for wastes determined to be nonhazardous. Contracted solid waste management company to collect material.	Uncontaminated waste to be disposed off-site at an approved Class III solid waste landfill.
Used Oil and Oil Filters	Spent oil filters and oil will be handled as a Specified California Hazardous Waste.	Used oil to be stored in 55-gallon containers.	Used oil to be stored in 55-gallon drums labeled "USED OIL/ HAZARDOUS WASTE" with an accumulation start date, and located within a secondary containment unit. A contracted waste oil recycler shall pick up used oil within 90 days of placement of first drop of oil.	If material is a hazardous waste, a hazardous waste manifest must be developed and waste will be transported as a DOT hazardous material. Must use a Cal-EPA permitted transporter. Must also have LDR certifications as necessary. Hazardous and nonhazardous waste manifests to be signed by the Navy. Individuals involved in overseeing or shipping hazardous materials must meet DOT and waste management training requirements.	Contracted Recycler to pick up and recycle used oil and empty filters.
Used Fuel and Air Filters	Run total analysis and STLC or TCLP, ignitibility test, or use process knowledge to make a waste	Fuel filters to be drained by vendor responsible for vehicle maintenance within a portable secondary	Spent fuel filters and fuel will be containerized in drums and stored within the specified waste accumulation area. All containers will be labeled with	If material is a hazardous waste, a hazardous waste manifest must be developed and waste will be transported as a DOT hazardous material. Must use a	The waste will be containerized and sent off-site for disposal at an appropriate treatment, storage, or disposal facility approved under the CERCLA Off-

TABLE 2-3
Waste Management Summary Requirements

Waste Types	Characterization Requirements	Containment Requirements	Accumulation Requirements	Transportation Requirements	Disposal Requirements
	determination.	containment unit.	the words "Hazardous Waste" and will have an accumulation start date.	Cal-EPA permitted transporter. Must also have LDR certifications as necessary. Hazardous and nonhazardous waste manifests to be signed by the Navy. Individuals involved in overseeing or shipping hazardous materials must meet DOT and waste management training requirements.	Site Rule.
Decontamination Pad Solid Residuals	Unless the disposal facility requires a different suite of analysis based on generator knowledge, the material will be sampled to determine appropriate management and disposal procedures. Samples will be run for total potential contaminants including: VOCs, SVOCs including PAHs, TPH, PCBs, explosives, dioxins/furans, total metals analysis including total chromium, and herbicides, with STLC or TCLP, as needed.	Residues accumulated in sump in designated decontamination area. Routinely removed and placed in containers. Residue must be free of free standing liquid.	Unless predetermined to be hazardous or known to be nonhazardous, containers will be marked as follows: "POTENTIALLY HAZARDOUS WASTE-ANALYSIS PENDING." The storage accumulation clock starts from the date that waste is first put into the container. Containers are to be labeled and stored in predesignated hazardous waste storage area with secondary containment.	If material is a hazardous waste, a hazardous waste manifest must be developed and waste will be transported as a DOT hazardous material. Must use a Cal-EPA permitted transporter. Must also have LDR certifications as necessary. Hazardous and nonhazardous waste manifests to be signed by the Navy. Individuals involved in overseeing or shipping hazardous materials must meet DOT and waste management training requirements.	The waste will be containerized and sent off-site for disposal at an appropriate treatment, storage, or disposal facility approved under the CERCLA Off-Site Rule.
Personal Protective Equipment (PPE)	Use process knowledge to make a waste determination of contaminated PPE. Decontaminated PPE can be managed as a nonhazardous solid waste.	Use double plastic bags at point of generation.	Labeling should consist of a completed commercial hazardous waste label. Containers will be sealed/covered when not being loaded/unloaded. Containers and roll-offs will be elevated to prevent contact with any ponded precipitation and/or liquids. Store in pre-designated hazardous waste storage areas with secondary containment.	If material is a hazardous waste, a hazardous waste manifest must be developed and waste will be transported as a DOT hazardous material. Must use a Cal-EPA permitted transporter. Must also have LDR certifications as necessary. Hazardous waste manifest to be signed by the Navy. Individuals involved in overseeing or shipping hazardous materials must meet DOT and waste management training requirements. Decontaminated PPE may be placed into nonhazardous solid waste roll-off to be picked up by contracted solid waste disposal contractor or disposed of with soils.	Decontaminated PPE may be disposed at an approved Class III solid waste landfill. If a hazardous waste, the PPE will be containerized and sent off-site for disposal at an appropriate treatment, storage, or disposal facility approved under the CERCLA Off-Site Rule.
Liner/sheeting	Liners used for containing hazardous soil will be presumed to be hazardous.	Liners will be stored in roll-offs or DOT 55- gallon drums or may be disposed of with soils.	Labeling should consist of a completed commercial hazardous waste label. Roll-offs will be marked as "HAZARDOUS WASTE" and include the accumulation date, composition and physical state of the waste, hazardous properties, and name and address of generator. Roll-offs will be sealed/ covered when not being loaded/unloaded. Roll-offs will be elevated to prevent contact with any ponded precipitation and/or liquids.	If material is a hazardous waste, a hazardous waste manifest must be developed and waste will be transported as a DOT hazardous material. Must use a Cal-EPA permitted transporter. Must also have LDR certifications as necessary. Hazardous and nonhazardous waste manifests to be signed by the Navy. Individuals involved in overseeing or shipping hazardous materials must meet DOT and waste management training requirements.	The waste will be containerized or included with soil and sent off-site for disposal at an appropriate treatment, storage, or disposal facility approved under the CERCLA Off-Site Rule.
Miscellaneous Debris Potentially Contaminated with Radioactive Isotopes	Debris suspected to contain radioactive material will be handled per the Radiological Materials Management Plan (RMMP) prepared under separate cover.	Segregate potentially contaminated debris from other construction debris.	Debris suspected to contain radioactive material will be handled per the RACP (see Appendix F).	Individuals involved in overseeing or shipping hazardous materials must meet DOT and waste management training requirements. Debris suspected to contain radioactive material will be transported and managed according to DOT and other appropriate and applicable requirements of radioactive material transport.	Use of any disposal facility for radioactive wastes is subject to approval by the DoD LLRW Executive Agency (Army). If radioactive waste is encountered, disposal will be arranged by the Navy.
Unidentified Waste Streams (i.e. waste streams that may be generated during site activities but have yet to be identified)	Unless a waste determination (e.g., RCRA hazardous, non-RCRA hazardous or nonhazardous) can be made based on generator knowledge, the material will be sampled to determine appropriate management and disposal procedures. Samples will be run for total potential contaminants including VOCs, SVOCs including PAHs, TPH, total metals analysis including total chromium, and herbicides, with STLC or TCLP, as needed.	DOT-approved 55-gallon metal drums (1A1 or 1A2) depending on whether a liquid or solid.	If hazardous waste, the words "hazardous waste – pending analysis" and the accumulation start date should be printed on the drum. Containers will be sealed/covered when not being managed. Containers will be elevated to prevent contact with any ponded precipitation and/or liquids. If a hazardous waste, the storage accumulation clock starts from the date that waste is first put into the container destined for off-site disposal (90-day	If material is a hazardous waste, a hazardous waste manifest must be developed and waste will be transported as a DOT hazardous material. Must use a Cal-EPA permitted transporter. Must also have LDR certifications as necessary. Hazardous and nonhazardous waste manifests to be signed by the Navy. Individuals involved in overseeing or shipping hazardous materials must meet DOT and waste	The waste will be containerized and sent off-site for disposal at an appropriate treatment, storage, or disposal facility approved under the CERCLA Off-Site Rule.

TABLE 2-3
Waste Management Summary Requirements

Waste Types	Characterization Requirements	Containment Requirements	Accumulation Requirements	Transportation Requirements	Disposal Requirements
			maximum allowed). Store in predesignated hazardous waste storage areas with secondary containment.	management training requirements.	

Notes:

Cal-EPA – California Environmental Protection Agency
CAM – California Assessment Metals
cy – cubic yard(s)
DOT – U.S. Department of Transportation
LDR – Land Disposal Restriction
LLRW – low level radioactive waste
PAH – polycyclic aromatic hydrocarbon
RMMP – Radiological Materials Management Plan
SAP – Uniform Federal Policy Sampling and Analysis Plan
STLC – soluble threshold limit concentration
SVOC – semivolatile organic compound
TCLP – toxicity characteristic leaching procedure
VOC – volatile organic compound

APPENDIX D

FIELD FORMS

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NOREAS
Environmental Engineering and Science

SUBSURFACE EXPLORATION LOG

BORING/WELL ID NUMBER:

Page __ of __

CLIENT:
PROJECT NUMBER:
LOCATION:

GEOLOGIST:
DATE DRILLED:
DRILLING COMPANY:

TOTAL DEPTH:
DRILLING METHOD:
SAMPLE METHOD:

Depth (ft bgs)		Time (24 hr)	FID/PID (ppm)		GEOLOGIC DESCRIPTION														USCS Soil Class. Symbol	Lithologic Contact (ft bgs)
			Soil Sample / Soil Cuttings	Breathing Zone	% gravel	% sand	% non-plastic fines	% plastic fines	Grading	Lithologic Name/Soil Type	Color	Moisture	Density	Consistency	Plasticity	Angularity	Max. grain size	Additonal Observations		
Notes:					> 1/4 inch	visible -1/4 in.	visible with hand lens	not visible	poorly vs. well	See USCS flow Charts. Describe sand and gravel grading, ie, fine to coarse grained	Use Munsell color chart if available	Dry Moist Wet	Course: v. loose loose md. dense dense v. dense	Fines: v. soft soft md. Stiff v.stiff hard	high med low non	A Sa Sr R	in inches	odor, staining, minerology, stucture, cementation, other distinctive charateristics		

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NOREAS
Environmental Engineering and Science

LOW-FLOW PURGING AND SAMPLING DATA SHEET

Project Name: _____ Well Number: _____
Project Number: _____ Equipment: _____
Date: _____ Sample ID: _____ Time: _____
Site Personnel: _____ Duplicate ID: _____ Time: _____

Reference: Top of Casing	Before	After
Depth to Water (ft)		
Depth of Well (ft)		
Depth to Top of Screen (ft)		
Screen Length (ft)		
Pump Depth (ft)		
Pump Rate (mL/min)		
Sample Pump Rate (mL/min)		
System Volume (mL)		

Total Volume Purged (mL): _____

System Volume (mL) = (2.4*H)+470
where
2.4mL/ft = tubing volume per foot (1/8" I.D.)
H = length of tubing in feet
470 mL = Bladder volume + Flowthru cell volume

Time	pH	Specific Conductivity (µS/cm)	Dissolved Oxygen (mg/L)	Temp. (^oC)	ORP (mV)	Turbidity (NTU)	Depth to Water (ft)	Cum. Volume (mL)	Comments
Stability:	± 0.1 units	± 3 %	± 0.3 mg/L	± 1^oC	± 20 mV	± 10 %			

Field Tests:

Note 1: Stabilization criteria may change based on project-specific requirements.

Note 2: Samples were collected directly from pump unless otherwise noted.

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APPENDIX E

RESPONSES TO AGENCY COMMENTS

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Responses to Agency Comments

Draft Remedial Investigation Work Plan for the South Shore Area,
Former Mare Island Naval Shipyard, Vallejo, California
Dated May 2014

The subject report has been made final based on two iterations of regulatory review and comment resolution. The following are responses to agency comments (RTCs) documenting the agency comments and Navy responses. The first set of RTCs (pages 1-80) includes responses to California Department of Toxic Substances Control (DTSC), San Francisco Bay Regional Water Quality Control Board (Water Board), and California Department of Fish and Wildlife (CDFW) comments received between July 8, 2014 and September 4, 2015 for the May 2014 Draft Remedial Action Work Plan. The second set (pages 81-102) includes responses to follow-on comments received from the DTSC, Water Board, and CDFW between April 24, 2015 and May 8, 2015. The RTCs were prepared by NOREAS, Inc.

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DRAFT REMEDIAL INVESTIGATION WORK PLAN, SOUTH SHORE AREA

FORMER MARE ISLAND NAVAL SHIPYARD
VALLEJO, CALIFORNIA

DATED MAY 2014

DCN: NRS-4812-0000-0008

Comments Provided By:	Responses Provided By:
Eric M. Sciullo, Ph.D. Staff Toxicologist Human and Ecological Risk Office (HERO) Department of Toxic Substances Date Comments Received: September 4, 2014	NOREAS, Inc.

General Comments

HERO General Comment 1. IR05 Shoreline. The Report describes the identification of a number of munitions and non-munitions items along the northeastern shoreline areas of IR05, directly adjacent to the South Shore Area. These items include two primer areas, large shell casings, and a number of partially buried drums. In addition a large mass of metallic debris, munitions, and concrete was found along the shoreline. The Report states that a response to the identification of these particular items has not been determined, these areas are not planned for investigation under this RI and it is anticipated that they will be addressed under a separate investigation. HERO feels a response to these items is warranted and justified due to their incorporation in the South Shore Area boundary and hence a part of the current RI. If these items will be handled under a separate future investigation this should be clearly described.	**Response.** The items located along the IR05 shoreline (now incorporated into the new SSA site boundary) will be addressed during a future investigation, the details of which are not available at this time. Section 2.4.7 (second paragraph of Page 2-17) includes the following statement: *"At the time of this RI Work Plan, the details of the response to the identification of these particular items have not been determined. As such, these areas are not planned for investigation under the SSA RI and it is anticipated that they will be addressed under a separate removal action. The boundary for the SSA now does, however, incorporate this shoreline area. While this area will not be included as part of this investigation, any information related to this area will be carried through and summarized in CERCLA documents for the SSA, including the RI Report."*

HERO General Comment 2. Oven/Primer Pit Areas. The Report states on page 4-15 that 20% of the soil samples collected from this area will be analyzed for dioxins/furans. Five boring locations are currently planned with soil samples at three distinct depths. What is the rationale for limiting dioxin/furan analysis to 20% of the planned 15 samples? Which 20% are planned for sampling, three out of five of the surface samples? HERO recommends sampling for dioxin/furans for all samples in this area.	**Response.** 100% sampling for dioxins and furans is not warranted at the site. Analysis for dioxins/furans is planned for the Oven/Primer Pit area due to historical burning of debris and trash in that location. However, because the debris and affected soil at the Oven/Primer Pit location was excavated during a previous removal action, burn material is not anticipated. Dioxins/furans were also analyzed in soil samples from one location (with drums) during the NTCRA but were not found in concentrations above screening criteria (ISR-JV, 2014). The selection of samples for dioxins/furans analysis will be based on observations in the field (visual evidence for charred materials in soil). If no evidence for burnt material is observed, samples will be selected to represent each of the three different sample depth intervals with a contingency to analyze additional samples if dioxins/furans are detected in the original samples. The last paragraph of Section 4.1.4 has been modified to describe this contingency as follows: *"In addition to the analytes described above, selected samples from the Oven/Primer Pit areas will also be analyzed for dioxins/furans given that visual evidence of discolored soils indicated that debris was once disposed by burning in these locations (Section 2.4.4). Although the affected (discolored) soil and debris within the pits was ultimately excavated and removed from the site (Roy F. Weston, 2003), a minimum of 20% of the soil samples collected from this area will be analyzed for dioxins/furans.* *The selection of samples for dioxins/furans analysis will be based on observations of soil conditions at the time of sampling. Specifically, samples where visual evidence of burnt material (discoloration) is observed will be analyzed for dioxins/furans. There are 15 soil sample locations planned for the SSA (with samples taken at 3 depths). In the event that evidence for burnt material is not observed, at least one soil sample will be selected from each of the three discrete sampling depths to provide information across the range of depths planned for the investigation."*

HERO General Comment 2. (Continued).	**Response (continued).** *"As a contingency, all of the soil samples from the Oven/Primer Pit Areas will also be archived by the analytical laboratory pending the results of the dioxin/furans analysis. If dioxins/furan are detected in the original 20% of the sample set from this area, additional analysis for dioxins/furans will be conducted on the remaining archived soil samples from the Oven/Primer Pit Area."*
HERO General Comment 3. Proposed Groundwater Monitoring Wells. HERO recommends the installation of an additional groundwater monitoring well near grids AA009/AA010 due to the uncertain nature of groundwater flow at the Site and the presence of buried drums in the vicinity.	**Response.** Well SSA-MW-06 was generally intended to provide coverage for the western portion of the SSA, and was not associated with a specific site feature. This well will be moved approximately 300 feet west to provide coverage of that location. Figures 4-1 and 4-7 have been revised to depict the new location of SSA-MW-06.
HERO General Comment 4. Toxicity Criteria. Section 7.2 describes the toxicity assessment approach toward the human health risk assessment (HHRA). The Office of Environmental Health Hazard Assessment (OEHHA) should be given top hierarchy for toxicity source criteria when conducting a HHRA for military facilities in California. In addition, the Regional Water Quality Control Board Environmental Screening Levels should be listed here.	**Response**. As a federal facility regulated by a federal oversight agency, the HHRA approach will give top priority to the federal (U.S. EPA) toxicity criteria. Where applicable, OEHHA and Water Board criteria may be used. As discussed during the October 30, 2014 teleconference, two sets of risk calculations will be provided in the RI Report, one set using federal EPA toxicity criteria, and the other using the State of California (DTSC) toxicity criteria. This approach is consistent with what has been done previously for the RIs completed at adjacent IA F1 and IR05 sites. Where applicable, OEHHA and Water Board criteria may be discussed in the HHRA Uncertainty Section. Please note that DTSC toxicity criteria include OEHHA-recommended criteria.

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HERO General Comment 5. Chemical of Potential Concern (COPCs) Selection. In general, HERO does not allow chemicals to be screened out of a risk assessment and all detected compounds should be included. Chemicals cannot be dropped out of a risk assessment solely based on presence below screening levels. The development of modern computerized spreadsheets facilitates carrying a larger number of chemicals through a risk assessment. Exceptions can be made for laboratory chemical artifacts as described in USEPA's Risk Assessment Guidance for Superfund Part A (RAGS) (http://www.epa.gov/oswer/riskassessment/ragsa/pdf/rags-vol1-pta_complete.pdf) and certain essential nutrients (sodium, potassium, calcium and magnesium only). Additionally, in some instances chemicals present at very low concentrations and detection frequency may be dropped after consultation with the HERO toxicologist. Factors needing to be weighed in dropping chemicals include the historical use of the chemical onsite, the frequency of detection, detection limits, chemical toxicity, and concentration detected, potential for bioaccumulation, spatial distribution, and essential nutrient status.	**Response.** Comment noted. Section 7.4.1 has been revised in the Work Plan to reflect the recommendations of HERO. It now reads: *"Consistent with the Screening Level HHRA, the following screening levels will be used to determine whether or not a chemical is retained for the BHHRA.* • *Applicable USEPA RSLs based on residential use for CERCLA constituents and site-specific Tier 2 SLs for TPH constituents, for soil and groundwater.* *The screening levels will also be used to select analytical methods with detection and reporting limits low enough to support the HHRA evaluation. However, the screening levels will not be used to eliminate COPCs as all detected compounds will be carried through the HHRA."*
HERO General Comment 6. Background Evaluations. The report indicates that a background evaluation may be conducted in the future evaluation of the Site. HERO recommends that any background studies conducted at the Site be submitted for agency review prior to performing the HHRA.	**Response.** No additional background studies are planned or anticipated at this time. Text related to this has been removed from the document. Section 7.4.2 has been abbreviated to indicate that existing background metals data will be used as part of the BHHRA.

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HERO General Comment 7. Exposure Assessment. A potentially complete exposure pathway exists for the construction worker exposed to pooled air while in a trench. If volatile organic chemicals (VOCs) are discovered in groundwater, a trench scenario should be included in the HHRA in order to evaluate this pathway. Please see the Virginia Department of Environmental Quality's approach to conducting a trench scenario (Section 2.4.3.2). http://www.deg.virginia.gov/Programs/LandProtectionRevitalization/RemediationProgramNoluntarvRemediationProgramNRPRiskAssessmentGuidance/Guidance.aspx	**Response.** As described in Section 7.5.2,the HHRA will consider the construction worker exposure scenario using similar risk evaluation/calculation methods used for the HHRA at the IA F1 area (located adjacent to the SSA), however this analysis will not include the use of the Virginia trench model.

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HERO General Comment 8. HHRA. Section 7.6.2 details the presentation of risk and hazards for the HHRA. Risks and hazards for the Site should be presented both incrementally and cumulatively across all investigated media. These summaries should be presented in the main body of the Report.	**Response.** The intent has always been to evaluate both incremental and cumulative risks and hazards and summarize the results in the main body of the BHHRA report. As such, Section 7.6.2 of the Work Plan has been modified to include the following statements: *"A summary of the risks and hazards, both incrementally and cumulatively, for the site across all investigated media and exposure scenarios will be presented in the BHHRA.* *All calculations of carcinogenic risk and non-carcinogenic hazard will be presented as an appendix to the BHHRA. These tables will identify exposure scenario, COPC specific risks and hazards, and total risks and hazards."*
HERO General Comment 9. Exposure Factors. In general, HERO does not concur with the proposed exposure factors presented in Table 7-1. For consistency purposes across military facilities in California, only exposure factors listed in DTSC HHRA Note 1 should be utilized in risk and hazard calculations. Any substitutions must be discussed with and approved by the HERO toxicologist assigned to the Site. Allowances will be made for recently updated exposure factors by the US EPA. http://www.dtsc.ca.gov/AssessingRisklupload/HHRA Note1 .pdf	**Response.** As a federal facility being addressed under the U.S Department of the Navy IR Program, with the Navy as lead agency, federal (EPA) exposure criteria will be given priority over State of California (DTSC) criteria. As discussed during the October 30, 2014 teleconference, two sets of risk calculations will be provided in the RI Report, one set using federal EPA exposure factors, and the other using the State of California (DTSC) exposure factors. This approach is consistent with what has been done previously for the RIs completed at adjacent IA F1 and IR05 sites. No changes to Table 7-1 are planned.

