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Additional Scrutiny Quality Assurance Project Plan
for
Operable Unit 4 (OU4)

at

Portsmouth Naval Shipyard
Kittery, Maine

Engineering Field Activity Northeast
Naval Facilities Engineering Command

Contract Number N62472-03-D-0057

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ADDITIONAL SCRUTINY QUALITY ASSURANCE PROJECT PLAN FOR OPERABLE UNIT 4

AT

PORTSMOUTH NAVAL SHIPYARD
KITTERY, MAINE

COMPREHENSIVE LONG-TERM
ENVIRONMENTAL ACTION NAVY (CLEAN) CONTRACT

Submitted to:
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Engineering Field Activity Northeast
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TABLE OF CONTENTS

SECTION **PAGE NO.**

ACRONYMS AND ABBREVIATIONS ..... **viii**

EXECUTIVE SUMMARY **ES-1**

1.0 INTRODUCTION **1-1**
1.1 OBJECTIVE AND SCOPE 1-1
1.2 REPORT ORGANIZATION AND DOCUMENT CONTROL 1-2
1.2.1 Additional Scrutiny QAPP Contents 1-2
1.2.2 USEPA-NE QAPP Worksheet No. 2 1-3
1.2.3 Document Control 1-3
1.3 FACILITY BACKGROUND INFORMATION 1-3
1.3.1 Facility Location and Description 1-4
1.3.2 Facility History and Background 1-4
1.3.3 Summary of Interim Offshore Monitoring Program 1-4
1.4 MONITORING STATION MS-01 1-7
1.4.1 Description of Monitoring Station 1-7
1.4.2 Summary of Interim Offshore Monitoring Program Data 1-7
1.4.3 Potential PNS Sources of Contamination 1-8
1.4.4 Non-PNS Sources of Contamination 1-12
1.5 MONITORING STATIONS MS-05 AND MS-09 1-12
1.5.1 Description of Monitoring Stations 1-12
1.5.2 Summary of Interim Offshore Monitoring Data 1-13
1.5.3 Potential PNS Sources of Contamination 1-14
1.5.4 Non-PNS Sources of Contamination 1-16
1.6 MONITORING STATION MS-11 1-16
1.6.1 Description of Monitoring Station 1-16
1.6.2 Summary of Interim Offshore Monitoring Program 1-16
1.6.3 Potential PNS Sources of Contamination 1-17
1.6.4 Non-PNS Sources of Contamination 1-20
1.7 MONITORING STATION MS-12 1-20
1.7.1 Description of Monitoring Station 1-20
1.7.2 Summary of Interim Offshore Monitoring Program Data 1-21
1.7.3 Potential PNS Sources of Contamination 1-21
1.7.4 Non-PNS Sources of Contamination 1-23

2.0 DATA QUALITY OBJECTIVES **2-1**
2.1 PROJECT PLANNING MEETINGS 2-1
2.2 MONITORING STATION MS-01 2-3
2.2.1 Problem Statement 2-3
2.2.2 Decision Statements 2-3
2.2.3 Decision Inputs 2-4
2.2.4 Study Boundaries 2-6
2.2.5 Decision Rules 2-7
2.2.6 Sampling Design and Rationale 2-8
2.3 MONITORING STATION MS-05 2-10
2.3.1 Problem Statement 2-11
2.3.2 Decision Statement 2-11

TABLE OF CONTENTS (Continued)

SECTION **PAGE NO.**

2.3.3 Decision Inputs 2-11
2.3.4 Study Boundaries 2-12
2.3.5 Decision Rule 2-12
2.3.6 Sampling Design and Rationale 2-12
2.4 MONITORING STATION MS-09 2-13
2.4.1 Problem Statement 2-13
2.4.2 Decision Statement 2-14
2.4.3 Decision Inputs 2-14
2.4.4 Study Boundaries 2-14
2.4.5 Decision Rule 2-15
2.4.6 Sampling Design and Rationale 2-15
2.5 MONITORING STATION MS-11 2-15
2.5.1 Problem Statement 2-16
2.5.2 Decision Statement 2-16
2.5.3 Decision Inputs 2-16
2.5.4 Study Boundaries 2-17
2.5.5 Decision Rule 2-17
2.5.6 Sampling Design and Rationale 2-18
2.6 MONITORING STATION MS-12 2-18
2.6.1 Problem Statements 2-19
2.6.2 Decision Statements 2-19
2.6.3 Decision Inputs 2-20
2.6.4 Study Boundaries 2-22
2.6.5 Decision Rules 2-22
2.6.6 Sampling Design and Rationale 2-23