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Comments Provided By:	Responses Provided By:
J. Michael Eichelberger, Ph.D. Staff Toxicologist Ecological Risk Assessment Section (ERAS) Human and Ecological Risk Office (HERO) Department of Toxic Substances Date Comments Received: July 8, 2014	NOREAS, Inc.

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ERAS General Comment 1. The report includes a sampling and analysis plan as well as a proposed human health and ecological risk assessment 'methodology'. The methodology sections do not represent a complete work plan for conducting these risk assessments. For example, the parameters for calculating the average daily dose for ecological receptors are not presented. Therefore, ERAS will need to see a risk assessment work plan which includes this information, along with a designation of habitat boundaries and Areas of Concern, prior to submittal of a risk assessment.	**Response.** The human health and ecological risk assessment methods provided in the RI Work Plan are intended to provide basic information with regard to the overall approaches that will be used to conduct these assessments. As discussed during the teleconference call on October 30, 2014, additional details on the SLERA approach will likely be discussed with Stakeholders once the RI chemical data are available. In the meantime, Section 8.0 of the RI WP has been modified to provide additional information regarding the ERA approach. Examples of dose parameters and dose equation are now provided in Table 8-8; examples of bioaccumulation models for different receptors are provided in Tables 8-2 through 8-7; and examples of biota soil accumulation factors (BASF) are provided in Table 8-5. The following dose equation, Eq. 4-23 from the US EPA Wildlife Exposure Factors Handbook (1993), will be used: $$ADD_{pot} = \left(\left[\sum_{k=1}^{m} \left(\frac{C_k \times FS \times IR_{total}\,(dry\ weight) \times FR_k}{BW} \right) \right] \right)$$ Where: ADD_{pot} = Potential average daily dose (e.g. mg/day) C_k = Ave contaminant concentration in soils in the kth foraging area (e.g. mg/kg dry weight) FS = Fraction of soil in diet (as percentage of diet on a dry-weight basis divided by 100; unitless) IR_{total} = Food ingestion rate on a dry-weight basis (e.g., in kg/day). Nagy's (2001) equations for estimating FI rates on a dry-weight basis can be used to estimate a value for this factor. If the equations for estimating FI rates are on a wet-weight basis are used, conversion to ingestion on dry-weight basis would be necessary. FR_k = Fraction of total food intake from the kth foraging area (unitless). This is also referred to as the Area Use Factor (site area/wildlife species home range), as suggested in Eq. 4-8 (Wildlife Dose Equations for Dietary Exposure [EPA, 1993]) k = counter m = Total number of foraging areas BW = Body weight (e.g., in kg)

ERAS General Comment 1 (continued).	**Response (continued).** A copy of the revised Section 8.0, including Tables 8-1 through 8-8, is provided as an Attachment to these RTCs. Complete descriptions of how the human health and ecological risk assessments are ultimately conducted will be provided in the RI Report.

ERAS General Comment 2. Contrary to the assumption in the report that ecological concerns are addressed by sampling solely the top 2 feet of soil, sampling depths need to address ecological receptor exposure pathways and the range of chemical concentrations in the soil. Most of the proposed sampling outlined in Appendix A of the Sampling and Analysis Report, Worksheet #18 does not propose soil sampling in the 2 foot soil profile interval. This should be included to ensure adequate sampling coverage protective of ecological receptors. Please see Specific Comments 3 and 4 below.	**Response.** Although providing data of sufficient quality for the proper assessment of ecological risks is a key objective for this RI, the overall sampling approach must consider other key objectives that include an overall evaluation of the nature and extent of potential contaminant impacts. As such, the sampling approach must not only consider the potential exposure pathways for ecological receptors, but it must also account for the source of potential contaminants encountered. In particular, the sampling depths must account for buried features such as USTs or pipelines. In these cases, samples must be collected from depths beneath the buried feature (typically 5 to 10 feet bgs) to properly evaluate potential impacts. Furthermore, the sampling approach for this RI has to remain flexible enough to allow for adjustment of final sampling depths to correspond with observations of potential impact that may be observed in the field at the time of the investigation. The sampling approach planned for this RI is consistent with that used at the recently completed RI at Investigation Area (IA) F1 where the ERA for that RI considered the results from the 0-2 feet bgs depth interval to screen for potential risks to plants, invertebrates, birds, and non-burrowing mammals. Data from the 0 to 6 feet bgs interval were used to evaluate the potential ingestion risks to burrowing mammals in the upland areas. As discussed with DTSC and ERAS in the 10/30/14 meeting, the current sampling approach proposed for the SSA will provide for a near surface sample collected at 0.5 feet bgs at all locations. The Navy agreed to preferentially sample the 0-6 inch interval. These samples will be used for the ecological surface risk assessment at 0-2 feet and the HHRA for surface soils which covers 0-0.5 foot bgs. Samples from this depth interval will be collected at all locations and will not be adjusted in the field based on field observations like many of the deeper samples might. These results will be used to evaluate the risks to plants, invertebrates, and non-burrowing mammals and birds.

ERAS General Comment 2 (Continued).	**Response (continued).** The mid-depth sample that is currently planned for a default depth of 5 feet bgs will provide data for the evaluation of risks to burrowing mammals and burrow-dwelling birds, but may be adjusted based on field observations. Regardless of field observations, the mid-depth sample will be collected at some depth above 6 feet bgs, most likely between 2 and 6 feet bgs. Based on these considerations, no adjustment to the sampling approach is planned at this time.
ERAS General Comment 3. Since the report introduces ecological risk assessment methodology, and sampling is proposed to support the risk assessment process, the report should introduce and discuss future land use for the site. Future land use will dictate sampling needs for evaluation of ecological risk.	**Response.** A discussion of future land use at the SSA is provided in Section 3.6.4 of the Site Conceptual Model (Section 3.6).
Specific Comments	
ERAS Specific Comment 1. Pdf page 17 of 186, Section 1.0 Introduction. The report states the *"SSA consists of approximately 38uplands [sic], wetlands, and tidal mudflat areas located on the southern end of the former MINS'.* The report should identify these 38 areas on a figure and indicate if these 38 areas will be treated as separate sampling areas.	**Response.** The statement was intended to describe that the SSA consists of "approximately 38 acres of upland, wetland, and tidal mudflat areas….," and has been modified as such to provide clarification.

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ERAS Specific Comment 2. Pdf page 18 of 186, Section 1.1, Purpose and Objectives. The report states *'The objective* of *this RI Work plan* is *to describe the procedures, methods, and approach used to investigate the nature and extent* of *potential contaminants at the SSA'.* Please explain how inclusion of a Human Health and Ecological Risk Assessment Work Plan in the report satisfies the stated goal to investigate the nature and extent of potential contaminants at the SSA. The logical process is to identify the nature and extent, and then issue a report containing the risk assessment work plans.	**Response.** The full sentence on page 1-2 (PDF page 18 of 186) has been updated to read: *"The objective for this RI Work Plan is to describe the procedures, methods, and approach used to investigate the nature and extent of potential contaminants at the SSA to ensure that data of sufficient quality and quantity are collected to evaluate current site conditions, conduct baseline human health and ecological risk assessments, and evaluate the potential need for further action to protect human health and the environment."* As noted in the response to HERO General Comment #1 above, the sections describing the Human Health and Ecological Health risk assessments are intended to provide some description of the general approaches that will be used for these evaluations. Modifications to these approaches may be warranted based on the analytical results of the investigation. Detailed descriptions of how the human health and ecological risk assessments are ultimately conducted will be provided in the RI Report rather than a separate Work Plan. Please see response to ERAS General Comment #1.
ERAS Specific Comment 3. Pdf page 19 of 186, Section 1.2, Scope of Work. The report states ' ...*soil samples will be collected from various depths at* a *total* of 46 *locations throughout the SSA'.* Please reference Figure 4-1 in the text as a reference for the sample locations within the SSA.	**Response.** The statement in Section 1.2 is intended to provide a general description of the level of effort involved in the RI. Given the level of detail associated with Figure 4-1, reference to that particular figure is deferred until later in the document, where the details of the scope are described.

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ERAS Specific Comment 4. Pdf page 104 of 186, Section 8.0 Ecological Risk Assessment Methodology, Step 3A. The report is not correct in stating that the CalEPA/DTSC soil interval of interest for ecological risk assessment is 0 to 2 feet below ground surface (bgs). The soil interval of concern is dependent on the receptor, the soil depth interval where exposure occurs and coincidentally the distribution of contamination within the soil profile. Generally speaking DTSC/ERAS considers soils of interest down to 6 feet bgs unless the soil profile is less than 6 feet or groundwater is encountered. Please see DTSC guidance at http://www.dtsc.ca.gov/AssessingRisk/upload/econote1.pdf. ERAS generally prefers to see soil sampling from three depths including 0-0.5 feet bgs, 2-3 feet bgs, and 5-6 feet bgs.	**Response.** Please refer to the response to ERAS General Comment #2 above. The sampling approach must consider all of the RI objectives to properly evaluate the nature and extent of the potential contaminant impacts to all potential receptors. It is acknowledged that CalEPA/DTSC's soil interval of interest for ecological risk assessment is as deep as 6 ft. bgs. In the 10/30/14 call with DTSC the Navy clarified that samples would be taken from depths 0-0.5 ft bgs and between 2-6ft bgs as warranted by site conditions including depth to groundwater and receptors on site.

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ERAS Specific Comment 5. Pdf page 105 of 186, Section 8.2 Ecological Conceptual Site Model. This section should include a discussion of future land use of the SSA as a whole and the 38 specific areas individually. If all of the SSA is to be left as open space suitable for habitat that should be stated, in which case a description of the end use for the 38 specific areas will be unnecessary. If certain areas are slated for immediate redevelopment other than habitat, a risk assessment for ecological receptors for that portion of the site is not necessary. If redevelopment is to be delayed for a period for example of 6 months or longer, than the site is considered an attractive nuisance posing a hazard to higher trophic levels in the interim prior to redevelopment. In this case an abbreviated risk assessment is recommended to evaluate potential risk to birds and mammals.	**Response.** Regarding the "38 specific areas" please see the response to ERAS Specific Comment #1. Reference to "38 specific areas" was a typographical error. The author meant to write "38 acres." The first paragraph of Section 8.2 has been modified to include the following statement: "*The area comprising the SSA remains the property of the U.S. Navy and is not currently in use. However, future plans for the site include transfer of the property from Navy control. Based on the Mare Island Specific Plan (City of Vallejo, 2008), the current reuse planned for the SSA includes redevelopment as a recreational area (park) and a wildlife preserve (Weston, 2011).*" The redevelopment of the area is not expected to take place for several years as sufficient time is necessary to investigate and address any environmental issues at the site. It is anticipated that the site will remain under Navy control until such time as the investigation and restoration activities are completed. Additionally, this area is being maintained as industrial until it is transferred. Mowing related to fire control is conducted as needed around buildings and along the roads at the site. As noted in response to General Comment #1, potential risks to birds and mammals will be included in the SLERA. An abbreviated risk assessment is not required because a SLERA will be completed. Once the RI analytical data become available, the Navy will work with BCT to ensure the CERCLA process is completed in a timely manner.

ERAS Specific Comment 6. Pdf page 105 of 186, Section 8.2, Ecological Conceptual Site Model. The California vole *(microtus californicus)* is not a deep burrowing species; in fact its burrows are shallow. A better choice for a deep burrowing mammal would be the California ground squirrel *(Spermophilus beecheyi)* for which the DTSC burrowing depth is actually based upon. The report will need to clarify which guild each of the list ecological receptors represents. For example, for the terrestrial habitat the northern harrier represents a carnivorous bird and the ornate shrew represents an invertivorous mammal. A designated species for each guild should be represented. The guilds that should be included are; generic plants, generic invertebrates, herbivorous birds, invertiverous birds, carnivorous birds, herbivorous mammals. Invertiverous mammals and carnivorous mammals. ERAS sees no need to evaluate receptors with omnivorous diets.	**Response.** The California ground squirrel is proposed as a mammalian burrowing species for the SLERA. Although this species has not been documented at the SSA (H.T.Harvey & Associates, 2011[1]), it may serve as a surrogate for other burrowing species such as the eastern grey squirrel that may be found in Coast Live Oak Forest that occurs at the site. As discussed in the October 30, 2014 teleconference, the SLERA will include up to seven wildlife receptors, as recommended, plus generic plants and soil invertebrates. The text of Section 8.2 of the RI WP (provided as an Attachment to these RTCs) has been modified to include this information. The final list of ecological receptors will be determined once the RI data become available.

[1] H.T.Harvey & Associates, 2011, Mare Island Production Manufacturing Area & South Shore Area Existing Conditions & Special –Status Species, February.

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ERAS Specific Comment 7. Pdf page 159 of 186, Table 8-1 Summary of Example Toxicity Reference Values for Soil. ERAS cannot locate a copy of the EFA West report. ERAS needs the report to verify the TRVs listed in Table 8-1. Please forward a copy of 'Engineering Field Activity, West (EFA West), 1998, Development of Toxicity Reference Values for Conducting Ecological Risk Assessments at Naval Facilities in California. Interim Final, EFA West, Naval Facilities Engineering Command, United States Navy, San Bruno, California' for ERAS to review.	**Response.** Table 8-1 was originally intended to provide examples of TRVs that have been used for previous ERAs on other federal facilities. However, example TRVs have been removed from the Work Plan, in lieu of the following hierarchy of TRVs that has been added to Section 8.4 of the text (a copy of the modified text has been provided as an Attachment to these RTCs): Potential TRV sources for wildlife toxicity will include the following,: • TRVs used for EPA Ecological Soil Screening Levels (EPA, online; EPA, 2007); • TRVs recommended by EPA Region 9 Biological Technical Assistance Group (2002, 2009), and DTSC (2000) Eco Note 4; • Oak Ridge National Laboratory (ORNL) databases of screening benchmarks for ecological risk assessment, that include Sample et al., (1996); • Los Alamos National Laboratory database (2014). TRVs for wildlife inhalation exposure will be based on values that have been used to evaluate risk for the Santa Susana Field Laboratory (MWH and CH2M-Hill, 2011). The document referenced in the Comment "EFA West 1998" was initially prepared under a Navy contract for development of TRVs for use in ERAs in the San Francisco Bay area, and was developed in consultation with EPA Region 9 BTAG. As stated in CH2M-Hill (2000[2]), these TRVs have been recommended by both Cal/EPA DTSC and EPA Region 9 for use in ERAs under their jurisdiction

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ERAS Specific Comment 8. Pdf page 175 of 186, Figure 2-8, Former Mare Island Naval Shipyard Vallejo California Remedial Investigation Work Plan Historical Soil Sampling Locations at SSA. Of the four color-coded sample locations, ERAS can only locate the green labeled samples. Please correct the figure with the addition of the other color-coded samples or include an annotation describing why the remaining three color-coded sample locations are not shown on the figure.	**Response.** Figure 2-8 has been corrected.
ERAS Specific Comment 9. Pdf page 180 of 186, Figure 4-5, Former Mare Island Naval Shipyard Vallejo, California Remedial Investigation Work Plan Proposed Soil Sampling Locations - Oven/Primer Pit Areas. Five soil boring locations are identified associated with the Oven/Primer Pit location, including three within the southern wetland of SSA. No other samples are proposed for the wetland areas. Please provide an explanation of why sampling is not necessary in the remainder of the wetlands.	**Response.** The three sampling locations noted are planned based on their proximity to the former Oven/Primer Pits. Apart from this area, no other activities involving the use, storage, or disposal of hazardous materials were conducted in the wetland areas; therefore investigation of the remainder of the wetlands is not warranted based on the current conceptual site model.
ERAS Specific Comment 10. Appendix A, Sampling and Analysis Plan Remedial Investigation South Shore Area, SAP Worksheet #15-1-Reference Limits and Evaluation Table (WATER). As with Specific Comment 11 below, the San Francisco Regional Water Quality Control Board (SF RWQCB) (see reference in Specific Comment 11) values may not be protective of aquatic life. For example, the National Recommended Ambient Water Quality Criteria Criterion Continuous Concentration (CCC) for arsenic (saltwater) is 0.036 mg/L whereas the SF RWQCB screening level is shown as 1.0 mg/L. For most organic molecules not listed under the National Ambient Water Quality Criteria, ECOSAR contained in EpiSuite (http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm) can be used to estimate a chronic screening level protective for aquatic organisms.	**Response.** The Navy has updated Worksheet 15.1 and 15.2 screening criteria to reflect the comparison criteria references in the IA F1 RI (Appendix A-ChaduxTt, 2012).

ERAS Specific Comment 11. Appendix A, Sampling and Analysis Plan Remedial Investigation South Shore Area, SAP Worksheet #15.2-Reference Limits and Evaluation Table (Soil). The table reports soil screening levels from the U.S. EPA RSL, Residential Soil Supporting Table, November 2013 (http://www.epa.gov/region9/superfund/prg/rsl-table.html), however these screening levels are not protective of ecological receptors. For example, the RSL screening criteria for copper is 310 mg/kg whereas the EcoSSL avian screening level is 28 mg/kg. Soil screening levels should be proposed for ecological receptors and the lower of the human health or ecological soil screening level where available, should be used to assist in determining the extent of sampling. Reporting limits should not exceed the screening levels. If this cannot be achieved, the report needs to discuss why the reporting limits exceed the screening levels and alternative methods need to be explored that may achieve data quality objectives that specify that the reporting limit should not exceed the screening level.	**Response.** As noted above, the screening criteria used for the SSA will be consistent with what were applied to the IA F1 area RI, which include the use of ambient values for metals in soil and groundwater that have been previously established for Mare Island. The concern for achieving reporting limits below the screening levels, when practical, is acknowledged. The analytical plan has been updated to include modified methods (such as use of EPA 6020 for metals), where practical, to achieve the lowest detection and reporting limits. In some cases it may not be possible to obtain reporting limits below the screening levels based on existing analytical methods/technology. Therefore, all analytical data will be reported down to the lowest detection limit and the results will be qualified in those circumstances where they are reported below the level of quantitation. The RI report will include a discussion of data quality objectives and provide explanation of those instances where reporting limits below a given screening level could not be achieved. The initial steps or evaluations of the human health and ecological risk assessments will consider all detected chemicals, regardless of whether or not they exceed selected screening criteria.

RESPONSE TO COMMENTS ON DRAFT REMEDIAL INVESTIGATION WORK PLAN, SOUTH SHORE AREA FORMER MARE ISLAND NAVAL SHIPYARD VALLEJO, CALIFORNIA DATED MAY 2014 DCN: NRS-4812-0000-0008	
Comments Provided By: Tami Nakahara, Senior Environmental Scientist (Specialist) California Department of Fish and Game (CDFW) Office of Spill Prevention and Response (OSPR) Date Comments Received: July 24, 2014	Responses Provided By: NOREAS, Inc.
CDFW Comment 1. Page 1-1, Section 1.0: *Introduction*. The text states, "*The SSA consists of approximately 38uplands, wetlands, and tidal mudflat areas…"* Please correct the typographical error.	**Response.** The text has been corrected to indicate *"…38 acres of uplands…."*
CDFW Comment 2. Appendix A Sampling and Analysis Plan (SAP), Page 17 of 154, *SAP Worksheet #3 – Distribution List (Continued).* For Tami Nakahara, please correct the organization name listed in the table from the *"California Department of Fish and Game"* to the *"California Department of Fish and Wildlife"* to reflect the name change of our Department on January 1, 2013. Please also correct the e-mail address listed in the table from tnakahara@ospr.dfg.ca.gov to Tami.Nakahara@wildlife.ca.gov.	**Response.** The text has been modified to reference California Department of Fish and Wildlife. The email address indicated in SAP Worksheet #3 has also been revised accordingly.
CDFW Comment 3. Appendix A Sampling and Analysis Plan (SAP), page 44 of 154, SAP Worksheet #14 – Summary of Project Tasks, subsection Biological Monitoring and Avoidance Procedures. The text states, *"The path to and from each sampling location will be cleared by a biologist before vehicles or heavy equipment drive off-road to ensure that there are special status special in the path of ingress or egress."* Please correct the text to state, "…*there are no special status species in the path of ingress or egress."*	**Response.** The word "no" has been added for correction. The statement now reads: *"The path to and from each sampling location will be cleared by a biologist before vehicles or heavy equipment drive off-road to ensure that there are no special status species in the path of ingress or egress."*

CDFW Comment 4. Appendix B Environmental Protection Plan, page 6-1, Section 6.1 Resource Evaluation. For the 5th bullet, please change the name of our organization to the California Department of Fish and Wildlife.	**Response.** The text has been modified to reference the California Department of Fish and Wildlife.
CDFW Comment 5. Appendix B Environmental Protection Plan, page 7-2, Section 7.3 Biological Monitor. The text states, *"the USFWS [U.S. Fish and Wildlife Service] and CDFW will also be notified if a rare plant species is observed."* a) Please capitalize the word *"the"* in the sentence b) Please add the following measures to the text: • If a rare plant species is observed in the field by the qualified biologist, the location will be noted in the daily monitoring report, appropriate avoidance and minimization measures will be recommended by the biologist, and the Navy will submit the report to the USFWS and CDFW-OSPR. If an access route, sampling location, or work area is affected by the presence of a rare plant species, the location will be offset to avoid the need to remove the rare plant. If this is not feasible and sampling or work must still be conducted at that location, the Navy will notify the USFWS and CDFW-OSPR, and the Navy will coordinate appropriate avoidance and mitigation measure with these agencies.	**Response.** a) The word "the" has been capitalized b) A new statement has been added to Section 7.3 and reads as follows : "If a rare plant species is observed in the work area, the USFWS and CDFW-OSPR will be notified and the Navy will coordinate appropriate avoidance and mitigation measures with these agencies. The location of the rare plant species will be noted in the daily biological monitoring report and reports will be submitted to the USFWS and DTSC for forwarding to the CDFW-OSPR."

CDFW Comment 6. Appendix B Environmental Protection Plan, page 7-2, Section 7.4 Pickleweed Removal. The text states, *"For any work that requires vegetation removal, a qualified biologist will visually inspect for rare plants that may be present prior to the start of field activities."* CDFW-OSPR does not normally consider rare plant surveys conducted outside of the flowering period of the species to be sufficient because of the difficulty in correctly identifying a species without the presence of the inflorescence. If the Navy has take of rare plants due to insufficient surveys and incorrect identification, they may not be in substantive compliance with State and Federal ARARs. Therefore, rare plant surveys should be conducted for the special status plant species listed in Table 1 of the PMA and SSA Existing Conditions and Special Status Species report (H.T. Harvey & Associates, 2011), during the flowering period of the species when they are evident and identifiable. Please revise the measure to state, *"For any work that requires vegetation removal, a qualified biologist will visually inspect for rare plants that may be present, during the time of year when the species are evident and identifiable, and prior to the start of field activities."*	**Response.** Based on the 2011 biological survey conducted by H.T. Harvey & Associates, Mason's lilaeopsis (*Lilaeopsis masonii*) is the only rare plant species that has been identified in the SSA and PMA where its presence was limited to the coastal salt marsh areas. The flowering period for Mason's lilaeopsis typically extends from April through November. The RI field activities are expected to take place sometime between May and August 2015 which falls within the flowering period for that plant species. As such, the plan for visual inspection for rare plants by the qualified biologist prior to the start of field activities, as described in the current statement in Section 7.4 of the EPP, will not be modified.

CDFW Comment 7. Appendix B Environmental Protection Plan, page 7-3, Section 7.6 Monitoring During Protected Species Nesting Season. The text states, *"If work is already occurring within the area when protected nesting season starts, a protected species nesting visual inspection will not be required."* Due to the potential for birds to start nesting after work has already commenced, please replace the above text with the following measure, *"The qualified biologist shall look for new nests at least twice per week, during remedial activities that occur during nesting season."*	**Response.** The approach to visual nest inspections described on page 7-3 (Section 7.6) of the EPP is consistent with what was implemented during the recently completed NTCRA work at the PMA and SSA as indicated in the following excerpt from Section 9.7 of the Final Environmental Protection Plan Waste Management Plan (EPP-WMP) for that effort (Battelle, 2012). "If work is already occurring within the area when protected nesting season starts, a protected species nesting visual inspection will not be required. If work is stopped for more than a reasonable time as determined by the qualified biologist during the protected species nesting season, staging and storage areas, work areas, and soil stockpile areas will be reassessed before a return to work activities." As such, this approach will be maintained for the implementation of the RI field activities and no changes the current text regarding the nest inspections in Section 7.6 of the EPP are planned.

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Comments Provided By:	Responses Provided By:
Eileen Hughes, P.G. 8170 Engineering Geologist, Geological Services Unit (GSU) Geological Services Branch Brownfields and Environmental Restoration Program Department of Toxic Substances Control	NOREAS, Inc.
Date Comments Received: August 28, 2014	Response:
General Comments	
GSU General Comment 1. RI completeness. MPPEH areas along the shoreline between the SSA and Investigation Area 5 (IR05) that were discovered during the NTCRA visual survey are not addressed by this RI WP (*1.1 Purpose and Objectives).* MPPEH areas include: the shoreline riprap where the MK6 depth charge was found; two primer areas in Grids Z006 and Z007; large shell casings in Grid Z008; drums partially buried in riprap in Grid Z007; and, a large mass containing munitions, metallic debris, and concrete in Grid Z005 (Figure 2-7 Areas where High Density of MEC Items Found – MEC NTCRA (2012-2013)). The large mass appears to be similar to dredge pond outfall masses found at other locations on MINS, which contained MEC and radiological items. a) To fill the data gap, the investigation of MPPEH areas along the shoreline for MEC and munitions constituents (MC) should be conducted prior to developing the comprehensive RI Report, and results should be summarized in the comprehensive RI Report. The shoreline riprap area, where the fully-loaded MK6 depth charge was recovered, should be investigated to determine if additional depth charges and other MPPEH have been incorporated into the riprap.	**Response.** 1 a) Please refer to the response to HERO General Comment #1. The areas identified along the shoreline of IR05 will be addressed under separate removal action and reporting mechanism to be determined at a future time.

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GSU General Comment 1b. MPPEH geophysical anomalies may be detected and debris may be encountered during the investigations proposed in the RI WP (i.e., during utility clearance; during magnetometer sweeps of the AF011 pit, boring locations, and well locations; and during downhole magnetometer measurements). The RI WP is not consistent with respect to how MPPEH will be addressed as shown below. *i.* *5.7 Management of MEC* says that subsurface anomalies will not be excavated for identification and disposition. However, in Section 5.7, procedures that apply to surface MPPEH are described, including: inspection, classification, onsite management of items unsafe to remove (presumably, blowing-in-place or detonation at the disposal range), storage, and disposition. *ii.* *Appendix A Sampling and Analysis Plan, Worksheet #14, Summary of Project Tasks* says: "If a surface anomaly is discovered on the site while employing anomaly avoidance techniques, the location and description will be reported to the Navy RPM (regional project manager). The specific boring location will then be moved to an area that is free of metal anomalies. The anomaly will not be excavated or handled." Subsurface borings will be screened using downhole equipment at 1-foot intervals, and: "If an anomaly is detected prior to completion of a boring, the boring will be terminated and the depth of detection and location of the boring will be recorded. The boring will not be excavated for identification." *iii.* *Appendix D Accident Prevention Plan/Site Health and Safety Plan, Attachment 1, 4.4.1 Residual UXO/MEC* says: "At no time will the ordnance item be moved or disturbed."	**Response.** 1 b) Based on the extensive nature of the MEC removal activities completed during the recent NTCRA, MPPEH is not expected to be encountered during the intrusive activities planned for the RI with the important exception of the additional delineation of the unresolved AF011 pit. As described in both Sections 5.2.3, 5.6, and 5.7, anomaly avoidance measures will be employed and any subsurface MPPEH encountered during intrusive activities will be left in place – no excavation of MPPEH or anomalies will be conducted under the RI Work Plan. Though the risk for encountering MPPEH at the surface is considered very low, Section 5.7 was prepared to describe how MPPEH found at the surface would be addressed. Any items determined as "not safe to move" will be left in place and the location will be secured pending proper disposition. i. Section 5.7.5 has been removed from the RI Work Plan as any movement or on-site treatment of MDEH or MEC items will be conducted under a separate plan. ii. Worksheet 14 states that the "anomaly will not be excavated for identification" and is consistent with the clarified approach in 5.7. iii. MPPEH will not be removed. It will be inspected and classified where it was found only to determine whether it is safe to move, but it will not be removed by NOREAS as part of the RI. Any movement will be conducted by DOD personnel or a separate MEC contractor.

Please resolve these discrepancies. In particular, if surface MPPEH is to be investigated (as per Section 5.7 et seq.), Appendices A and D should be revised accordingly. **GSU General Comment 1c.** With respect to MPPEH and debris that is not addressed in the RI WP, the RI WP says that further investigation will be addressed under a separate work order. Work plans for additional MPPEH and debris investigations should be submitted to DTSC for review and approval. **GSU General Comment 1d.** The delineation of the extent of a disposal pit in DGM grid AF 011 is proposed using a magnetometer and ground penetrating radar (GPR) (5.2.3 Additional Delineation of Disposal Pit – DGM Grid AF011). If the pit cannot be delineated using these methods, potholes will be excavated in the area surrounding the pit to depths of approximately four feet to locate the top of the buried debris. Excavation will stop if either an anomaly is detected or debris is encountered. This approach differs from the NTCRA approach (and from the approach for surface MPPEH described in 5.7 Management of MEC). In the NTCRA, anomalies were intrusively investigated (i.e., excavated) and debris was removed down to at least 4 feet below the ground surface (ft bgs). Even if delineation of the AF011 is successful, a data gap will remain in AF011 and the RI will not be complete because the anomalies and debris will be left in place. Therefore, it may be more cost effective to include the delineation and intrusive investigation of the AF011 pit with the investigation of MPPEH investigations along the shoreline (discussed in 1a, above).	**Response.** 1c) If MPPEH is encountered, work plans to address the MPPEH will be submitted to the DTSC. However, the Navy does not anticipate providing these WPs during the RI effort. 1d) Comment noted. The objective of this task is to provide a preliminary delineation of the pit only. Removal of any residual MPPEH in DGM Grid AF011 is not an objective of the Remedial Investigation. This area will be remediated during the remedial action phase if appropriate to protect human health and the environment.

GSU General Comment 1e. The results of this investigation are to be included with results of other investigations in a comprehensive RI Report (10.0 RI Report). It is recommended that a separate field report for this investigation be submitted, with all necessary documentation, prior to inclusion of the results of this investigation in the comprehensive RI Report. Similarly, if additional investigations are conducted (e.g., the MEC investigation in the shoreline area), it is recommended that separate work plans and field reports for those investigation be submitted, with results of all investigations summarized in the comprehensive RI Report.	**Response.** The investigation and removal of potential MEC items in the unresolved areas of the Grid AF011 debris pit, as well as those items located along the IR05 shoreline, will be addressed in the future. In the event that the removal action is completed before the completion of the RI report, the results will be included. If the investigation/removal action is not complete by the RI report is created, a summary of actions and information to date will be provided to move the area to the FS if there is a potential threat to human health and the environment.
GSU General Comment 2. MEC Explosives Safety Submission (ESS). The ESS describes essential elements of the proposed field work (listed below). DTSC relies on the review and approval of the ESS by the Naval Ordnance Safety and Security Activity (NOSSA) to ensure that appropriate MEC safety measures are used. Critical elements of the ESS (as identified in DoD 2008) should be summarized in the text of the RI WP (and in Appendices A and D) and illustrated on figures. Critical elements include: explosive safety quantity distances (ESQDs), munition with greatest fragmentation distance (MGFD), the maximum fragmentation distance (MFD), MEC exclusion zones (EZs) for each location and activity, clearance techniques, depth of clearance for each area, blow-in-place restrictions/requirements, detonation areas, inhabited building distances, public transportation routes, minimum separation distance (MSD), team separation distance (TSD), reuses on which the ESS was based, and presumed land use controls. Include the ESS and NOSSA approval as an appendix.	**Response.** The ESS is an internal Navy document and is not intended for distribution to the public domain. The ESS and NOSSA approval documents will not be included in the RI Work Plan or RI Report.

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GSU General Comment 3. MEC avoidance. The text says that it is not expected that MEC will be encountered during the proposed field work (4.0 Remedial Investigation, second paragraph). However, although significant MEC has been removed and the potential for encountering MEC has diminished, MEC still exists at SSA. For example, all MPPEH locations were not cleared during the NTCRA. At other MPPEH locations, clearance generally was to 4 fbgs. Moreover, during the NTCRA visual survey, significant MPPEH was identified on the surface of the SSA (e.g., the MK6 depth charge). The proposed investigations will penetrate up to 20 ft. bgs. Proposed MEC avoidance measures for boring and well installations include surface sweeps and downhole detectors (5.6 MPPEH Avoidance and Appendix A Sampling and Analysis Plan [SAP], Worksheet #14 – Summary of Project Tasks). In addition to the measures described in 5.6 MEC Avoidance, other measures may be warranted (e.g., shielding of equipment operators and maintaining safe distances during drilling).	**Response.** Comment noted. The Navy PMO office has consulted with its munitions specialists at NOSSA and its experts contracted to perform the fieldwork. Appropriate precautions will be taken in the field to ensure worker safety and health. However, no changes to the RI Work Plan and related documents are planned at this time.

GSU General Comment 4. MEC geophysical instrumentation. Magnetometers and GPR will be used for MEC avoidance activities. a) Include a section that more fully describes the geophysical equipment that will be used for surface and downhole investigations (e.g., instrument makes and models, operating principles, limitations, and interferences). b) Describe the surveying approach for surface magnetometer and GPR surveys (e.g., distance between transects, height above ground, rate of travel, penetration distance) and for downhole measurements (e.g., rate of travel, penetration distance, et cetera). c) Identify the consultant and the qualified personnel who will be conducting the GPR survey.	**Response.** General response to items 4a) through 4c): The objective of the limited geophysical survey of the Grid AF011 pit is to provide a preliminary delineation of the unresolved eastern portion of the pit for order of magnitude quantification for incorporation into the Feasibility Study if appropriate to protect human health and the environment. It is not intended to constitute a formal DGM survey. The first paragraph of Section 5.2.3 has been revised to emphasize the objectives and now reads as follows: "To delineate the approximate lateral extent of the pit, a limited non-intrusive geophysical survey will be conducted using a combination of methods, including electromagnetic (EM) (all-metals detectors and magnetometer) and ground-penetrating radar (GPR) techniques. As the western portion of the pit has already been delineated and excavated, the objective of the geophysical survey is limited to delineating the lateral extent of the remaining debris to the east for order of magnitude quantification for incorporation into the Feasibility Study if appropriate to protect human health and the environment. It is not intended to constitute a DGM survey." The GPR and EM survey will be conducted by Bristol Environmental Remediation (BERS) personnel under subcontract with NOREAS. The qualified personnel who will be conducting the survey will be identified prior to mobilization.

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GSU General Comment 4.	**Response.**
d) To be consistent with the NTCRA, an instrument verification strip (IVS) should be used to determine the lowest settings required to detect all industry standard objects (ISOs), or seeds. Include the IVS location on a figure. e) Describe the geophysical instrument calibrations and checks that will be performed and the required frequency of the calibrations and checks. Records of geophysical instrument calibration and checks should be included in the field report. f) Include data quality objects (DQOs) for the IVS and for equipment tests. For example, during the NTCRA, tests included: equipment warm-up, personnel test, cable connection test, static background, static spike, and repeat data.	General responses to items 4d) through 4f): As noted above, the objective of the delineation effort is limited to determining the approximate boundaries of the eastern extent of the debris that remains in the AF011 pit but it is not intended as a formal DGM survey or MEC intrusive investigation. No MPPEH or debris will be moved or handled as part of the delineation effort and MEC avoidance procedures will be implemented. Based on the limited scope, there are no DQOs associated with the delineation effort. Therefore, the IVS and instrument calibration standards used for the NTCRA will not be required.
g) A function check for magnetometers at each borehole is included on SAP Worksheet #22: is the function check identical to the tests performed during the NTCRA (noted above)?	4g) The function check will be performed to ensure that the detector is functioning in accordance with the manufacturer's specifications and will be conducted according to the instructions in the user's manual for that specific make and model of the equipment.
h) In addition to the magnetometer, an all-metals detector should be used for surface surveys.	4h) An all metals detector will be used for the delineation effort. A statement to that effect has been added to the Work Plan text (see response to items 4a through 4c above).
i) To facilitate MPPEH reacquisition and to be consistent with the NTCRA, a real-time kinematic/differential global position system (RTK/GPS) should be used to record MPPEH and debris locations. Include the required accuracy for the RTK/GPS. Identify the location of the benchmark control point, and include the benchmarks on a figure. The RTK/GPS should be verified twice daily at the benchmark control point.	4i) As noted above, the delineation will not constitute a formal DGM survey. Based on the results of the delineation effort, the limits of the AF011 pit will be surveyed and documented on appropriate figure(s) in the RI Report.

GSU General Comment 4. j) A figure showing all MPPEH discovered during the investigation should be included in the field report. Tabulated locational data should also be included. Figures and tables should be consistent with those provided in the NTCRA completion reports, so that the data can be merged.	**Response.** With the exception of the AF011 debris pit delineation effort, MPPEH is not anticipated during the RI field activities. However, if encountered during the field activities, the location of any MPPEH will be marked (flagged) and surveyed by a California licensed land surveyor. The RI Report will provide location coordinate data for any MPPEH that is discovered and those locations will be included on the relevant figures and tables.
GSU General Comment 5. Abrasive blast material. ABM was observed during SSA investigation. The extent of ABM has not been determined. Include a section on ABM in the RI WP. Discuss the conceptual site model (CSM) for ABM. Identify how ABM will be addressed in the RI Report and in the feasibility study. Include a figure showing locations where ABM has been observed.	**Response.** A new Section 4.1.7 has been added to the RI WP as follows: **4.1.7 Abrasive Blast Material (ABM)** Abrasive blast material (ABM) was identified in the SSA during the recent excavation and removal activities conducted as part of the MEC NTCRA. As indicated in the Draft Removal Action Completion Report (ISR-JV, 2013), the majority of the ABM was found beneath the edges of roads, along buried utility corridors. The locations of the ABM found in the SSA during the MEC NTCRA are depicted in Figure 4-1. As can be seen on Figure 4-1, several of the planned soil sampling locations coincide with where ABM was found during the MEC NTCRA activities. In the event that ABM is found in the soil core or cuttings samples, the Navy will be notified immediately. In addition, the following information will then be documented in the appropriate field forms and log book: • Location where ABM was recovered • Date and time • Depth at which ABM was encountered • Estimated thickness of zone where ABM was recovered • Approximate volume of ABM recovered

GSU General Comment 5. (continued)	**Response (continued).** For those locations where ABM or soils mixed with possible ABM are observed, a sample of soil beyond or below the ABM will be collected and analyzed for metals, PCBs, and organotins (monobutyltin, dibutyltin, and tributyltin). The locations of the ABM found during the RI sampling activities will be combined with those documented during the MEC NTCRA to evaluate the nature and extent of the ABM at the SSA and update the current CSM for the RI Report. A human health and ecological risk assessment of ABM was previously conducted at IR Site 4 to evaluate the risks posed by exposure to ABM in backfill material placed around utility lines (Tetra Tech, 1999). The results of the evaluation, as provided in a technical memorandum, indicated that the ABM used to backfill utility trenches does not pose a significant risk to human or ecological receptors at Mare Island (Tetra Tech, 1999). Analytical results of soil near ABM sampling completed as part of the RI will be evaluated at part of the risk assessment activities and a refined conclusion about ABM at the site will be incorporated into the RI Report.

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GSU General Comment 6. Soil borings locations along pipelines. Soil borings with sampling at 3 depths are proposed along the sanitary system pipeline (8 locations) and along the storm water system (5 locations). However, it is difficult to determine if the proposed locations are sufficient or appropriate because information essential for the evaluation is not provided, as discussed below. • Industrial and sanitary wastes were historically disposed to the SSA storm water system • The MINS Industrial Waste Water Treatment Plant was constructed in 1972. However, the date of installation of the industrial waste water system at SSA is not provided. Moreover, the SSA industrial waste water system is not shown on figures (e.g., Figures 4-1 and 4-3).	**Response.** General Response: It is important to note that the investigative approach to both the Storm Sewer (SWMU 93) and Sanitary Sewer (SWMU 106) systems at the SSA includes analysis for a full range of constituents, including VOCs, SVOCs, PAHs, TPH-g, TPH-d, TPH-mo, PCBs, and metals for all soil samples collected at these features. This approach is designed to account for typical wastes that may have been discharged to these systems in the past. Response to Bullet #2: The operations at the SSA did not involve the generation of industrial wastes therefore industrial wastes were not discharged to the piping systems at the SSA. The site was predominantly used for munitions storage, loading and unloading from ships. The MINS industrial waste water system does not extend into the SSA.

GSU General Comment 6 (continued).	**Response.**
• Several industrial facilities that may have discharged hazardous wastes to the combined sanitary/storm water/industrial waste water system are identified, along with the specific hazardous wastes that may have been discharged. However, the facilities which are mentioned (e.g., on Table 4-1) are outside SSA. • The MINS sanitary waste treatment plant was operated from 1959, and the MINS sanitary system was connected to the City of Vallejo publicly-owned treatment works (POTW) in 1972. However, the date when SSA sanitary system was installed (i.e., the date when the sanitary system was separated from the combined sanitary/storm water/industrial waste water system) is not provided. • Storm water pipelines (and drains and catch basins) are not shown on figures (except for pipelines lines connected to Outfalls 207 and 208). For example, pipelines connected to Outfalls 40, 41, and 42 are not shown. • It is not clear why the proposed investigation along the sanitary pipeline is more extensive than the proposed investigation for the storm water system (which was historically used for industrial waste). • Two boring locations for the storm water system are proposed near Buildings A195 and A259. However, storm water pipelines near these buildings are not shown on figures. • Building A153 is described as a sewer pump station. However, pipelines connecting to the storm and/or industrial and/or sanitary systems are not shown on figures. The discharge location is also not shown.	Response to Bullets #3 and #4: As noted above, the industrial waste water system did not extend into the SSA. The storm sewer and sanitary sewer systems in the SSA are independent of one another and are not connected. In addition, the sanitary sewer system flows north, away from the SSA, into the upland areas of Mare Island where it eventually connects to the POTW. Any discharges of industrial wastes to the sanitary system that may have occurred due to historical activities in the manufacturing areas north of the SSA would not be connected to the SSA. It should also be noted that the SSA was historically used for storage and logistics, all of the manufacturing and other industrialized operations were conducted on other portions of the island, to the north. However, for the purposes of the investigation, the sampling approach is designed to address the potential that hazardous wastes may have been discharged and/or released in the SSA through the storm and sanitary sewer systems in the SSA (see the general response to GSU General Comment 6 above).