3.0 PROJECT ORGANIZATION 3-1
3.1 PROJECT ORGANIZATION CHART 3-1
3.2 COMMUNICATION PATHWAYS 3-1
3.2.1 Modifications to the Approved QAPP 3-2
3.3 PERSONNEL RESPONSIBILITIES AND QUALIFICATIONS 3-2
3.4 SPECIAL TRAINING REQUIREMENTS AND CERTIFICATIONS 3-3
3.5 ASSESSMENTS AND RESPONSE ACTIONS 3-3
3.5.1 Planned Assessments 3-3
3.5.2 Assessment Findings and Corrective Action Responses 3-4
3.5.3 Additional QAPP Nonconformances 3-5
3.6 QA MANAGEMENT REPORTS 3-5
3.7 PROJECT SCHEDULE 3-7

4.0 FIELD SAMPLING AND ANALYSIS PLAN 4-1
4.1 SITE UTILITY CLEARANCE AND DIGGING PERMIT 4-1
4.2 SEDIMENT/CATCH BASIN SAMPLING 4-1
4.3 SOIL SAMPLING 4-6
4.4 SURVEYING 4-7
4.5 SAMPLE IDENTIFICATION SYSTEM 4-7
4.5.1 Environmental Samples 4-7
4.5.2 Field Quality Assurance/Quality Control Sample Nomenclature 4-8
4.6 FIELD QUALITY CONTROL SAMPLES 4-9

TABLE OF CONTENTS (Continued)

SECTION **PAGE NO.**

4.7 SAMPLE HANDLING AND MANAGEMENT 4-10
4.7.1 Sample Custody 4-10
4.7.2 Field Custody 4-11
4.7.3 Transfer of Custody 4-11
4.7.4 Sample Shipment Procedures 4-12
4.7.5 Laboratory Sample Custody 4-13
4.8 EQUIPMENT DECONTAMINATION 4-13
4.9 INVESTIGATIVE-DERIVED WASTE MANAGEMENT 4-14
4.10 FIELD DOCUMENTATION AND DOCUMENTATION RESPONSIBILITIES 4-14
4.11 SAMPLING SOP MODIFICATIONS 4-15
4.12 FIELD EQUIPMENT MAINTENANCE, TESTING, AND INSPECTION REQUIREMENTS 4-15

5.0 FIXED-BASE LABORATORY ANALYTICAL PLAN 5-1
5.1 METHOD DETECTION/QUANTITATION LIMITS 5-1
5.2 ANALYTICAL METHODS/SOPs AND MODIFICATION 5-1
5.3 CALIBRATION AND PREVENTATIVE MAINTENANCE OF LABORATORY INSTRUMENTS 5-2
5.4 INTERNAL QUALITY CONTROL CHECKS 5-2
5.4.1 Laboratory Control Samples 5-3
5.4.2 Laboratory Duplicates 5-3
5.4.3 Laboratory Method Blanks 5-3
5.4.4 Matrix Spikes 5-4
5.4.5 Post-Digestion Spikes 5-4
5.4.6 Performance Evaluation Samples 5-4
5.5 REQUIREMENTS FOR SUPPLIES/SAMPLE CONTAINERS 5-5