GSU General Comment 6 (continued). a) Explain why the proposed investigation of the sanitary system (which presumably did not convey industrial wastes) is more extensive than the proposed investigation of the storm system (historically used for industrial waste) and the industrial waste system. b) Identify SSA facilities that discharged industrial wastes and describe the wastes. c) Include the full extent of the industrial waste, storm water, and sanitary systems on figures showing proposed borings and monitoring wells. Distinguish historical uses from current uses on a figure. d) Provide dates of operation of industrial waste water and sanitary systems at SSA including dates of separation from the combined system.	**Response (continued).** a) Data from soil and sediment samples collected in the IAK at the storm water outfalls do not indicate significant impacts from discharges. The sampling plan considers that the storm water pipeline in the SSA has a smaller footprint than the Sanitary Sewer system (so the relative number of samples is less for the storm water system), and that the Sanitary System has not been previously sampled in the SSA. b) Historical records of site activities do not indicate the discharge of industrial wastes from the SSA and none of the buildings in the SSA were connected to the industrial wastewater lines. Information provided in the Environmental Baseline Survey (Mare Island Naval Shipyard, 1994) indicates that Buildings A195 and A259 were connected to the sanitary sewer system but there are no records indicating that industrial wastes were discharged to that system from these buildings. As described in Section 4.1.2. soil samples will be collected from the storm drains located throughout the SSA. This includes samples at storm drain catch basins located outside Buildings A195 and A259. As noted above, these samples will be analyzed for a full suite of chemical constituents. c) As noted above, the industrial wastewater system did not extend into the SSA. The extent of the Sanitary Sewer and Storm Water systems in the SSA is depicted on Figures 4-1 and 4-3 that also include the boring locations planned as part of the investigation for these features. d) As noted above the industrial wastewater system did not extend into the SSA. The discussion of the Storm Sewer System (SWMU 93) in Section 4.1.2 provides the following description with respect to the dates of operation for the Storm and Sanitary Sewer systems:

GSU General Comment 6 (continued).	**Response (continued).** d) Continued. "SWMU 93 consists of the storm sewer system for the former MINS. It was designed to handle, collect, convey, and discharge excess surface water runoff into Mare Island Strait, Carquinez Strait, and San Pablo Bay at 46 different outfalls. Information provided in the PA/SI indicates that the domestic sanitary sewer system and storm sewer system at MINS were completely combined until 1959, after which a domestic wastewater sewage plant was built (PRC, 1995b). The domestic wastewater sewage plant provided primary waste water treatment, including aeration, grit removal, sedimentation, and chlorination prior to discharging treated water to San Pablo Bay. In 1976, the MINS sanitary sewer system was connected to a publicly-owned treatment works (POTW) in the City of Vallejo, California. Until that time, most of the industrial waste water generated at MINS was discharged to Mare Island Strait and San Pablo Bay through the storm sewer system (PRC 1995b)." The following text was added to provide additional detail: "Between 1959 and 1972, the storm sewer system and sanitary system were partially interconnected, and some raw wastewater (both sanitary and industrial wastewater) was discharged directly to Mare Island Strait (though not from the SSA). Before an industrial wastewater treatment plant (IWTP) was built in 1972, most of the industrial wastewater was discharged directly to Mare Island Strait and San Pablo Bay through the storm sewer system.

GSU General Comment 6 (continued).	**Response (continued).** d) Continued. As depicted in Figures 4-1 and 4-3, the storm sewer system in the SSA consists of five separate lateral lines that convey storm water runoff captured in drains and catch basins located near buildings and roads in the upland areas to a series of outfalls along the shoreline. The storm sewer system in the SSA was not connected to other portions of the base where industrial wastes were generated and discharged as part of historical industrial activities at other part of MINS.
e) Identify the wastes that were pumped at Building A153. Include the dates of pumping. Include pipeline connections and discharge locations on figures.	e) Based on the available information for Building A153, it was used to pump sanitary sewage from Buildings A195 and A259. The piping associated with Building A153 is depicted on Figures 4-1 and 4-3. Several new soil boring locations were added to evaluate this line. The locations of these samples are indicated on Figures 4-1 and 4-3.

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GSU General Comment 7. Chemical Analytical Program. The following revisions to the chemical analytical program are recommended. a) Industrial wastes disposed to the combined pipeline system (SWMU 93) included several wastes that may have contained hexavalent chromium (Cr VI). Identify wells for Cr VI analyses and add Cr VI analyses to text and tables. b) Because the uses of the tanks and dry wells in Grid AJ 015 are not known, include energetics as analytes for boring locations along the perforated pipeline. c) Analysis for dioxins and furans is proposed for all groundwater samples (Table 4-3), and for 20% of the soil samples collected in the Primer/Oven Pits area. Analyses for dioxins/furans in groundwater is warranted at SSAMW-05, near the Primer/Oven Pits area (where munitions have been burned), and for other locations where dioxins/furans have been detected in nearby soil. However, groundwater analyses for dioxins/furans can be postponed at other wells, pending review of soil and groundwater results. d) Analyzing soil samples collected at 0.5 ft bgs for VOCs is not recommended. VOC concentrations in soil collected at 0.5 ft bgs may be low-biased because VOCs are likely to have evaporated from such shallow soils. Low-biased results will not be appropriate for risk assessments.	**Response.** a) If the analytical results from the initial round of groundwater sampling at the SSA monitoring wells indicate concentrations of total chromium in excess of the current Mare Island ambient value (22 ug/L), analysis for Cr VI will be included in future groundwater sampling events. b) Energetics have been sampled for at the site during the Oven/Primer Pit excavation and in 4 locations (6 samples) representing the pathway of energetics to the soil per the CSM (buried munitions). All samples for energetics have been non-detect. Energetics at the site are well understood and will not be sampled for in this phase of the CERCLA investigation. c) Dioxins/Furans will only be considered for analysis in groundwater samples in the event that the soil sampling results from Primer/Oven Pit area indicate their presence above the soil screening criteria. d) No changes for this depth interval are planned. Please refer to the response to ERAS General Comment 2.

GSU General Comment 7 (continued).	**Response (continued).**
e) General Minerals are inconsistently identified as an analytical group for groundwater samples. Confirm that groundwater samples will be analyzed for General Minerals. f) Pesticides and herbicides may have been used historically to control vegetation and vermin in SSA. Analysis of shallow soil samples for herbicides and pesticides which have been detected at MINS (including SSA) should be considered. Groundwater samples for pesticides/herbicides can be archived pending review of soil sampling results.	e) Analysis for general minerals is not currently planned for the RI. Reference to the sampling for sulfate, nitrate/nitrite, and other MNA parameters in the sampling procedures described in Item # 16 of Section 5.3.3 has been removed. f) Pesticides and herbicides have been added to the analytical list for the surface samples collected in the areas where they most likely to have been used and the soil has not been reworked during the MEC NTRCA activities. As such the 0.5 feet bgs soil samples collected adjacent to Bldgs. A195, A259, and A296 will be analyzed for pesticides and herbicides. Pending the results from these locations, additional selected archived soil and groundwater samples may be analyzed for these parameters. In the paragraphs of Section 4.1.1.2 of the Work Plan describing the analytical methods that will be applied to the investigation at Bldgs A195, A259, and A296, the following statement has been added: "In addition to these analytes, the soil samples collected from 0.5 feet bgs will also be sampled for selected pesticides and herbicides." In addition, Table 4-3 of the Work Plan and relevant worksheets in the SAP have been revised to include these analyses.

GSU General Comment 8. Continuous soil cores. Collection of continuous soil cores at boring locations is proposed. However, collection of continuous cores for monitoring wells is not proposed (Appendix A Sampling and Analysis Plan [SAP], Worksheet #14 – Summary of Project Tasks). a) Continuous cores should be collected at monitoring well locations. b) Include photos of the continuous cores in the report.	**Response.** a) Continuous soil core samples will be collected during the advancement of the pilot boreholes for the soil sampling and groundwater monitoring wells. b) The continuous core samples will be described in detail in the boring logs. Photographs of the core will not be necessary and will not be provided in the RI Report.
GSU General Comment 9. Soil sampling depths. Soil sampling at 0.5 fbgs, 5.0 fbgs, and 10.0 fbgs is proposed. Explain why these depths have been selected and how the data sets will be used. For example, will only the soil and sediment samples collected at 0.5 fbgs be used for determining risks associated with sediment and surface soil (defined as 0.0 to 2.0 fbgs), or will both the 0.5 fbgs and 5.0 fbgs samples be used (because the 5.0 fbgs data set represents a portion of the soil volume between 0.5 fbgs and 10.0 fbgs)? Sediment and surface and subsurface soil depths for the human health risk assessment (HHRA) and the ecological risk assessment (ERA) are shown on *Figure 7-1 Preliminary HHRA Conceptual Site Model and Figure 8-1 Preliminary Ecological Conceptual Site Model*.	**Response.** Please see response to ERAS General Comment #2.

GSU General Comment 10. Soil boring locations. a) **Buildings A193, A195, A259, and A296 (Explosives Safe Haven).** Two boring locations are proposed for each building. Boring locations were selected to provide overall coverage (i.e., not because specific boring locations are associated with specific activities that warrant investigation) (Section 4.1.1.2 Buildings Proposed for Investigation as Part of the RI). In lieu of sampling locations chosen for overall coverage, biased sampling locations near drains and pipelines that conveyed industrial waste should be considered. For example, metal surface preparation (degreasing), painting, and welding/cutting occurred at Building A259; however, it is not clear whether the proposed soil sampling at Building A259 will occur near locations of these activities, or near waste drains or pipelines that conveyed wastes from these activities. Activities at Building A193 were similar to those at Building A259. Building A193 has been demolished and the Navy says that information on the building interior is not available. Soil sampling at two locations within the former building footprint is proposed. However, soil sampling near drains and pipelines exiting the former Building A193 should be considered. Inspection of the undersides of existing buildings (e.g., Buildings A195 and A259) may be useful for locating possible piping connections from interior to exterior of the buildings, which are preferred soil sampling locations. Similarly, soil sampling near drains and pipelines for A296 should be considered.	**Response.** a) As noted in the responses to GSU General Comment 6, the majority of the historical activities at the SSA were based on the storage and loading/unloading of munitions. Though some repair and assembly work was conducted here, the SSA was not used for the manufacture and production of weapons. As such, the SSA was never connected to the industrial wastewater treatment system as historical activities did not involve the large scale use, generation, or discharge of industrial wastes. However, due to historical activities at Buildings A193, A195, and A259, it is clear that some small quantities of hazardous materials were used and/or stored in these locations in the past. With respect to A195 and A259, impacts from the historical presence of USTs at both locations have been addressed and ruled out during the tank removal and closure process. Although Building A195 was once used for storage of hazardous materials, it was regulated, maintained, and closed under the RCRA program with no documented violations. The flooring at both Buildings A195 and A259 consist of sealed concrete and do not contain floor drains. Sampling for discharges to the storm drains around these buildings is already planned under SWMU 93, therefore the planned samples are intended to provide broader coverage around these buildings in the event that a potential release or discharge to the ground surface may have occurred in the past. Where warranted, sample locations for these buildings may be moved to locations where drains or pipelines or evidence of impact is observed in the field. Bldg 259 is still intact. Bldg. 193 has been demolished. A296 (Explosives Safe Haven) is a berm constructed of soil and does not have associated drains or piping.

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GSU General Comment 10. b) **MEC disposal pits.** i. Borings for MEC disposal pits (except near Building A259) are located within excavations, which were backfilled with excavated soil. Therefore, some of the samples will be collected from backfill and some from underlying soil. Sampling (for energetics and metals) at 0.5 ft bgs, 5.0 ft bgs, and 10.0 ft bgs is proposed. Samples collected from backfill are composite samples and may approximate average concentrations; however, samples collected from underlying soil will be discrete samples. Boring logs should note whether each sample is collected from backfill or from underlying soil. ii. The two borings near Building A259 appear to be located adjacent to (not within) MEC disposal pit excavations. Please explain why Building A259 borings are located adjacent to (not within) excavations.	**Response.** b) i. Where possible, the boring logs will denote backfill from underlying soil intervals though it may not be possible in locations because the disposal pits were backfilled with reworked native soils and the differences between the backfill and underlying, undisturbed material may be too subtle to detect. ii. The two borings associated with MEC near Bldg. 259 will be located just outside the edges of the unresolved AF011 pit where potential MPPEH may remain in place. As discussed above this fieldwork will not involve investigation or removal of MPPEH, only avoidance.

GSU General Comment 10 (continued).

c) **Primer/Oven Burn Pits**

i. Borings at 5 locations in the vicinity of former burn pits are proposed. Presumably, the purpose of the borings is to delineate that soil above criteria has been removed, with respect to zinc, copper, and lead and additional analytical groups. One boring is located within an excavation (for the Primer Pit). Four borings are located outside Oven Pit 1 (excavated to 9.5 fbgs), Oven Pit 2 (excavated to 7 fbgs), and the Primer Pit (excavated to 7 fbgs). Please explain why one sample has been located within the Primer Pit excavation and the other four samples have been located outside the three excavations. If the intent is to demonstrate that the depths of excavations were sufficient, samples should also be collected at the bottoms of the Oven Pit excavations.

Response.

c)

i. Additional borings have been added within the footprints of Oven Pit 1 and Oven Pit 2 to evaluate conditions in the native soils below the former excavations. The locations of the additional borings have been added to Figures 4-1 and 4-5. Section 4.1.4 of the text has been revised to include the two new borings and provide clarification regarding sampling rationale as follows:

> *"Based on the potential for other hazardous non-ordnance materials (solvents, oils/grease, paints, etc.) to have been disposed in the burn pit operations, additional soil sampling will be conducted at eight boring locations (six soil borings and two monitoring wells) in the Oven/Primer Pit Areas (Table 4-2) Five of these borings will be placed outside the footprints of the former excavations to delineate the lateral and vertical extent of potential impacts outside the pits. At these five locations, soil samples will be collected from planned depths of 0.5, 5, and 10 feet bgs and analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, and metals (Table 4-3).*
>
> *Three boring locations will be placed with the footprints of the Oven and Primer Pits to confirm the vertical extent of potential impacts below the former excavations (one boring each within Oven Pit 1, Oven Pit 2, and the Primer Pit). Soil samples at these three locations will only be collected from a depth of 10 feet bgs to evaluate conditions in the native soils below the former excavations; samples will not be collected from the backfill materials in the shallower depth intervals. Samples from these three locations will be analyzed for VOCs, SVOCs (including PAHs), TPH-g, TPH-d, TPH-mo, dioxins/furans, and metals (Table 4-3)."*

GSU General Comment 10 (continued).	**Response.**
ii. Sampling for dioxins/furans is proposed at 20% of the soil sampling locations. Please explain what criteria will be used for selection of samples for dioxin/furan analysis and why 20% was considered to be the appropriate subset. For example, will samples for dioxin/furan analyses be archived, with selection pending review of other analytes? Or, will shallow samples (at 0.5 fbgs and 5.0 fbgs) be preferentially analyzed because of the relevance of shallow samples for risk assessments.	ii. As agreed upon during the October 30, 2014 teleconference, analysis for dioxins/furans are planned for this location because wastes were once disposed or reduced by burning here. 20% is considered an appropriate subset for dioxins/furans because the buried debris and discolored soils were removed. The plan includes analysis for dioxins/furans for any samples visually observed to contain residual debris or burnt material. If no such material is observed, 20% of the samples from this area will be analyzed with a contingency to analyze 100% of the sample set if dioxins/furans are detected. The selection of the 20% will include at least one sample from each of the three depth intervals. See response to HERO General Comment #2.
iii. Sample SSA RI-PPB01 (Figure 4-5) is close to SSAMW-05 (Figure 4-1). For better coverage, move SSA RI-PPB01 to the wetlands (about 70 feet to the east) and add dioxin/furan analysis for the soil samples collected for SSAMW-05.	iii. Boring SSA RI-PPB01 has been moved as recommended. Figures 4-1 and 4-5 have been revised to depict the new location. Dioxin/furans are not planned for the groundwater sample from SSA-MW05, but will be analyzed in event that they are detected in the soil samples collected from the Oven/Primer Pit areas

GSU General Comment 10 (continued).

iv. The Primer Pit sample at 5.0 fbgs will be collected from backfill. Has the source of the backfill of the Primer Pit and Oven Pits 1 and 2 been identified?

d) **Underground Storage Tanks and Dry Wells Found in DGM Grid AJ015.** Soil sampling is proposed at 2.0 fbgs and 5.0 fbgs (4.1.5 Other Area). Three locations are near the tanks and a perforated pipeline that connects to two dry wells (i.e., SSARI-STB01, SSARI-STB02, and SSARI-STB03). Six locations are along a non-perforated pipeline to the tanks that does not connect to the dry wells (i.e., SSARI-STB04 to SSARI-STB09). The waste/liquid conveyed to the tanks through the non-perforated pipeline is unknown, and the source of the liquid/waste is unknown. Geophysical techniques or hand-digging will be used to determine the extent of the non-perforated pipeline leading to the tanks.

i. Because the two dry wells were 12 feet deep, sampling at 12 fbgs should be considered – at least at the three soil locations which are near the dry wells and the tanks (i.e., SSARI-STB01, SSARI-STB02, and SSARI-STB03).

ii. Soil samples near the dry wells should be moved downgradient of the dry wells.

Response.

c)

iv. As noted in the response to GSU General Comment 10c) i) above, samples will be collected from approximately 10 feet bgs in the three borings located within the footprints of the Oven and Primer Pits to evaluate conditions below the former excavations. As described above, the text of Section 4.1.4 has been revised to clarify that samples will not be collected from depths corresponding to the backfill at these locations.

d)

i. Although it was initially believed that the wells extended to depths of approximately 12 feet bgs, they were found to terminate at 5 feet bgs during their excavation and removal. Because of this sampling will not be considered at 12 ft bgs.

ii. Although it is reasonable to assume that groundwater likely flows from the uplands towards the Strait in the SSA, there are currently no groundwater wells in the area. Thus, the actual direction and magnitude of the hydraulic gradient at the site is unknown at this time. However, the soil sampling locations associated with the dry wells will be moved to the south of these former features, downgradient of the presumed groundwater flow direction. Figures 4-1 and 4-6 have been revised to reflect this change.

GSU General Comment 10 (continued).	**Response.**
iii. Shallow soil samples were previously collected at the locations of SSARI-STB1, SSARI-STB02, and SSARI-STB03 and analyzed for semi-volatile organic compounds (SVOCs), including polynuclear aromatic hydrocarbons (PAHs); for total petroleum hydrocarbons quantified as gasoline, diesel, and motor oil (TPH-g, TPH-d, and TPH-mo); and for metals. Deeper soil samples at the locations of SSARI-STB01, SSARI-STB02, and SSARI-STB03 were not previously collected. Therefore, deeper soil samples at SSARI-STB01, SSARI-STB02, and SSARI-STB03 should be analyzed for SVOCs, TPH-g, TPH-d, TPH-mo, and metals, as well as for VOCs and polychlorinated biphenyls (PCBs).	iii. See Response to GSU Comment 10d(i) above. The wells were ultimately found to extend to 5 feet bgs only during their removal. Following the removal of the wells and tanks, soil samples were collected from between 4.5 and 6 feet bgs. Only trace concentrations of TPH-motor oil and metals were detected, all of which were reported in concentrations below their respective residential RSL or ambient values. As such, the collection of deeper soil samples at this feature is not warranted.
iv. It may be prudent to collect deeper samples (i.e., at 12 fbgs, the depth of the dry wells) at SSARI-STB04 to SSARI-STB09: deeper samples at these locations may be archived, pending results from other samples (i.e., shallow samples at these locations and shallow and deep samples at the upgradient locations).	iv. See response to GSU Comments 10d (i) and 10d(iii)above. The wells were ultimately found to only extend to 5 feet bgs.

GSU General Comment 11. Well Locations.	**Response.**
a) Installation of additional wells is recommended to investigate areas downgradient of potential release areas: i. Immediately downgradient of the hazardous waste storage area in Building A195 near the location of the two proposed soil borings for SWMU 93 (Figure 4-3); ii. Immediately downgradient of the 3 USTs and 2 dry wells north of Building A292 (Figure 4-6); iii. Along the shoreline, downgradient of the buried drums and the area of high-density of MEC south of Building A165 (Figure 2-8); and, iv. Downgradient of the Primer/Oven Pits. SSAMW-05 is upgradient of the Primer/Oven Pits area and will not suffice for evaluating water quality downgradient of the Primer/Oven Pits. However, if well installation in the wetlands is not acceptable or is problematic, collection of grab groundwater samples at four locations surrounding the Primer/Oven Pits will suffice. b) Relocation of two wells is recommended: i. Move SSAMW01 closer to the disposal pits in Grids AI014 and AI015 (Figure 4-1); and, ii. Move SSAMW03 downgradient of the disposal pits in Grids AF011 and AG011, or add another well in this location.	a) See response to GSU Comment #10d(ii) above. Although it is reasonable to assume groundwater flows towards Carquinez Strait, actual gradient/flow information for the SSA has not been determined as of yet. i. The location of SSAMW-07 has been moved to the south side of Bldg. A195. Figures 4-1 and 4-7 have been revised to reflect this change. ii. Well SSAMW-01 is already planned for that general location. It will be moved approximately 50 feet to the north to satisfy this recommendation. Figures 4-1 and 4-7 have been revised to reflect this change. iii. The location of SSAMW-06 has been moved closer to the shoreline south of Building 165. Figures 4-1 and 4-7 have been revised to reflect this change. iv. Monitoring well SSAMW08 will be installed approximately 50-75 feet south of the Primer Pit, near the edge of the wetlands. Permanent wells will not be placed in the wetlands. The location of SSAMW08 has been added to Figures 4-1, 4-5, and 4-7. b) i. The location of SSAMW-01 was moved approximately 50 feet to the north to be closer to both the USTs and the disposal pits. ii. SSAMW-03 has been moved approximately 50 feet south of the AF011 and AG011 pits. Figures 4-1 and 4-7 have been revised to reflect this change.

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GSU General Comment 12. Well installation and construction. a) Installation of 4-inch diameter wells using 8- to 10-inch hollow stem augers (HSAs) is proposed (SAP Worksheet #14). In lieu of HSA installation (if acceptable to the county), installation of 2-inch diameter wells using direct push methods may be more efficient and may result in cost savings. Use of pre-packed filters may simplify installation and minimize turbidity, while increasing sample quality. Conducting cone penetrometer tests (CPTs) prior to well installation would help identify zones of higher hydraulic conductivity. If CPTs are used in lieu of continuous coring at well locations, a continuous core should be collected at least at one well location for correlation purposes. b) Soil samples from monitoring wells are proposed at 0.5 fbgs, 5.0 fbgs, and 10.0 fbgs. The screened intervals of the wells are nominally from 5.0 fbgs to 20.0 fbgs. Soil samples for monitoring wells should be collected from higher permeable zones within the screened intervals of the wells as identified from CPTs or continuous cores. c) Well screens with lengths of 15 feet are proposed. Generally, shorter screen lengths (less than 10 feet) are preferred, to minimize the potential for cross-contamination between water-bearing zones. However, longer screen lengths may be acceptable in areas where the water table fluctuates significantly, provided the well screen does not cross multiple water-bearing zones. For each well, the continuous core (or CPT results) should be evaluated to determine an appropriate screened interval that does not cross multiple water-bearing zones.	**Response.** a) Based on our experience, the installation of small diameter wells using direct push techniques often results in wells that do not set up properly or are difficult to develop sufficiently. Given the shallow depths required at the SSA, the use of direct push to install smaller diameter wells will not likely result in significant cost saving over the use of hollow stem auger methods. As such, the current plan to install the larger diameter wells by hollow-stem auger will be maintained. b) Section 4.1.6 has been modified by addition of the following statement: *"The actual depth of the two deeper soil samples at these pilot borings may be adjusted in the field based on observations of evidence for contaminant impacts (staining, elevated PID readings, etc.) or variations in lithology (bias for higher-permeability zones)."* c) We do not have information regarding multiple water-bearing zones at this time. Given the limited total depth of the wells (20 feet bgs) and proximity to the shoreline, significant tidally-influenced water level fluctuations are anticipated. In this case a 15 ft screen interval is considered reasonable. However, the final screen length may be reduced in the event that evidence for multiple water-bearing zones is observed in the core samples.

GSU General Comment 12 (continued).	**Response.**
d) The top of the well screen will be located about 1 foot above the water table as observed during high tide as (4.2 Investigative Approach – Groundwater). Please clarify whether 1 foot above the water table at high tide will suffice to intersect free product during the wet season at all well locations (including upland well locations).	d) Documentation and soil sampling from previous UST removals do not indicate a significant release from any of the known tanks. In addition, no evidence for significant petroleum hydrocarbon impacts or free product were observed during the extensive excavations completed during the NTCRA, some that extended to depths of 10 ft bgs. Therefore, free product is not anticipated. In the event that LNAPL is discovered, the screen lengths will be reconsidered to accommodate fluctuations, where possible.
e) Depth to groundwater is shallow, between 2.5 fbgs to 6 fbgs (4.2 Investigative Approach – Groundwater), which suggests that in fact it may not be possible to construct wells to intersect floating product (because the water table is too close to the ground surface). To prevent surface water infiltration to shallow groundwater, wells should be constructed with at least 5 feet of annular sealant (or more, if required by the county) between the well screen and the ground surface.	e) See response to GSU General Comment 12 d) above. This is accounted for in the current design.
f) Specify the composition of the bentonite seal and the bentonite grout.	f) The bentonite seal will consist of 100% bentonite; the grout will consist of 95% Portland cement and 5% bentonite. Section 5.3.1 has been modified with the following statement: *"The remaining annular space will be backfilled with a grout mixture up to 2-feet bgs. The grout mixture will consist of 95% Portland cement and 5% bentonite.*"
g) Identical slot sizes and filter pack are proposed for all wells. Provide a rationale for selection of slot size and filter pack.	g) Based on the location and history of the development at the SSA, fine-grained soils are anticipated at most locations. The slot size and filter pack specifications were chosen to optimize the flow of water but retain fine-grained silt/sediments from entering the well. A similar well design has successfully been employed at IR05.
h) Figure 5-1 Proposed Groundwater Monitoring Well Construction Details i. Flush mount well vaults are shown. In areas where the water table approaches the ground surface (e.g., near wetlands), above-ground completions are recommended. ii. Include a locking well cap. iii. Label the annular material that is six inches thick.	h) Figure 5-1 and the text in Section 5.3.1 have been modified to provide for the following. i. The surface completions for the wells will include above-ground monuments. ii. Locking caps will be installed on all wells. iii. The upper 6-inch layer has been labelled as concrete.

GSU General Comment 13. Groundwater sampling. Table 4-3 Summary of Planned Sampling Locations and Analytical Parameters, Footnote 2 says that groundwater samples will be collected within a few feet below the water table in each well. Because the water able fluctuates, sampling at a depth below the water table will result in sample collection at different depths for each event and at different depths for each well. Groundwater sampling at a consistent depth is preferred. Well screen intervals are nominally from 5.0 fbgs to 20 fbgs. Sample collection from the middle of the screened interval could be considered (i.e., at about 12.5 fbgs). The depth of sample collection should be noted on the field form for groundwater sampling. Samples should be collected from the same depth in subsequent events.	**Response.** Footnote 2 of Table 4-3 has been modified to read as follows: *"Groundwater samples will be collected from the depth corresponding with the middle of the screened interval for each well, as determined from the total depth as installed."*
GSU General Comment 14. Baseline data set for groundwater. Eight rounds of water level gauging and groundwater sampling are recommended to capture the variability of water elevations and of chemical concentrations (e.g., two years of quarterly sampling). At the minimum, four rounds should be conducted prior to decision-making (e.g., quarterly sampling for one year or biannual sampling for two years).	**Response.** For the purposes of the RI, the initial sampling data will be used to establish preliminary information with respect to hydraulic gradient and contaminant nature and extent.
GSU General Comment 15. Tidal study. Several rounds of groundwater elevation gauging are discussed in Worksheet #17 – Sampling Design and Rationale, to assess tidal effects on groundwater elevations, gradients, and flow at the SSA. However, a tidal effects study is not discussed elsewhere in the RI WP. Please resolve this discrepancy. Describe the tidal study in more detail.	**Response.** A formal tidal study is not planned at this time. The text in Worksheet #17 has been revised accordingly..
Specific Comments and Recommendations	
GSU Specific Comment 1. Cover and title page. Include the name of the consultant that prepared the RI WP (i.e., NOREAS, Inc.) on the cover and the title page.	**Response.** NOREAS has been added to the cover and title pages of the Work Plan.

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GSU Specific Comment 2. 1.0 Introduction. The first sentence of the fourth paragraph contains an incomplete phrase: "The SSA consists of approximately 38uplands [sic], wetlands and tidal mudflat areas…" Perhaps the acreage is missing. Please revise the text.	**Response.** The text has been revised to indicate: *"…approximately 38 acres of uplands, wetlands, and tidal mudflat areas…."*
GSU Specific Comment 3. 2.2 South Shore Area Description and History. The text says (third paragraph): "Ordnance was not manufactured or refurbished in the SSA." However, on Figure 4-1, Building A259 is described as being used for "Mine Anchor Assembly and Advanced Weapons Container Maintenance." Renovation of containers was conducted in Building A259 (Table 4-1). Similar site history is associated with Building A193 (Table 4-1). Maintenance and renovation of advanced weapon containers seems to imply refurbishing. Please resolve this apparent discrepancy between the text, Table 4-1, and Figure 4-1, and describe what is meant by advanced weapons container maintenance.	**Response.** The text of Section 2.2 has been revised to remove reference to refurbishing of ordnance. The second to last sentence of paragraph three now reads as follows: *"Ordnance was not manufactured in the SSA."* This statement is now consistent with Table 4-1 and Figure 4-1.
GSU Specific Comment 4. 2.4.3 Preliminary Assessment/Site Inspection Final Summary Report – Non-Radiological Sites (1995). The titles of the individual SWMUs vary throughout the RI WP. For example, SWMU 93 is referred to as "Storm Sewer System" (Section 2.4.3), "Storm/Sewer Outfalls" (Table 4-1), and "Storm/Sewer Drains" (Table 4-2). SWMU 101 is referred to as "Ordnance Sites including Magazines" (Section 2.4.3) and "Concord Annex Ordnance and Additional Sites" (Table 4-1). For consistency, use SWMU titles assigned in the Preliminary Assessment/Site Investigation (PA/SI) report.	**Response.** References to the individual SWMU titles have been made consistent throughout the document.

GSU Specific Comment 5. 2.4.7 Munitions NTCRA for PMA and SSA (2012-2013). a) **Munitions Constituents.** The text says that soil samples collected during the NTCRA are included on Figure 2-8 Historical Soil Sampling Locations, including samples collected in Grids AE008, AF011, and AI012. However, soil samples from Grids AE008, AF011, and AI012 are not included on Figure 2-8. Also, the description for two soil samples collected from a disposal pit in Grid AI015 does not agree with the descriptions of two composite and seven discrete soil samples collected under buried drums in Grid AI015 on Figure 2-8. Please resolve these discrepancies and include all soil sampling results on Figure 2-8. b) **Non-Munitions Items Found. Buried Cans in DGM Grid AE010.** Identify the propellant in the cans. If the cans were empty but labels were legible, identify propellants as identified on the labels.	**Response.** a) Figure 2-8 has been revised to include the NTCRA sampling locations. The discrepancy between the soil sample descriptions for Grid AI015 in the text and on Figure 2-8 have been resolved. b) The propellant cans were empty and degraded. Propellant labels were either not present or were not legible due to corrosion/degradation.
GSU Specific Comment 6. 4.0 Remedial Investigation Approach. Include a discussion of Pier 35 (also known as the Mine Wharf). Identify munitions and materials loaded and unloaded at Pier 35.	**Response.** The following statement has been added to end of Section 4.1.1.1: "***Pier 35*** *Pier 35, also known as the Mine Wharf Pier extends southward from the SSA into Carquinez Strait, between Dike 12 (the IR05 shoreline) and Dike 14 (see Figure 2-1). Built in 1942, the pier was used historically to transfer mines from Building A-195 to Navy ships (Battelle, 2009). The pier remains in place but is currently not in use.* *Because of its location over the waters of Carquinez Strait, the potential for contaminant impacts associated with past activities at Pier 35 is being addressed as part of the offshore investigation at IA K (Figure 2-1). As such, no investigation of Pier 35 is planned for the SSA RI."*

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GSU Specific Comment 7. 4.2.1 Potential Chemical Constituents. Analysis of one well (SSAMW05) for dioxins/furans is described in this section. However, all well samples are specified for dioxins/furans on Table 4-3. Please resolve this discrepancy.	**Response.** A footnote has been added to Table 4-3 to indicate that SSAMW05 will be sampled for dioxins/furans in the event that they are detected in the soil samples from the Oven/Primer Pit areas in concentrations above their respective screening levels, with a contingency to analyze other samples based on the soil sampling results.
GSU Specific Comment 8. 5.3.2 Well Development Procedure. Development by bailing and surging/swapping will continue until turbidity of 50 nephelometric turbidity units (NTUs) is achieved and 5 casing volumes have been removed. Ideally, development would continue until turbidity of 5 NTUs is achieved.	**Response.** Comment noted. Reasonable effort will be made to achieve the turbidity target of 5 NTU or less during the development phase. However, given the setting, a turbidity goal of 5 may not necessarily be achievable.
GSU Specific Comment 9. 5.3.3 Groundwater Monitoring and Sampling, Number 17. Specify that groundwater samples for VOC analysis should be collected with a pump rate of about 100 milliliters per minute.	**Response.** The following sentence has been added to Item number 17 of Section 5.3.3: *"Prior to collecting samples for VOCs, reduce the flow rate to approximately 100 mL/min. "*
GSU Specific Comment 10. 5.9 Investigation-Derived Waste (IDW). Identify storage locations for IDW, and show locations on a figure.	**Response.** The staging area for the IDW will be determined during the pre-mobilization of the field activities. The handling and storage of the IDW will be in accordance with the Waste Management Plan (Appendix C of the Work Plan)

GSU Specific Comment 11. 7.4.1 Screening Levels. Use of USEPA's regional screening levels (RSLs) is proposed for soil and groundwater. DTSC's Preliminary Endangerment Assessment Guidance Manual (PEA Manual: DTSC 2014) and DTSC's Human and Ecological Risk Office (HERO) HHRA Notes 3 and 4 (which are updated as needed) provide general guidance for conducting a baseline HHRA, including use of RSLs. The PEA Manual states: "It is imperative that RSLs be used with modifications as discussed in DTSC's HHRA Note 3 so that the screening levels utilized are those specifically recommend by the DTSC. For a limited number of constituents, DTSC HHRA Note 3 recommends use of alternate screening levels, other than the RSLs. The limitation of the RSLs are discussed as follows. 1) The inhalation of VOCs intruding indoors from the sub-surface is not included as an exposure pathway in the soil RSLs. Thus, the soil RSLs for VOCs cannot be used in a PEA screening evaluation to evaluate the indoor air pathway. Soil RSLs for VOCs maybe be used to evaluate soil ingestion and outdoor ambient air exposure. Since the inhalation of vapors intruding into indoor air is not included in the development of the soil RSLs, this exposure pathway must be evaluated separately, as discussed in Section 2.5.4.5.3. 2) RSLs do not consider ecological receptors. 3) The derivation of soil RSLs does not consider the potential for contaminants to migrate to groundwater or surface water from soil however, the RSL Tables do list risk-based and MCL-based screening levels in soil (SSLs), representing chemical concentrations in soil that may affect the groundwater through leaching. The DTSC geologist and the RWQCB should be contacted regarding the protection of groundwater and surface water."	**Response.** Section 7.4.1 has been revised in response to HERO General Comment #5.

GSU Specific Comment 11 (continued). Please revise Section 7.4.1 to be consistent with the PEA Manual and HHRA Notes 3 and 4. For example, review the text of HHRA Note 3 regarding use of LeadSpread 8 for evaluating lead and, for other compounds, review *Table 1. Alternate soil and tapwater screening values currently recommended in lieu of the Spring 2013 RSL.* This section says that chemicals that do not exceed RSLs will be eliminated from further evaluation. However, the PEA Manual does not recommend eliminating chemicals that do not exceed RSLs. Chemical that do not exceed background concentrations may be eliminated. Background determinations are discussed in *Appendix B – Strategies for Establishing and Using Background estimates of Metals in Soil in the Proven Technology and Remedies Guidance – Remediation of Metals in Soil* (DTSC 2008).	**Response.** Comment acknowledged. Please refer to response to HERO General Comment #5 above. Section 7.4.1 has been revised to reflect the recommendations of HERO.
GSU Specific Comment 12. 7.4.2 Background Evaluation. Include the reference provided above (i.e., DTSC 2008) as a bullet.	**Response.** As noted above, Section 7.4.1 has been revised in response to HERO General Comment #5.

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GSU Specific Comment 13. Table 4-1 Summary of Information for SSA from Previous Site Assessments/Investigations. a) Buildings A162, A163, A169, A194 and A227. Under *Comments*, replace "TCRA" with "TSCA". b) Structure A296 High Explosives Safe Haven. Include the date of construction c) SWMU 101 Concord Annex Ordnance and Additional Sites. The text is not clear regarding the relevance of SWMU 101 with respect to SSA. Please revise the text to clarify whether SWMU 101 exists in the SSA and provide a detailed description. d) SWMU 125 South End of Island. Include SWMU 125 on Table 4-1. e) A link to the RWQCB's GeoTracker site is provided for UST A259 but not for USTs A195, A292, and A296. Provide GeoTracker ID#s and links for all USTs.	**Response.** a) The change has been made throughout Table 4-1. b) The construction date of 1941 has been added to the comments section of Table 4-1. c) After additional research the Navy has determined that SWMU 101 only applies to the IR05 area and not the SSA. Reference to SWMU 101 has been removed from the WP. d) SMWU 125 has been added to Table 4-1. e) References to the GeoTracker ID#s and links have been added to all of the USTs in Table 4-1.
GSU Specific Comment 14. Table 4-2 Summary of Proposed Approach to Soil and Groundwater Sampling RI at South Shore Area. a) Former MEC Sites. Under *Basis for Proposed Investigations*, include the SWMU 93 sample that will be analyzed for energetics and metals (i.e., SSARI-SS93B03). b) 3 USTs and 2 Dry Wells in Grid AJ015. Include the depths of the dry wells (12 feet) in the last column. c) Groundwater at SSA. To be consistent with the description in the last column, add General Minerals to the analytical parameters for groundwater.	**Response.** a) Reference to this sample is included in Table 4-2. b) The actual depth of the dry wells was confirmed to be 5 feet bgs during their removal. Reference to this depth has been added to the Basis for Proposed Investigation in Table 4-2. c) The current sampling plan for groundwater does not include analyses for general minerals. Please refer to the response to GSU General Comment # 7e above.

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GSU Specific Comment 15. Table 4-3 Summary of Planned Sampling Locations and Analytical Parameters. a) SWMU 106. Two samples are identified as SSARI-S106B04-0.5. Change one sample to SSARI-S106B05-0.5. b) Soil Samples from Monitoring Well Borings. To be consistent with Table 4-2, add General Minerals to *Analytical Group*.	**Response.** a) The change has been made to Table 4-3 to clarify. b) The current sampling plan for soil does not include analyses for general minerals. Please refer to the response to GSU General Comment # 7e above.
GSU Specific Comment 16. Table 8-1 Summary of Example Toxicity Reference Values for Soil. Expand Table 8-1 to include all analytical groups (e.g., dioxins/furans, energetics, and possible Cr VI, pesticides, and herbicides).	**Response.** See response to ERAS Specific Comment #7.
GSU Specific Comment 17. Figure 2-8 Excavation Results MEC NTCRA at SSA (2012-2013). Locations of recovered MEC (shown as red dots) on Figure 2-8 are too small to read and the font is also illegible. For the hardcopy of the report, to be retained in the administrative record, please provide a large plate for Figure 2-8.	**Response.** We assume that this comment is in reference to Figure 2-6 that depicts all of the MEC items found during the NTCRA. Figure 2-6 will be provided in a larger plate format for the next hard copy version of the Work Plan.

GSU Specific Comment 18. Figure 4-1 Summary of Proposed Soil and Groundwater Sampling Location. a) To evaluate the proposed soil and groundwater sampling locations, accurate depiction of the extent of recovered MEC is necessary. However, all recovered munitions are not shown on Figure 4-1. And, locations of munitions items are depicted in various ways, which results in an impression that fewer MEC items have been recovered examples are provided in the bullets below. • "Removed munitions and explosives of concern (MEC) locations" are shown as black crosses on Figure 4-1. However, hundreds of location where MEC was recovered in 2012 and 2013, which are shown as red dots on *Figure 2-6 Excavation Results MEC NTCRA at SSA (2012-2013)*, are not shown as black crosses on Figure 4-1. • "Non-Pit Ares where High Density of MEC Items Removed" are shown on Figure 4-1 as two red circles and two red ovals. But the magnitude and full distribution of MEC recovery is not depicted using the circles/ovals. Moreover, recovered MEC outside the circles and ovals is not depicted. • Black crosses, representing recovered MEC, are also shown on *Figure 2-3 Munitions Emergency Response Actions (1990-1995), Figure 2-5 Recovered Munitions and Explosives of Concern (MEC), and Figure 2-7 Area where High Density of MEC Items Found – MEZ NTCRA (2012-2013)*; however, these recovered MEC locations are not shown on Figure 4-1.	**Response.** a) Based on the number of recovered items (including MEC and debris), it is difficult to represent all of the NTCRA results on the proposed sampling map. The black crosses were used to represent those areas where a substantial amount and/or density of MEC items was removed.

GSU Specific Comment 18 (continued).	**Response.**
• Black crosses within yellow circles on Figure 2-7 that represent "Munitions Items Identified during Visual Survey (Not Removed)", are not shown on Figure 4-1. These locations are identified as: Propellant Charge Cans, Large Shell Casings, Primer Area 1, Primer Area 2, and Large Debris Mass. These areas have not been investigated. The MK6 depth charge was removed. However, because the MK6 depth charge was disposed in riprap, riprap areas also need to be investigated. The message that riprap should be investigated should be conveyed on Figure 2-7 and 4-1. i) Revise Figure 4-1 to include all recovered MEC. One symbol should be used for all MEC locations. Also include areas identified during the visual survey that were not investigated (including riprap areas). Distinguish uninvestigated areas (identified on Figure 2-7) from locations where MEC was recovered (e.g., by using a different symbol). Describe uninvestigated areas as potential MEC areas in the legend. In the hardcopy of the report, a large plate will be necessary to show all recovered MEC locations, as well as all uninvestigated potential MEC locations. b) Three SWMUs are shown on Figure 4-1: SWMU 91 Hazardous Waste Storage Unit in Building A195, SWMU 93 Outfalls (40, 41, 42, 207, and 208), and SWMU 106 Sanitary Sewer Pipeline. However, SWMU 101 Concord Annex Ordnance and Additional Sites and SWMU 125-South End of Island are not shown. Revise Figure 4-1 to state that SWMUs 101 and 125 are not shown on Figure 4-1 because SWMUs 101 and 125 do not have specific locations within SSA.	i. Figure 4-1 has been revised to a larger format to include the recovered MEC items. In addition, the uninvestigated areas are indicated on the revised figure. b. A footnote has been added to Figure 4-1 indicating that SWMUs 101 and 125 are not shown as they do not have specific locations identified within the SSA.

GSU Specific Comment 18 (continued).	**Response.**
c) Include Dike 14 on Figure 4-1.	c) Dike 14 has been added to Figure 4-1.
d) A symbol that is used for USTs in Figure 2-8 (i.e., a square within a square) is not explained in the legend for Figure 4-1. To be consistent with Figure 2-8, add another UST symbol at the location for three suspected USTs (i.e., T-194) on Pier 35.	d) An explanation of the UST symbol has been added to the legend of Figure 4-1. The UST symbol has not been used for the 3 suspected USTs as no evidence for their existence has been found.
e) The red diamond symbol is explained in the legend as “SWMU 93 Boring also used for MEC Sites”. However, the red diamond is shown only at one location, east of the unresolved MEC pit area in AF011. The 4 other SWMU 93 boring locations are shown as red squares. Please use either red diamonds or red squares for all SWMU 93 boring locations on Figure 4-1 (and Figures 4-3 and 4-4). Similar comments apply to SWMU 106, for which red squares and red crosses are both used: please use one symbol for SWMU 106 boring locations.	e) Figures 4-1 through 4-6 have been revised to simplify the representation of boring locations
f) The arrow for the approximate location of the deck marker is not pointing to the red circle location. Please change the arrow to point to the red circle.	f) The location of the arrow has been moved to point to the red circle
g) Building A292 should be shown with dashed lines, indicating that Building A292 has been removed.	g) The figure has been adjusted to improve legibility.

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GSU Specific Comment 19. Appendix A Sampling and Analysis Plan. a) Worksheet #5 – Project Organization Chart i. Bristol Environmental is subcontractor (to NOREAS) with responsibility for MEC. However the MEC team is not shown on the organization chart. To demonstrate that the composition of the MEC team is consistent with requirements for the work to be performed, expand the box under Bristol Environmental to include UXO personnel (i.e., identify the senior UXO supervisor [SUXOS], UXO quality control [QC] officer, UXO safety officer, and UXO technicians). ii. Include the biological monitoring team on the organization chart. b) Worksheet #7 – Personnel Responsibilities and Qualifications Table i. Include Scott Bailey from Bristol Environmental (as shown in Worksheet #5) and other Bristol Environmental personnel. ii. Documentation of training for munitions personnel should be provided, as per Department of Defense Explosives Safety Board's (DDESB's) *Minimum Qualifications for Unexploded Ordnance (UXO) Technicians and Personnel, DDESB TP18.* c) Worksheet #8 – Special Personnel Training Requirements Table. Include UXO team requirements. d) Worksheet #11 – Project Quality Objectives/Systematic Planning Process Statements. Include MPPEH objectives and processes. e) Worksheet #12 – Measurement Performance Criteria. Include performance criteria for geophysical investigations and locational data.	**Response.** a) SAP Worksheet #5 i. The Project Organization Chart in Worksheet #5 has been modified to include the Bristol support team. ii. The Project Organization Chart in Worksheet #5 has been modified to include biological monitoring team. b) SAP Worksheet #7 i. Scott Bailey and other Bristol personnel have been added to Worksheet #7. ii. As noted above, the RI field activities do not involve the investigation or removal of MPPEH. The Bristol team will be providing MEC avoidance support for health and safety purposes only. As such, their UXO training will not be included in the SAP. c) The UXO team requirements have been added to SAP Worksheet #8. d) SAP Worksheet #11 has been updated to include the objectives and processes. As emphasized in the responses to previous GSU comments, the primary objective of the UXO team is to provide anomaly avoidance during intrusive activities. Handling, movement, and disposal of MPPEH is outside the scope of this investigation. e) Performance criteria, where applicable, have been added to Worksheet #12 of the SAP. As described in the responses to previous GSU comments, the geophysical investigation will be limited in scope.

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GSU Specific Comment 19. f) Worksheet #15 – Reference Limits and Evaluation Table. The screening criteria for water and soil are not necessarily the most conservative or appropriate, as indirectly acknowledged in footnotes to the table. The purpose of the screening criteria is to ensure that project-required quantitation limits (QLs) are appropriate. In the future, when site-specific criteria are established in the RI Report, QLs exceeding RI criteria should be evaluated.	**Response.** f) Please see response to ERAS Comments #10 and #11.
GSU Specific Comment 20. Appendix B Environmental Protection Plan. Field notes of the qualified biologist, documenting compliance with the biological monitoring plan, should be included as an appendix in the field report.	**Response.** The Navy has responded to comments from Cal FWS as appropriate.
GSU Specific Comment 21. Appendix C Waste Management Plan, Table 2-3 Waste Management Summary Requirements. Under "Wastewater", the last column (Disposal Requirements) says: "Wastewater will be treated by NBSD in the onsite treatment facility, unless characterized as a RCRA hazardous waste." Define "NBSD". Clarify whether onsite treatment is planned. If so, include the location of the treatment plant.	**Response.** The statement has been revised to indicate that all wastes will be characterized for appropriate disposal off-site. The last column of Table 2-3 now reads as follows: *"The wastewater will be containerized and sent off-site for disposal at an appropriate disposal facility, depending on waste classification results."*
GSU Specific Comment 22. Appendix D Accident Prevention Plan/Site Health and Safety Plan (APP/SHSP). Installation of five wells in described in Section 7.0 of APP and Section 1.0 of SHSP. Installation of seven wells is described elsewhere in the RI WP. The number of wells to be installed should be consistent throughout the RI WP.	**Response.** Comment noted.

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Comments Provided By:	Responses Provided By:
Elizabeth K. Wells, PE Water Resource Control Engineer Regional Water Quality Control Board (Water Board) San Francisco Bay Region	NOREAS, Inc.
Date Comments Received: August 15, 2014	Response:
General Comments	
Water Board General Comment 1. Revise the text in the Work Plan and Sampling and Analysis Plan to be consistent regarding the distance (in miles) between San Francisco and Mare Island. The text states that Mare Island is located both 25 and 30 miles northeast of San Francisco.	**Response.** The text of the Work Plan and SAP have been revised to indicate that Mare Island is located “northeast of San Francisco”.
Water Board General Comment 2. Change “RWQCB” to “Water Board” thought the entire document (including appendices).	**Response.** All references to RWQCB have been changed to “Water Board” in the Work Plan and associated plans located in the appendices.

Water Board General Comment 3. Provide the rationale for the proposed depths (0.5, 5, and 10 feet bgs) of the soil samples at each location. In areas where soil was excavated, confirm the soil samples will be collected from native soil. In areas where samples are proposed near pipelines (e.g., storm and sanitary sewers), confirm soil samples will be collected from 1 to 2 feet below the bottom of the pipeline.	**Response.** The proposed sample depths are intended to provide sufficient data to evaluate both human and ecological risks, and to allow for an evaluation of the nature and extent of potential impacts based on possible contaminant sources. A new paragraph four has been added to Section 4.0 and reads as follows: *"It should be noted that soil samples will be collected from three discrete depths intervals at all locations except for those few associated with shallow features. As noted in Table 4-3, a shallow soil sample will be collected at approximately 0.5 feet bgs in all locations for the purpose of evaluating potential risks to ecological and human receptors. The depths for the deeper samples are currently planned for five and ten feet bgs, but will be adjusted in the field based to provide adequate coverage below buried features (USTs, pipelines, etc.) or imported backfill. In addition, the deeper sample depth intervals may also be adjusted based on evidence for potential contaminant impact (staining, elevated headspace readings, etc.) as observed in the field."*
Water Board General Comment 4. All modifications and edits to the text should be reflected in both the main work plan and the applicable appendices (e.g., Sampling and Analysis Plan).	**Response.** Comment noted; the document will be updated as applicable..
Specific Comments – Work Plan	
Water Board Specific WP Comment 1. Section 1.0: Correct the sentence that states "The SSA consists of approximately 38upland, wetland, and tidal mudflat areas…"	**Response.** The text has been revised to state: ***"****The SSA consists of approximately 38 acres of upland, wetland, and tidal mudflat areas…"*
Water Board Specific WP Comment 2. Section 1.1: State when the Navy intends to investigate the impacts along the shorelines of the South Shore Area (SSA) and IR05.	**Response.** The items identified along the IR05 shoreline will be addressed at some point in the future under a Time-Critical Removal Action (TCRA), the timing and details of which have yet to be determined. All available information and status for these areas will be summarized in the RI Report and carried through to other CERCLA documents associated with the SSA.

Water Board Specific WP Comment 3. Section 2.2: Clarify whether only upland fill material was used to create the SSA, or if dredge material also was used. This section states that rock and soil taken from upland areas was used for fill. However, Section 2.3 states that MEC could have been included in fill material used to expand the facility boundaries.	**Response.** The statement in the first paragraph of Section 2.2 had been modified to be consistent with Section 2.3 and now reads as follows: *"The material used to construct the SSA consisted primarily of rock and soil taken from the upland areas that was placed over the clays and silts that had been deposited at the edge of Mare Island. However, dredge materials may also have been used to expand portions of the SSA in the past."*
Water Board Specific WP Comment 4. Section 2.4.1: Clearly describe the seven emergency munitions response actions. It appears that only four of these actions are described in the text.	**Response.** A total of seven emergency response actions were completed at the PMA and SSA, four of which involved the SSA. To provide clarification, the text of Section 2.4.1 has been revised as follows: *"Four separate emergency munitions response actions were completed at the SSA by Explosive Ordnance Disposal Mobile Unit Nine (EODMU9) between August 1990 and May 1995 (Weston, 2011)."*

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Water Board Specific WP Comment 5. Section 2.4.4: Specify at what depths the MEC and radioactive items were found, and define "surface" and "near-surface." In addition, state whether the Primer Pit and two Oven Pits were backfilled, and if so, specify the source of the backfill.	**Response.** The actual depths at which the MEC items and deck marker were found are not specified in the UXO Intrusive Investigation Report (Roy F. Weston, 2003), but it contains a general statement that the investigation cleared MEC items down to a minimum depth of 4 feet bgs in most locations, and down to 10 feet bgs in others. No additional specifics are given. The following sentence has been added to the first paragraph of Section 2.4.4 for clarification: *"The MEC items were removed down to a minimum depth of four feet bgs and up to ten feet bgs in locations near active or maintained utilities."* Only one radioactive item was found (the deck marker). The third paragraph of Section 2.4.4 contains the following statement regarding the find: *"The item was identified during the screening of soil excavated near Dike 14 to remove ordnance. As a result of the finding, all of the soil removed from the excavation, several hundred cubic yards, was screened for radioactive material; no additional radioactive material was identified."* The information provided in Section 2.4.4 was summarized directly from the 2003 UXO Site Investigation Report (Weston, 2003), however it does not quantify the terms "surface" and "near-surface". For purpose of clarity, reference to surface and near-surface have been removed from the second paragraph of Section 2.4.4. The 2003 UXO Investigation report indicates that the excavations were backfilled with clean soil, but does not specify the source of the fill (Weston, 2003). No additional information regarding the backfill is provided within the report.

Water Board Specific WP Comment 6. Section 2.4.6: Confirm whether the wetland areas and debris piles were investigated at a later date (if so, state in what section of the report they are discussed).	**Response.** Information included in the ISR-JV Final Remedial Action Completion Report indicates that approximately 3.5 acres of the PMA and SSA (including wetlands and some debris piles) that were not accessible during the 2006 DGM survey were surveyed prior to the start of the NTCRA. All of the Category A anomaly locations and a minimum of 20% of the Category B anomalies were subsequently excavated (including step out requirements) in accordance with the Action Memo. The following statement has been added to the first paragraph of Section 2.4.6: *"However, prior to the start of the MEC NTCRA, approximately 3.5 acres of accessible data gap area were subject to a DGM survey in 2012 and 2013 (ISR-JV, 2014). Additional details regarding the data gap survey are provided in Section 2.4.7."* A short paragraph has been added to Section 2.4.7 as follows: "*Data Gap Geophysical Surveys* *Due to issues associated with accessibility or disturbances of critical habitat, several portions of the PMA and SSA were not included in the 2006 DGM survey. Therefore, in 2012 and 2013, prior to the initiation of the NTCRA, a total of approximately 3.5 acres of accessible data gap areas were subject to a DGM survey (ISR-JV, 2013). This included areas along the shoreline that could not be surveyed using the standard EM61-MK2™ system, but were therefore surveyed with hand-held equipment.* *All of the accessible Category A anomaly locations were subsequently excavated. Category B anomaly locations were selected and excavated as appropriate, to achieve a removal rate of 20 percent or greater, including step out requirements."*
Water Board Specific WP Comment 7. Section 2.4.7: State when the Navy intends to address the IR05 shoreline, including the partially buried drum.	**Response.** Please refer to response to Water Board Specific Comment 2 above.

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Water Board Specific WP Comment 8. Section 3.6: Confirm that the conceptual site model includes any revisions that have been made in response to comments on the recent SSA Remedial Action Completion Report.	**Response.** The current conceptual site model considers all revisions to the Final RACRs.

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Water Board Specific WP Comment 9. Section 4.1.1.1: a) Sewer Pump Station (A153): Clarify if building A153, which is called a "sewer" pump station was ever used to pump sewage, including industrial waste water. b) Ordnance Warehouse (A164): Include the use of the other two portions of the building. The text only identifies the use of one of the three building compartments.	**Response.** a) Building A153 was indicated as a sewer pump station in the Environmental Baseline Survey Report (Mare Island Naval Shipyard, 1994) and is presumed to have been used for pumping sanitary wastes. Because the building sits on pilings over the water adjacent to Pier 35, no investigation of the structure is planned. However, the associated pipelines in the onshore area will be addressed under the investigation for SWMU 106 (Sanitary Sewer System). Section 4.1.1 has been modified to include the following: *"…the building is currently boarded up and not in use. Building A153 was not included in the 1995 PA/SI, therefore no additional information is provided in the 1995 PA Final Summary Report (PRC, 1995a). However, information provided in the Final Environmental Baseline Survey (EBS) Report (Mare Island Naval Shipyard, 1994) indicates that the pump station was connected to the sanitary sewer system. No reports of past leaks or releases at Building A153 were reported in the EBS."* *"…no further investigation of Building A153 is planned. Piping associated with the pump station will be addressed as part of the investigation planned for SWMU 106 (Sanitary Sewer System)…"* b) The other two portions of the building were used to stage/store ordnance. The third sentence in that section has been modified to read as follows: *"The building is divided into three compartments, one of which was used as an office; the other two were used to store ordnance."*

Water Board Specific WP Comment 9 (Continued).	**Response.**
c) Ordnance Warehouse (A165): State what kinds of cleaners were stored. Clarify whether the "evidence" for chemical impacts includes observation of staining or releases from the stored chemicals (lube oils and cleaners).	c) Information in the 1995 PA/SI only indicates that cleaners and lube oils were being stored at the time; however it does not include additional details with respect to the nature of the cleaners. Moreover, the report does not indicate any staining or other evidence for releases were observed. The report does recommend no further action for the building based on the results of the inspection, but is silent on the reason.

Water Board Specific WP Comment 10. Section 4.1.1.2: a) Ordnance Segregation/Hazardous Waste Storage (A195): State whether the 1000-gallon diesel underground storage tank (UST) was used to fuel the boiler. If not, clarify how the boiler was fueled, where the fuel was stored, and what action was taken to remove and close the fuel storage equipment. b) Mine Anchor Assembly and Advanced Weapons Container Maintenance (A259): Provide the rationale for the location of the borings outside the building. Based on the past uses of the building, it is not clear why samples are not being collected from beneath the footprint of the building.	**Response.** a) Based on information contained in the T-195 closure report package, the 1,000 gallon UST was used to store fuel for the boiler. The first sentence of paragraph four of Section 4.1.1.2 has been modified to read as follows: *"A 1,000 gallon capacity UST was formerly located adjacent to the northwest corner of Building A195 and was used to store diesel fuel that was used by the boiler for heating the building. The UST was removed in July 1990. The Water Board closed the UST with a letter dated October 1, 2009 (GeoTracker No. T0609560708)."* b) The last paragraph of the A259 description has been modified to emphasize the rationale at this building and now reads as follows: *"In addition, a storm drain associated with SMWU 93 is located just south of Building A259. Soil sampling will be conducted adjacent to this drain as part of the investigation for SMWU 93 (see Figure 4-3). Another soil boring will be advanced adjacent to the southwest portion of Building A259 to evaluate conditions near the DGM Grid AF011 disposal pit. The analytical data from both of these locations will also be used to evaluate subsurface soil conditions south of A259. As such, a total of four sampling locations are planned at A259 to provide information with respect to those locations around the perimeter of the building."* Based on information provided in the PA/SI, there are no floor drains in the building and the concrete floor was observed to be intact. As such, the actual locations of the two soil borings that are dedicated to A259 will be selected at the time of sampling based on observations of potential impacts to surface soil or to coincide with piping or other appurtenances that may extend from the building.

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Water Board Specific WP Comment 11. Section 4.1.2:	**Response.**
a) SWMU 93 (Storm Sewer System): Include the depths of the storm sewer pipelines and, specifically those near the proposed locations. Provide the rationale for the number of borings.	a) The depths of the SWMU 93 Storm Sewer System pipelines in the SSA are not indicated in either the 1987 RCRA Facility Assessment (A.T. Kearney, 1987) or the 1995 PA/SI (PRC, 1995) documents. However, based on the relatively shallow nature of groundwater at Mare Island, it is presumed that the pipelines are buried no deeper than approximately 5 feet bgs. The following statement has been added to the discussion of SWMU 93 sampling in Section 4.1.2: *"Although the results of the outfall sampling did not indicate evidence for discharge of industrial wastes through the storm sewer in the SSA, soil samples for the RI will be collected adjacent to the storm drains to evaluate the potential for discharges or releases of industrial or other hazardous wastes from historical activities. Given that extent of the storm sewer system in the SSA limited and is not connected to other waste discharge systems that serviced the more active, upland portions of the shipyard in the northern portion of the island, the storm drains are considered the most likely location where wastes could potentially have been discharged at the SSA in the past. In addition, at least one soil sample will be collected adjacent to each of the storm sewer lines approximately every 100 to 150 feet downstream of the catch basins to provide additional information regarding potential impacts between the storm drains and outfall locations. The spacing of samples between 100 to 150 feet along the pipelines is adequate because impacts limited to areas between the samples are unlikely to produce unacceptable risk. "*

Water Board Specific WP Comment 11. Section 4.1.2: b) SWMU 106 (Sanitary Sewer System): Include the depths of the sanitary sewer pipelines and, specifically those near the proposed locations.	**Response.** b) As indicated for SWMU 93 above, the depth of the SWMU 106 (Sanitary Sewer System) pipeline in the SSA is not indicated in the RFA or PA/SI documents. However, the samples planned for those locations along the SWMU 106 pipeline will extend down to a minimum of 10 feet bgs and will be collected from deeper depths to obtain samples approximately 1 to 2 feet below the piping, if warranted based on observations in the field. The discussion of SWMU 106 sampling in Section 4.1.2 has been modified to read as follows: "*Soil samples from the 21 borings located near the SWMU 106 sanitary sewer line will be collected from depths of 0.5, 5, and 10 feet bgs. In some locations, the deepest sample may be collected from depths below 10 feet bgs to provide a sample from at least 1 to 2 feet below the bottom of the pipe*."
Water Board Specific WP Comment 12. Section 4.1.3: If disposal pits were excavated and backfilled, explain the purpose of the 0.5-foot sample.	**Response.** The disposal pits were excavated and backfilled with native soil. Although it is clear that the soil in these locations has been reworked, the 0.5-foot bgs sample will be necessary to conduct the ecological risk assessment in accordance with DTSC protocols. Though reworked, the soil at 0.5 feet does represent current conditions of the near surface soil that would be encountered by ecological receptors that forage in the near surface soil. The following sentence has been added to the end of paragraph 4 of Section 4.1.3: *"Although the debris pit excavations were backfilled with reworked native soils following the debris removal, samples from the 0.5 feet bgs depth interval will be necessary to conduct ecological risk assessment evaluations for current conditions."*

Water Board Specific WP Comment 13. Section 4.1.4: If the primer pit areas were excavated, include the depth of excavation and explain the purpose of the 0.5-foot sample.	**Response.** As noted in the response to GSU General Comment 10(b)(iv) above, all of the samples from the Oven/Primer pit areas will be collected from outside the footprint of the excavations. Figures 4-1 and 4-5 have been revised such that boring SSARI-PPB04 will be collected from outside the Primer Pit excavation area. The 0.5-foot samples will be used to represent surface soil for the purposes of the human health and ecological risk assessments.
Water Board Specific WP Comment 14. Section 4.1.5: Buried Drums in DGM Grid AA009: Include the depth at which the PAHs were detected.	**Response.** As noted in Section 4.1.5, the PAHs were detected in two of the four samples collected from approximately 6 feet bgs following the excavation and removal of the drums.

Water Board Specific WP Comment 15. Section 4.2: Unless deeper groundwater will be sampled, clarify objective (3) to state that the evaluation of general quality will be of "shallow" groundwater. Discuss how seven wells will provide sufficient data for the entire SSA area and provide the rationale for not collecting groundwater samples downgradient of all potential source areas.	**Response.** The first sentence of Section 4.2 has been revised to clarify that the objective applies specifically to shallow groundwater and now reads as follows: *"…and (3) to evaluate the general quality of shallow groundwater at the SSA."* Although it is reasonable to assume that groundwater likely flows southward from the uplands towards Carquinez Strait, the actual flow direction and hydraulic gradient are not known at this time. The locations of the seven planned wells have generally been selected to evaluate potential contaminant source areas (presuming a south/southeasterly flow pattern) and to determine groundwater flow and gradient conditions across the SSA. One additional monitoring well (SSAMW-08) has been added to provide additional coverage south of the Oven/Primer Pit area. Each of the likely source areas has a groundwater well associated with it down gradient of the likely groundwater flow. A new Table 4-4 has been added to the Work Plan to summarize the rationale for each of the eight well locations. A copy of Table 4-4 is provided as an attachment to the RTCs along with updated Figures 4-1 and 4-7 showing the well locations. The following statement has been added to the third paragraph of Section 4.2 as follows: "The rationale for each of the groundwater monitoring wells is described in Table 4-4."

Water Board Specific WP Comment 16. Section 4.2.2: Clarify how the locations of the wells were "selected to provide information with respect to hydrogeologic conditions." State whether an evaluation of tidal influence will be conducted, and if so, how.	**Response.** With respect to the rationale for the well locations, please see the response to Water Board Comment #15 above. Under the current plan, a total of eight wells will be located across the SSA in both the upland and near shoreline areas. The wells are expected to provide a good cross-sectional view of groundwater conditions from the uplands to nearshore (north to south), as well as east to west. This network of wells is expected to provide sufficient coverage from which groundwater flow and gradient conditions at the site can be evaluated. Tidal influence will be inferred from the results of data collected at nearby sites such as IR05 and PMA. .
Water Board Specific WP Comment 17. Section 5.3.1: Site-specific lithology should be considered in well construction, including screen interval and total depth. Based on the proposed well construction details, it is assumed that groundwater will be present at more than 5 feet bgs (1 foot of sand above screen, plus 2 feet of bentonite pellets, plus 2 feet of bentonite grout). Discuss how the well will be constructed if groundwater is encountered at depths shallower than 5 feet bgs.	**Response.** The lithology at each well location will be taken into consideration in determining the total well depth and screen intervals. In the event that groundwater is encountered during drilling at depths shallower than 5 feet bgs, a minimum seal of 1-foot of bentonite will be maintained. Section 5.3.1 has been modified by adding the statement below to the end of paragraph five, which now reads: *"In the event that groundwater is encountered at depths of less than 5 feet bgs during drilling, the filter pack sand will be installed to a minimum of 6-inches to 1-foot above the top of the screened interval, and a minimum 1-foot thick bentonite seal will be maintained."*

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Water Board Specific WP Comment 18. Section 5.3.3: a) Water Board staff recommend modifying the sampling protocol to measure water levels in all wells first, before sampling groundwater. This allows for consistent data to be used when developing the potentiometric surface maps. b) Clarify why samples are being analyzed for natural attenuation parameters (nitrates/nitrites, sulfate, ferric iron, etc.). Section 4.2.1 did not include these analytes.	**Response.** a) The following paragraph has been added to Section 5.3.3 as paragraph two: *"Prior to sampling, groundwater level measurements will be collected from all monitoring wells first. Once groundwater levels have been measured in all of the wells, groundwater purging and sampling activities will be initiated."* b) Natural attenuation parameters are not part of the scope of this RI; reference to them in Item #16 of Section 5.3.3 was made in error. Item #16 has been revised and now reads as follows: *"Next, collect samples for analysis of VOCs first, followed by TPH-g. Collect samples for all other parameters (SVOCs, TPH-d/TPH-mo, PCBs, metals, and dioxins/furans)."*
Water Board Specific WP Comment 19. Section 5.4: Confirm that analytical detection limits will be less than screening levels.	**Response.** Please refer to the response to ERAS General Comment #11 above.
Water Board Specific WP Comment 20. Table 4-1: For UST A296, the 1998 report documenting removal of the tank (Removal of Summary Report for Underground Storage Tank Site A-296, Former Mare Island Naval Shipyard, Vallejo, California, SSPORTS Environmental Detachment, May 8, 1998) states the tank was "apparently used to store diesel fuel." In addition, the report states the tank was less than 1,100-gallons. Modify the text in the table to reflect this information.	**Response.** We understand the Removal Summary report was not specific so, Table 4-1 has been revised to include the information from the SSPORTS Closure Report. The description of UST A-296 now reads: *"A 420 gallon fuel oil/diesel UST that was located adjacent to Structure A296. The tank was removed on January 9, 1998. The Water Board closed this tank in a letter dated October 22, 2009 (GeoTracker No. T0609560708)."*
Water Board Specific WP Comment 21. Table 4-2: For the groundwater evaluation, discuss how 7 wells provide "sufficient spatial coverage" for the entire SSA area. In addition, provide the rationale for not collecting groundwater samples downgradient of all potential source areas.	**Response.** Please see response to Water Board Specific WP Comment #15 above.

Water Board Specific WP Comment 22. Table 4-3: Include the rationale for the soil sample depths. If source areas are being investigated, site-specific (source-specific) depths may be more appropriate.	**Response.** The 0.5 feet bgs sample is intended to provide near surface data necessary to perform the ecological and human health risk assessment in accordance with DTSC protocols. The deeper soil sampling depths (5 and 10 ft bgs) are generally intended to provide general coverage of the upper 10 feet of soil but are not intended to be the final sampling depths in all locations. The final sampling depths will be adjusted in the field based on observations of lithology and any evidence of potential contaminant impact (staining, elevated headspace readings, etc.). The following footnote has been added to Table 4-3: 1. *Planned depth only, actual depth may be adjusted in the field based on observations of potential sources or evidence of contaminant impact (staining, elevated head space measurements. etc.).*
Specific Comments – Sampling and Analysis Plan	
Water Board Specific SAP Comment 1. Worksheet #3: Correct Tami Nakahara's email address to tami.nakahara@wildlife.ca.gov	**Response.** Worksheet#3 of the SAP has been updated to include Ms. Nakahara's current email address.

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Water Board Specific SAP Comment 2. Worksheet #11:	**Response.**
a) Former Tanks and Dry Wells: Clarify why samples are being analyzed only for VOCs and PCBs. Include analysis for TPH, SVOCs, and metals as well. b) If the investigation results suggest that groundwater in the SSA, or portions of the SSA, meet the beneficial use criteria for drinking water, the proposed screening criteria will not be appropriate.	a) Following the removal of the former tanks and dry wells, a total of 11 confirmation soil samples were collected from beneath these features and analyzed for TPH-g, TPH-d, TPH-mo, SVOCs (including PAHs), and metals. Based on the uncertainty surrounding their former use, additional soil samples will be collected in the locations of the former dry wells and tanks and analyzed for VOCs and PCBs. This rationale is described in Sections 2.4.7 and 4.1.5 of main RI Work Plan document. The VOC, PCB, TPH, SVOC, and metals results from the confirmation sampling, following the tank removal, will be included in the data summary and evaluation for the RI Report. b) Comment noted. If investigation results suggest that groundwater at the SSA meets the beneficial use criteria, screening criteria will be updated. The footnotes for Worksheet #15.1 have been updated to include the following: *"In the event that groundwater is determined to be a current or potential source of drinking water, the screening levels will be updated accordingly."*

Water Board Specific SAP Comment 3. Worksheet #14: a) Monitoring well borings should be continuously cored for soil to collect lithologic information to assist in determining the appropriate depths for well screens. b) Measure water levels in all wells first, before sampling groundwater.	**Response.** a) Continuous core samples will be collected at all of the soil boring locations, including the pilot boreholes for the monitoring wells. Paragraph three of the Soil Sampling Procedures in Worksheet #14 already describes the use of continuous cores. b) Water levels will be measured in all of the monitoring wells prior to sampling the wells. Worksheet #14 has been revised to include the following statement: *"Groundwater level measurements will be collected from all monitoring wells before groundwater sampling is initiated."*
Water Board Specific SAP Comment 4. Worksheet #15.1: Analytes that have a detection limit greater than the screening level will need to be further evaluated to determine the level of risk posed. While a non-detect determination suggests the chemical is not present at a concentration greater than a specified limit, it could be present at a level that poses a potential risk to receptors.	**Response.** Please refer to the response to ERAS Comment #11 above.
Water Board Specific SAP Comment 5. Worksheets #15.1 and #15.2: Confirm the ESLs being referenced are from the most recently updated Water Board document. In addition, reference the document in which the Navy calculated site-specific "Tier 2 Screening Levels."	**Response.** As consistent with the approach described in the responses to HERO General Comments 4 and 9 above, Worksheet #15.1 and #15.2 have been revised to give priority to federal screening criteria (EPA RSLs and NAWQC where applicable). Site-Specific Screening Levels established at the adjacent IA FI area will be applied to TPH compounds and were derived from the following document that is referenced in the footnotes for Worksheet #15.1: *Final Addendum to Technical Memorandum and Responses to Agency Comments and Additional Supporting Information for TPH Areas 2B, 2C, 6, 9, and 10, Investigation Area F1 TPH Evaluation* (Tetra Tech, 2012)

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Water Board Specific SAP Comment 6. Worksheet #17: State why only general coverage samples for groundwater are being collected and why no samples from downgradient of potential sources are proposed.	**Response.** Please see response to Water Board Specific WP Comment #15 above.
Water Board Specific SAP Comment 7. Worksheet #18: Include the rationale for the proposed sample depths.	**Response.** Please refer to the response to Water Board Specific WP Comment #22 above. The following footnote has been added to SAP Worksheet #18: 1. Planned depth only, actual depth may be adjusted in the field based on observations of potential evidence for contaminant impact (staining, elevated head space measurements. etc.).

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Comments Provided By:	Responses Provided By:
Patrick Hsieh Department of Toxic Substances Additional Comments Dated: May 8, 2015	NOREAS, Inc.
Page 5, Response to HERO General Comment 7, Exposure Assessment: HERO concurs with using similar risk evaluation/calculation methods used for the HHRA at the IA F1 area, presumably the VLEACH trench model approach, but HERO would like the current Report to indicate its use at the South Shore Area. Please add a statement to Section 7.5.2 regarding the evaluation of trench air using the VLEACH model. HERO has no additional Comments at this time.	**Response.** The following will be added to Section 7.5.2 of the Final RI Work Plan: "The Navy developed a model approved by the DTSC during the IA FI RI (Chadux Tt, 2012) to simulate migration of chemicals in groundwater through the soil into a trench to estimate the vapor concentrations in the trench. The model consists of two parts: (1) calculation of volatile emission rates from groundwater into a trench, using the VLEACH model (Ravi and Johnson 1996), and (2) calculation of vapor concentrations in the trench air using the calculated emission rates and simple air dispersion (box) model. A full description of the model used to estimate volatilization into a construction trench will be provided in the RI Report."

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Comments Provided By: J. Michael Eichelberger, Ph.D. Staff Toxicologist Ecological Risk Assessment Section (ERAS) Human and Ecological Risk Office (HERO) Department of Toxic Substances Additional Comments Dated: May 1, 2015	Responses Provided By: NOREAS, Inc.
General Comments	
ERAS Additional Comment 1 (re: Navy Response to ERAS General Comment 1). Comment noted with the provision that ERAS may request changes to the RI depending on the exposure parameters that are presented.	**Response.** Comment noted. The Navy has agreed (in meeting 5/20/15 with DTSC) to coordinate the input and exposure parameters with the ERAS group prior to the production of the draft RI.
ERAS Additional Comment 2 (re: Navy Response to ERAS General Comment 2). **(Part 1):**ERAS agrees that nature and extent is the foremost concern during early sampling of a site. However, sampling also needs to consider the requirements necessary for conducting a risk assessment. These requirements include sufficient samples at the appropriate depth to develop a statistically acceptable exposure point concentration. The analysis of the data must also be conducted at ecologically relevant reporting limits that are appropriate for relevant ecological screening levels. The screening levels are used as a guide to determine the extent of contamination.	**Response (Part 1).** Comment noted.

ERAS Additional Comment 2 (Continued) **(Part 2):** The section of the response that ERAS has underlined above is not clear. The response indicates that the 0-0.5 ft bgs interval will be collected. However the underlined sentence appears to indicate that the 0-2 ft bgs interval will be used for evaluation of surface soil exposure to ecological receptors. The 0-0.5 ft bgs interval is the portion of the soil profile that presents the highest exposure to ecological receptors. ERAS again requests that if the 0-0.5 bgs interval is available, it is the interval that should be used for the surface soil exposure interval. **(Part 3):** Comment accepted.	**Response(Continued)** **(Part 2).** Soil samples from the 0-0.5 ft bgs sampling interval will be used to evaluate surface soil exposures for ecological receptors. **(Part 3).** Comment noted.
ERAS Additional Comment 3 (re: Navy Response to ERAS General Comment 3). Comment noted.	**Response.** No action needed.
Specific Comments	
ERAS Additional Comment 1 (re: Navy Response to ERAS Specific Comment 1). The response does not indicate if the different areas will be assessed as separate exposure units in the risk assessment. For example, the mud flat samples should not be grouped with all other samples on site for establishing an exposure point concentration.	**Response.** The majority of soil sampling is planned for the uplands areas, with the exception of 6 locations within and around the former Oven and Primer Pits. Given their locations in the wetland areas, they will be treated separately from the upland area samples with respect to the ecological risk evaluations, including the establishment of exposure point concentrations.
ERAS Additional Comment 2 (re: Navy Response to ERAS Specific Comment 2). The potential danger to this approach is the possibility that DTSC/ERAS may not agree with input parameters to the risk assessment after the risk assessment has been performed. ERAS could potentially not be able to recommend acceptance of the risk assessment findings to the DTSC project manager if there has not been prior agreement to the technical inputs to the risk assessment.	**Response.** Comment noted. The Navy has agreed (in meeting 5/20/15 with DTSC) to coordinate the input and exposure parameters with the ERAS group prior to the production of the draft RI.
ERAS Additional Comment 3 (re: Navy Response to ERAS Specific Comment 3). Comment noted.	**Response.** Noted, no action required.

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ERAS Additional Comment 4 (re: Navy Response to ERAS Specific Comment 4). Please respond to ERAS Specific Comment Number 2.	**Response.** As noted above, soil samples from the 0-0.5 ft bgs sampling interval will be used to evaluate surface soil exposures for ecological receptors.
ERAS Additional Comment 5 (re: Navy Response to ERAS Specific Comment 5). **(Part 1):** Comment Accepted. **(Part 2):** If contamination was detected that posed a significant exposure and threat to ecological receptors, and development was delayed, the existing exposure pathway would necessitate some interim measure that would sever the exposure pathway.	**Response.** **(Part 1):** Noted, no action required. **(Part 2):** Comment noted.
ERAS Additional Comment 6 (re: Navy Response to ERAS Specific Comment 6). To ERAS' knowledge the eastern grey squirrel, along with other introduced non-native fox squirrel and the native western grey squirrel, do not burrow underground, but rather build nests in tree canopies. As the name implies the California ground squirrel burrows underground and is not a good surrogate for 'tree' squirrels. Although all three of the tree squirrel species forage on the ground, the exposure for a ground burrowing species should be expected to be much greater than an arboreal species.	**Response.** Comment noted. The California ground squirrel will be used as a surrogate burrowing mammals at the site.
ERAS Additional Comment 7 (re: Navy Response to ERAS Specific Comment 7). **(Part 1):** ERAS would like to have a chance to review and comment on the selected TRVs prior to a risk assessment being conducted.	**Response.** **(Part 1):** Comment noted. As discussed during the May 20, 2015 teleconference call, TRVs will be provided to ERAS for review and coordination with Navy prior to initiating the ecological risk assessment activities.

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ERAS Additional Comment 7 (Continued). **(Part 2).** ERAS concurs with the use of Santa Susana Field Laboratory inhalation screening levels. ERAS is reticent about using the Navy BTAG high TRVs for establishing clean up goals since they are largely based on mid-range effects rather than Lowest Observable Adverse Effect Levels. However, ERAS would like to have a dialog on the TRVs.	**Response (Continued).** **(Part 2):** Comment noted. As discussed during the May 20, 2015 call, the Ecological Risk assessment will evaluate screening levels/clean-up goals using TRVs based on LOAELs, where applicable. In addition, the TRVs will be provided for review and discussion and coordination prior to the initiation of the ecological risk assessment activities.
ERAS Additional Comment 8 (re: Navy Response to ERAS Specific Comment 8). Comment noted.	**Response.** Noted, no action required.
ERAS Additional Comment 9 (re: Navy Response to ERAS Specific Comment 9). ERAS understands the sampling strategy for the burn pits. However, If no sampling is proposed for the wetlands, there needs to be a discussion of fate and transport from shore to the wetlands and if sampling adjacent to the wetlands exceeds relevant ecological screening levels, sampling within the adjacent wetlands should be considered.	**Response.** Comment noted. In addition to the sample locations planned for the burn pits, there are additional soil sampling locations proposed adjacent to the former pits in the wetland area. There are also samples proposed just upgradient of the wetlands along the piping (Figure 4-1). If sampling at the edge of the wetlands indicates the presence of contamination, this will be discussed along with fate and transport in the RI. Additional sampling may be suggested at that time.
ERAS Additional Comment 10 (re: Navy Response to ERAS Specific Comment 10). ERAS is not sure where Worksheet 15.1 and 15.2 are in the report. ERAS conducted a pdf 'Find' query and did not note a reference to a 'worksheet'.	**Response.** Worksheets 15.1 and 15.2 are part of the Sampling and Analysis Plan (SAP) that constitute Appendix A of the Work Plan. Copies of the worksheets are included as an attachment to these RTCs. The relevant portions of the worksheets have been updated to include the ecological screening levels (Eco-SLs).

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ERAS Additional Comment 11 (re: Navy Response to ERAS Specific Comment 11). ERAS concurs that screening levels should not be lower than the Mare Island DTSC approved ambient fill concentrations. However, it does not agree with the use of human health screening levels for assessing ecological risk. This is not a sound approach and ERAS will not recommend to the DTSC project manager that these are acceptable screening levels.	**Response.** The Navy has clarified that it agrees that human health screening levels (HHSLs) should not be used for assessment of ecological risk. The samples will be compared to HHSLs and EcoSLs as part of the nature and extent (N&E) discussion in the RI. The analytical methods and associated detection limits identified in the Sampling and Analysis Plan (SAP) are appropriate for both human health and ecological SLs. No COPECs will be screened out based on the comparison to screening levels. All COPECs will be carried forward and evaluated in the ecological risk assessment portion of the RI. The approach for the selection of initial screening level criteria is consistent with what was approved and used at the IA F1 Area RI (Chadux Tt, 2012). However, based on discussions between the Navy and DTSC in the 5/20/15 call and clarifications in the 5/28/15 BCT meeting, the Navy has agreed to include EcoSLs for soil in worksheet 15.2 attached along with worksheet 15.1 to these RRTCs. (Worksheet 15.1 has not been modified as the RI will involve groundwater sampling only, no surface water sampling, in which case EcoSLs would not be applicable). The initial phases of the Human Health and Ecological risk assessments will include an evaluation of all detected chemicals. For the ecological risk assessment, appropriate ecological screening criteria will be applied as described in Section 8.0, as follows: "Potential ecological risk will be evaluated by comparing soil data with the ecological soil screening levels (Eco-SSL) (EPA 2008b) and the lowest available ecological screening levels from Oak Ridge National Laboratory (Efroymson and others 1997a, 1997b) or (Talmage and others, 1999). Conservative assumptions will be used, including using the maximum detected soil and groundwater concentrations and a Site Persistence Factor (SPF) of 1.0 (meaning that wildlife will be assumed to spend 100 percent of their time at the site)."

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ERAS Conclusions to Navy Responses. The report does not provide sufficient information to facilitate media sampling that will identify nature and extent of chemical contamination that might be injurious to ecological receptors. To ensure that sampling does identify levels of chemicals that might be injurious, media concentrations need to be compared to relevant ecological screening levels and these screening levels should not exceed the laboratory reporting limits. Soil sampling depths should be performed at 0-0.5 feet, 2-3 feet and 5-6 feet. Although methodology has been offered for performing an ecological risk assessment, the methodology is not complete and does not represent a work plan for conducting an ecological risk assessment. An ecological risk assessment work plan will need to be conducted at a later date following completion of the media sampling.	**Response.** As noted in the responses above, it was agreed during the October 31, 2014 teleconference call, and confirmed during the May 20, 2015 call, that the Navy will coordinate with ERAS prior to the preparation of the ecological risk assessment to provide essential input parameters and discuss appropriate methodologies. As such, a separate stand-alone risk assessment work plan will not be provided. It was further agreed that the coordination and submittal of risk assessment parameters would not need to be completed prior to the initiation of the field sampling activities, as long as it takes place before the risk assessment activities begin in earnest. With regard to the soil sampling depths, it was agreed during the May 20, 2015 call that the current plan to collect soil samples from 0.5 feet, 2-5 feet, and below 5 feet bgs would be sufficient to conduct the ecological risk assessment.

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Comments Provided By:	Responses Provided By:
Tami Nakahara, Senior Environmental Scientist (Specialist) California Department of Fish and Game (CDFW) Office of Spill Prevention and Response (OSPR) Comments Dated: April 24, 2015	NOREAS, Inc.
CDFW Specific Comment 1. Specific Comment #6. Appendix B Environmental Protection Plan, page 7-2, Section 7.4 Pickleweed removal. CDFW-OSPR requested the Navy's avoidance measure be revised to state, "For any work that requires vegetation removal, a qualified biologist will visually inspect for rare plants that may be present, during the time of year when the species are evident and identifiable, and prior to the start of field activities." The Navy responded that the measure will not be modified because, "Based on the 2011 biological survey conducted by H. T. Harvey & Associates, Mason's lilaeopsis (Lilaeopsis masonii) is the only rare plant species that has been identified in the SSA and PMA where its presence was limited to the coastal salt marsh areas." According to the 2011 biological surveys, "The purpose of the surveys was to describe the existing conditions of the site and determine the potential for occurrence of special status species" (H.T. Harvey & Associates, 2011), not to confirm the presence or absence of special status species at the PMA and SSA.	**Response.** Consistent with previous agreements between the Navy and CDFW, plants that are listed as rare under the Federal and State Endangered Species Acts and present in the work areas are afforded mitigation measures during response actions as appropriate. Of the 13 different plant species identified as having potential to occur at the SSA, only 4 are listed as rare or endangered under Federal and California regulations. These include: • Mason's lilaeopsis (blooms April-November) - **State listed Rare** • California seablite (July-October) - **Federally listed Threatened and State-listed Endangered** • Contra Costa goldfields (March-June) - **Federally listed Endangered and State listed Rare** • Soft bird's beak (July-November) - **Federally listed Endangered and State listed Rare**

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CDFW Comment to Navy Response (continued).	**Response (continued).**
However, CDFW-OSPR does not agree the surveys are adequate for determining the absence of rare plants on or adjacent to the site because the survey was conducted on December 8, 2010 when none of the rare species surveyed for were in bloom. These rare species include: • Mason's lilaeopsis (blooms April-November) • California seablite (July-October) • Contra Costa goldfields (March-June) • soft bird's beak (July-November) • San Joaquin saltbush (April-October) • Congdon's tarplant (May-October) • Marin knotweed (May-August) • Suisun Marsh aster (May-November)	Additionally, in 1993 a study of soft bird's beak conducted on behalf of CDFW concluded this species had been extirpated at Mare Island and that the soil salinity was too high to support this species (Napa Botanical Survey Services, 1993). The biologist also noted that historic information suggested that the river was much fresher at one time. The USFWS agreed with the 1993 survey in an email to the Navy in 2012 (Raabe, 2012) and the USFWS withdrew its request for a soft bird's beak survey prior to the PMA and SSA Munitions NTCRAs. Inspections will not include soft bird's beak. The sampling is scheduled to begin late June/ early July 2015, is limited in scope, and vegetation removal is not planned. However, in order to provide information for future work, the qualified biologist will perform a visual inspection for Mason's lilaeopsis California seablite, and Contra Costa goldfields in June. An additional visual inspection will be conducted in early July 2015, prior to the field activities, to overlap the blooming periods of the California seablite.

CDFW Comment to Navy Response (continued).	**Response (continued).**
• Pappose tarplant (May-November) • Point Reyes bird's-beak (May-June) • round-leaf filaree (March-May) • fragrant fritillary (February-April) • chaparral ragwort (January-April). In addition, Table 1 of the survey lists the potential for occurrence on site for most of the rare plant species as "presumed absent, not "confirmed absent, due to lack of visual confirmation during the flowering periods. The survey also uses the lack of past observations in the California Natural Diversity Database (CNDDB) to support their presumptions that a species is absent from the sites. Please note, CNDDB only contains records of species occurrences that have been submitted to the database. If species have been observed, but not reported to CNDDB, then these records are not contained in the database. Therefore, a lack of records in CNDDB cannot be used to assert that a rare plant species is not present on or within the vicinity of the project site. Based on the information in Table 1, potential habitat exists on or adjacent to the sites for these rare species. As a result, there is the potential for rare plant species, in addition to Mason's lilaeopsis, to be on site and to be affected by remedial activities. CDFW-OSPR again requests a qualified biologist "visually inspect for rare plants that may be present, during the time of year when the species are evident and identifiable, and prior to the start of field activities." CDFW-OSPR will conduct site visits during remedial activities to document any take of State and Federally-protected species that may occur due to the Navy's actions.	Section 7.4 of Appendix B Environmental Protection Plan has been revised to read as follows: “Inspections for Mason's lilaeopsis California seablite, and Contra Costa goldfields will be performed in June and an additional visual inspection will be conducted in early July 2015, prior to the field activities to overlap the blooming periods of the California seablite.”

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CDFW Specific Comment 2. Specific Comment #7. Appendix B Environmental Protection Plan, page 7-3, Section 7.6 Monitoring During Protected Species Nesting Season. The text states, "If work is already occurring within the area when protected nesting season starts, a protected species nesting visual inspection will not be required." CDFW-OSPR requested the measure be revised to state, "The qualified biologist shall look for new nests at least twice per week, during remedial activities that occur during nesting season." The Navy responded that their approach to visually inspect for nests is consistent with what was implemented during the recently completed NTCRA work at the PMA and SSA and no changes to the text are planned. Please note, according to the NTCRA PMA-SSA Biological Monitor Daily Reports, the qualified biologist observed birds starting to nest after remedial activities had begun during the previous NTCRA work at the PMA and SSA (Integrated Solutions for Remediation, JV, 2014). Therefore, it is likely birds will start nesting after remedial activities commence during the RI work at the SSA. CDFW-OSPR again requests the qualified biologist "look for new nests at least twice per week, during remedial activities that occur during nesting season." CDFW-OSPR will conduct site visits during remedial activities to document any take of State and Federallyprotected species that may occur due to the Navy's actions.	**Response.** Section 7.6 of Appendix B Environmental Protection Plan has been revised to indicate the following: The proposed activities are not response or remedial actions but rather a field sampling effort. There will be no staging, storage or stockpile areas. The field investigation consists of collecting samples at individual locations and the onsite biologist will visually inspect for nesting birds prior to work. The field crew will not return to that sampling area after the samples have been collected and therefore multiple inspections of the sampling locations will not be required. The Navy will have a biologist onsite to conduct inspections on a daily basis during work in potential habitat areas.

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Comments Provided By: Eileen Hughes, P.G. 8170 Engineering Geologist, Geological Services Unit (GSU) Geological Services Branch Brownfields and Environmental Restoration Program Department of Toxic Substances Control Comments Dated: May 8, 2015	Responses Provided By: NOREAS, Inc.
Comments and Recommendations (Non-MEC Issues)	
GSU Comment 1. In general, the RTCs are responsive to GSU's comments. Approval of RTCs is recommended, provided the following comments are addressed. Also, it is recommended that GSU review the final work plan to that the final work plan is consistent with the RTCs.	**Response.** Comment noted. In the 5/20/15 meeting the GSU representative indicated this was meant as an internal comment. Additionally, during this meeting the DTSC agreed to review these RRTCs and reply to the Navy within one week.

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GSU Comment 2. RTC re: GSU General Comment 1e. GSU had recommended that a field report summarizing the results of this investigation be provided. The field report should include all the necessary documentation of the field activities (e.g., well construction diagrams, boring logs, sampling forms, field notes, investigation-derived waste documentation [i.e., for storage, transport, and disposal] documentation, laboratory reports, etcetera). The field report for this investigation should be distinguished from the final remedial investigation report (RI Report) for the SSA, which would contain summaries of all field investigations, including this field investigation and any future investigations. Recommendation a) Please clarify: Does the Navy intend that the report for this investigation will be a field report for this investigation or the final RI Report for the SSA? If the report of this field investigation is intended to be the final RI Report for the SSA, then the data gaps identified in GSU's comments (e.g., GSU General Comment 1) will continue to exist and, because the site characterization is incomplete, the final RI Report will be incomplete. Additional discussion regarding the final RI Report may be warranted.	**Response.** As discussed during the May 20, 2015 teleconference call, a separate field and/or data report will not be provided. Summaries of the field activities, data, and documentation (including recommendations for additional investigation, where warranted) will be provided in the RI Report. In addition, the RI report will provide summaries of all available historical data obtained at the SSA prior to the RI activities. These historical data will be incorporated into a comprehensive evaluation of environmental conditions that will be provided as a key component of the RI Report.

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GSU Comment 3. RTC to GSU General Comment 7e. Pesticides and herbicides may have been used as vegetation and animal control measures in munitions areas, to minimize the potential for fire and explosion, as well as biological hazards. GSU recommended analysis of shallow soil samples for pesticides and herbicides. In response, the Navy added pesticides/herbicides to samples to be collected at 0.5 feet below the ground surface (fbgs) at Buildings A195, A259, and A296. These locations were selected by the Navy because they were considered to be most likely areas for pesticide/herbicide applications and because these areas have not been re-worked during recent field activities. This approach is acceptable to GSU. However, analysis for pesticides and herbicides should also be considered for the wetland areas and for upland areas adjacent to the wetlands.	**Response.** Based on discussions during the May 20, 2015 teleconference call, analyses for organochlorine pesticides (OCPs) will be added to the analytical suite planned for the 0.5 feet bgs soil samples collected at 5 upland locations around Buildings A195, A259, and A296. These locations were chosen to represent the areas where pesticides would most likely have been applied. In addition, the surface soil sample from planned well MW05 will also be analyzed for pesticides due to its proximity to the wetlands area. As a contingency measure, all of the soil samples collected during the RI will be temporarily archived by the analytical laboratory. If pesticides are detected above screening levels in the samples from the upland areas, additional archived soil samples from locations near and/or within the wetlands may be analyzed for pesticides. During the May 20, 2015 call, ERAS commented that herbicides would not likely represent a concern for this area. Therefore, herbicides will not be included as part of the planned analytical suite at this time.
GSU Comment 4. RTC to GSU General Comment 7d. GSU had noted that sampling at 0.5 fbgs for volatile organic compounds (VOCs) (e.g., in the Oven/Primer Pit area) is not recommended because VOCs are likely to have evaporated from such shallow soils. The Navy responded that analyzing the 0.5 fbgs samples for VOCs will not be changed. GSU reiterates that samples collected at 0.5 fbgs for VOC analysis will be considered low-biased for VOCs: such samples will not demonstrate the absence of VOCs in the sampling vicinity (e.g., at depths below 0.5 fbgs).	**Response.** Based on discussions during the May 20, 2015 teleconference call, DTSC agreed that VOC results from the 0.5 ft bgs sample would likely be biased low and would not provide value to either the human health or the ecological risk assessment evaluations. As such, DTSC and the Navy agreed that VOCs would not be analyzed at any of the surface soil samples (0.5 ft bgs) during the RI. This change has been made in the appropriate sections of the Final Work Plan and SAP documents.

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GSU Comment 5.	**Response.**
RTC to GSU General Comment 10ci a) The RTC says that samples will be collected at 10 fbgs only below the three excavations (i.e., for Oven Pit 1, Oven Pit 2 and the Primer Pit) to determine the vertical extent of potential impacts below the excavations. However, there is no soil boring location within the Primer Pit shown on Figure 4-5 Proposed Soil Sampling Locations, Oven/Primer Pit Areas. Please resolve this discrepancy. b) Three sampling locations in the pits will be analyzed only at 10 fbgs. Therefore, only four surface samples (at 0.5 fbgs) and four shallow samples (at 5 fbgs) will be collected. Four surface samples and four shallow samples are not sufficient for characterizing the surface and shallow soil in this area.	a) Figure 4-5 has been revised to illustrate the planned location of soil boring SSARI-PPB04 within the footprint of the Primer pit. b) The soil samples from this area are intended to confirm the results of the previous investigation conducted following the removal of the debris from the area. 3 samples will be collected from within the footprint of the former debris pits at approximately 10 ft bgs. Another 6 soil sampling locations are planned for this area at 3 depths (soil samples will be collected from the soil boring locations shown on the figure and also from the pilot borehole for the 2 groundwater monitoring wells in the area). These 6 locations include 2 locations upgradient of the pits, 1 location between the pits, and 3 locations downgradient of the pits (See Figure 4-5). Including the 3 locations where the soil at the base of backfilled debris pits is being sampled, a total of 9 locations will be sampled for soil in this area. Based on the results of the previous confirmation sampling and discussions with the DTSC on the 5/20/15 and 5/28/15 meeting calls, this level of coverage is expected to be sufficient to characterize any potential residual impacts to the area.

GSU Comment 5 (continued). c) GSU questioned why only 20% of samples would be analyzed for dioxins/furans and requested clarification on how samples for dioxin/furan analysis would be selected. And, HERO General Comment 2 recommended that all samples from the area be analyzed for dioxins/furans. A total of fifteen samples will be collected in this area; therefore, only three samples (i.e., 20% of 15) will be analyzed for dioxins/furans. The Navy says that if burned materials are observed, the samples containing burned material will be selected for dioxins/furans analysis. And, if no burned material is observed, one sample from each depth will be selected (i.e., 0.5 fbgs, 5 fbgs, and 10 fbgs). One sample from each depth will not be sufficient to characterize the distribution of dioxins/furans in the vicinity.	**Response (continued).** c) Based on discussions during the May 20, 2015 teleconference call, additional analyses for dioxins/furans will be added to the samples from all 3 depth intervals the 3 locations in the wetlands surrounding the pits as well as from the 3 samples collected from below the former pits. Section 4.1.4 for the Final Work Plan has been revised to reflect this change as now reads follows: "In addition to the analytes described above, selected samples from the Oven/Primer Pit areas will also be analyzed for dioxins/furans given that visual evidence of discolored soils indicated that debris was once disposed by burning in these locations (Section 2.4.4). Although the affected (discolored) soil and debris within the pits was ultimately excavated and removed from the site (Roy F. Weston, 2003), soil samples from the three borings located in the wetlands surrounding the former pits, as well as those collected from beneath each of the three former pits, will be analyzed for dioxins/furans. In particular, soil samples from all three discrete depth intervals (0.5, 5.0, and 10.0 feet bgs) at the three borings located in the wetlands surrounding the former pits will be analyzed for dioxins/furans. In addition, at the borings located within the footprints of the former pits, the soil samples collected from beneath the bottom of the former excavations (at the 10 feet bgs interval) will also be analyzed for dioxins/furans. The final selection of samples for dioxins/furans analysis may be biased in the field based on observations of soil conditions at the time of sampling. Specifically, samples where visual evidence of burnt material (discoloration) is observed may be selected for analysis for dioxins/furans. The approximate locations of the soil samples proposed for this area are depicted on Figure 4-5."

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GSU Comment 6. RTC to GSU General Comment 12hiii. Regarding Figure 5 Proposed Groundwater Monitoring Well Construction Details, GSU had asked that the Navy label the 6-inch layer between the filter pack and the bentonite seal. In the RTC, the upper 6-inch layer has been identified as concrete. However, installation of 6 inches of concrete between the filter pack and the bentonite seal is not acceptable. Fine sand or bentonite pellets should be installed as a transition zone between the filter pack and the bentonite seal, to prevent intrusion of the bentonite seal into the filter pack. Please provide a revised Figure 5.	**Response.** The response assumed that GSU was referring to the uppermost region of the annular space near the surface (above the grout mixture and was made in reference to that near surface completion. The 6-inch layer above the top of the screen was previously unlabeled as it consists of filter pack material (#2/16 sand or equivalent). The call-out for that 6-inch area on Figure 5-1 was intended to illustrate that the filter pack will extend a minimum of 6 inches above the top of the screen. A revised Figure 5-1 is provided as an attachment to this document.
GSU Comment 7. RTC to GSU Specific Comment 10. GSU requested that storage locations for investigation-derived waste (IDW) be shown on a figure. The Navy responded that the IDW storage location will be determined during pre-mobilization of the field activities. When the IDW storage location is determined, please provide a figure showing the IDW storage location.	**Response.** Comment noted.
Comments and Recommendations (MEC Issues)	
GSU Comment 1 (MEC). In general, the RTCs are responsive to GSU's comments. Approval of the RTCs is recommended, provided the following comments are addressed. Also, it is recommended that GSU review the final work plan to check that the final work plan is consistent with the RTCs. For example, revisions to Worksheet #7 regarding the unexploded ordnance (UXO) team's qualifications and training could not be checked because a revised Worksheet #7 was not provided.	**Response.** Comment noted. In the 5/20/15 meeting the GSU representative indicated this was meant as an internal comment.

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GSU Comment 2 (MEC Issues). The Navy responded that the ESS is an internal Navy document, is not intended for public distribution, and will not be included in the RI Work Plan or the RI Report. Communications with the Navy regarding the SSA ESS parallel previous communications with the Navy regarding the Investigation Area K (IAK) ESS. Previously, GSU had requested that the ESS for IAK be included in the IAK work plan. Initially, the Navy's RTC to GSU's request for the IAK ESS was similar to the current RTC to GSU's request for the SSA ESS. However, GSU reiterated the request for the IAK ESS. GSU also provided several examples of ESSs which existed within the public domain (e.g., on the internet), including examples from Mare Island. The Navy then provided the IAK ESS as a separate document (i.e., the IAK ESS was not included within the IAK work plan). Recommendation a) GSU reiterates the request for the SSA ESS. Similar to the IAK ESS, the SSA ESS can be submitted under separate cover (with NOSSA approvals and communications with NOSSA regarding revisions to the ESS). However, critical elements of the SSA ESS (described in the quote above) should be identified in the work plan.	**Response.** The DDESB approval of the ESS-DR will be provided to the DTSC separately for reference. As discussed during the May 20, 2015 teleconference and subsequent calls between the Navy and DTSC, the Navy clarified the MEC related activities for the RI field work will involve anomaly avoidance measures only. Munitions and/or related debris will not be handled as part of the RI.

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GSU Comment 3 (MEC). RTC Specific Comment 19 b ii. GSU had requested that training requirements for the unexploded ordnance (UXO) team be included. For example, a UXO Technician II (or higher) is usually required to lead an anomaly avoidance team. The Navy replied that because the Bristol team will be used for anomaly avoidance only (not for the investigation and removal of material potentially presenting an explosives hazard [MPPEH]), documentation of their UXO training will not be included in the sampling and analysis plan (SAP). This response is not sufficient. Please identify the position descriptions of the UXO team (e.g., UXO Safety Officer, UXO Technician II) and the minimum qualification standards for each member of the UXO team, as per Department of Defense Explosives Safety Board's (DDESB's) Minimum Qualifications for Unexploded Ordnance (UXO) Technicians and Personnel, DDESB TP18 (TP18: dated December 20, 2004). TP18 describes the training that is required for all UXO team members. For example, the training required for the lowest position on a UXO team, UXO-Sweep Personnel (UXOSP), is as follows: "Such training shall, at a minimum include training in: explosives safety; recognition of munitions and explosives of concern (MEC), particularly UXO; and the proper use of personal protective equipment (PPE). UXOSP are not involved in .the execution of explosives operations and shall not have intentional physical contact with MEC."	**Response.** DTSC staff have identified the correct Navy document (TP-18) that describes the appropriate qualification standards for each member of the munitions safety team. The training and qualifications for the anomaly avoidance team will not be provided as part of the Work Plan.

RESPONSE TO ADDITIONAL COMMENTS ON DRAFT REMEDIAL INVESTIGATION WORK PLAN, SOUTH SHORE AREA FORMER MARE ISLAND NAVAL SHIPYARD VALLEJO, CALIFORNIA DATED MAY 2014 DCN: NRS-4812-0000-0008	
Comments Provided By: Elizabeth K. Wells, PE Water Resource Control Engineer Regional Water Quality Control Board (Water Board) San Francisco Bay Region Comments Dated: April 27, 2015	Responses Provided By: NOREAS, Inc.
Water Board Specific WP Comment 6. Section 2.4.6: The response adequately states that additional investigation was conducted. However, the way the new text is written, it is not clear if the total area that was inaccessible in 2006 was 3.5 acres, or if only 3.5 acres of the total inaccessible area was later investigated.	**Response.** To clarify, the total data gap area for the PMA and SSA that was inaccessible in 2006 was 5.3 acres. Of that total, 100% of Category A (3 acres) and 20% of Category B (0.46 acres, rounded up to 0.5 acres) were investigated for munitions. The total data gap area in the SSA was 1.6 acres, of which 1.2 acres of Cat A and 0.08 acres of Cat B were investigated for munitions.

RESPONSE TO ADDITIONAL COMMENTS ON
DRAFT REMEDIAL INVESTIGATION WORK PLAN, SOUTH SHORE AREA

FORMER MARE ISLAND NAVAL SHIPYARD
VALLEJO, CALIFORNIA

DATED MAY 2014

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Water Board Specific WP Comment 11. Section 4.1.2: **(Part 1):** No technical basis is provided for the statement that "impacts limited to areas between the samples are unlikely to produce an unacceptable risk." In general, Water Board staff consider a sample spacing of 20 linear feet adequate to provide a measure of confidence in the assessment of environmental conditions/quality along a pipeline. Either change the sampling interval or provide a supporting argument for why the proposed spacing of 100-150 feet is sufficient. In addition, confirm the piping will be physically located (laterally and vertically) before the sampling will be conducted such that the Navy is confident that samples are collected at and beneath the piping.	**Response. (Part 1):** There are approximately 3,350 linear feet of sanitary and storm sewer pipelines at the SSA. The current sampling plan will provide a sample spacing of 100-150 feet while also providing focus on those locations with the greatest potential for release, such as joints and bends in the pipeline. This sampling plan is considered adequate based on the following: • The WB has clarified that their comment regarding a 20-feet spacing interval was provided as part of their oversight of the petroleum program and was primarily meant for the investigation of pipelines wherein petroleum product may have been conveyed. • The majority of the pipelines proposed for investigation during the RI were used to convey sanitary sewage and storm water run-off generated at the SSA only. • Historical activities at the SSA largely involved the staging and loading of munitions; only limited quantities of hazardous materials were used or stored at the SSA. • Other investigations of the sanitary sewer at Mare Island where there were reasons to suspect potential contamination did not identify substantial evidence for releases along the pipelines (CH2M Hill 2005). Based on the above, there is no reason to suspect that large quantities of hazardous materials were disposed of and/or conveyed through the sanitary or storm sewer systems at the SSA. However, these features are being sampled out of an abundance of caution. The lateral and vertical locations of the pipelines will be verified in the field prior to sampling. Samples beneath the remaining suspected UST piping will be conducted at 20 ft intervals.

Water Board Specific WP Comment 11. Section 4.1.2: (continued) **(Part 2):** Confirm the piping will be physically located (laterally and vertically) before the sampling will be conducted such that the Navy is confident that samples are collected at and beneath the piping.	**Response (continued).** **(Part 2):** The lateral and vertical extent of the piping will be verified in the field prior to sample collection.
Water Board Specific WP Comment 15. Section 4.2: Water Board staff appreciate the addition of Table 4-4, which provides the rationale for the location of each proposed monitoring well. Based on review of the new table and the figures included in RTCs, Water Board staff have the following additional comments: • Confirm that all potential chemical source areas have a well located such that groundwater quality will be evaluated at and downgradient of that source. • If water level measurements in the new monitoring wells indicate that groundwater flow direction is different than currently anticipated by the Navy such that the new wells are not downgradient of on-site sources, Water Board staff expect the Navy to propose additional monitoring well locations. • Water Board staff question whether sufficient groundwater sampling locations have been proposed downgradient of Building 195. No monitoring well is proposed between SSAMW04 and SSAMW07; if groundwater elevation measurements show a groundwater flow direction of south-southwest, this could be a potential data gap.	**Response.** See responses below. • The planned groundwater monitoring well locations will provide adequate coverage to evaluate groundwater quality downgradient of the areas with potential for contaminant impacts. • Comment noted. • A new well, SSAMW09, has been added to the RI groundwater sampling network between SSAMW04 and SSAMW07. The location of SSAMW09 has been added to Figure 4-7 (see attached).

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