6.0 DATA MANAGEMENT AND QUALITY ASSESSMENT PLAN 6-1
6.1 DOCUMENTATION, RECORDS, AND DATA MANAGEMENT 6-1
6.1.1 Documentation and Records of the Analytical Program 6-1
6.1.2 Field Analysis Data Package Deliverables 6-1
6.1.3 Fixed-Base Laboratory Data Package Deliverables 6-1
6.1.4 Data Reporting Formats 6-1
6.1.5 Data Handling and Management 6-1
6.1.6 Data Tracking and Control 6-2
6.2 DATA VERIFICATION AND VALIDATION 6-4
6.2.1 Verification 6-5
6.2.2 Data Validation 6-6
6.3 DATA USABILITY AND RECONCILIATION WITH PROJECT QUALITY OBJECTIVES 6-7
6.3.1 The PARCC Parameters 6-7
6.3.2 Data Quality Assessment 6-10

REFERENCES R-1

TABLE OF CONTENTS (Continued)

APPENDICES

A SUPPORTING INFORMATION
B TECHNICAL MEMORANDUMS AND RESPONSES TO COMMENTS
C STANDARD OPERATING PROCEDURES AND FIELD FORMS
D PAH FORENSICS QUALITY ASSURANCE PROJECT PLAN
E RESPONSES TO COMMENTS, CONFERENCE CALL NOTES, AND MEETING MINUTES RELATED TO THE QAPP

TABLES

NUMBER		PAGE NO.
1-1	Distribution List	1-31
1-2	Example Project Personnel Sign-off Sheet	1-32
3-1	Personnel Responsibilities and Qualifications	3-9
3-2	Special Personnel Training Requirements	3-10
3-3	Project Assessment	3-11
3-4	Quality Assurance Management Reports	3-12
4-1	Summary of Standard Operating Procedures	4-17
4-2	Summary of Samples Proposed for Collection	4-18
4-3	Sample Containers, Preservation Methods and Holding Times	4-22
4-4	Aqueous Semivolatiles, pesticides, and Metals Field Sampling QC	4-23
4-5	Summary of QA/QC Samples and Analysis	4-24
5-1	Soil/Sediment MDLs and Laboratory Reporting Limits - PAHs	5-7
5-2	Aqueous PQLs and Laboratory Detection Limits - PAHs	5-8
5-3	Soil/Sediment MDLs and Laboratory Reporting Limits - Pesticides	5-9
5-4	Aqueous PQLs and Laboratory Detection Limits - Pesticides	5-10
5-5	Soil/Sediment IDLs and Laboratory Reporting Limits - Metals	5-11
5-6	Aqueous IDLs and Laboratory Reporting Limits - Metals	5-12
5-7	Example Laboratory Analytical Methods/SOP Reference Table	5-13
5-8	Example Laboratory Analytical QC Sample Table - PAHs and Pesticides	5-14
5-9	Example Laboratory Analytical QC Sample Table - Metals	5-16
6-1	Sampling and Analytical Program Documentation and Records	6-11
6-2	Data Validation Summary Table/Modification	6-12

FIGURES

NUMBER		PAGE NO.
1-1	Portsmouth Naval Shipyard Vicinity Map	1-33
1-2	Overview of Monitoring Station Locations	1-35
1-3	Overview of Reference Station Locations	1-37
1-4	MS-01 Location and Potential Contaminant Migration Pathways	1-39
1-5	MS-05, MS-08, and MS-09 Locations	1-41
1-6	MS-11 Location and Potential Contaminant Migration Pathways	1-43
1-7	MS-12 Location and Potential Contaminant Migration Pathways	1-45
3-1	Project Organization Chart	3-13
4-1	Proposed Sample Locations for Additional Scrutiny at MS-01	4-25
4-2	Proposed Sample Locations for Additional Scrutiny at MS-05	4-27
4-3	Proposed Sample Locations for Additional Scrutiny at MS-09	4-29
4-4	Proposed Sample Locations for Additional Scrutiny at MS-11	4-31
4-5	Proposed Sample Locations for Additional Scrutiny at MS-12	4-33
4-6	Proposed Locations of Sediment Samples at RS-02	4-35
4-7	Proposed Locations of Sediment Samples at RS-03	4-37
4-8	Proposed Locations of Non-PNS Sediment Samples	4-39

ACRONYMS AND ABBREVIATIONS

bgs	Below ground surface
BSAF	Biota-sediment accumulation factor
CA	Corrective action
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CIA	Controlled Industrial Area
CLEAN	Comprehensive Long-Term Environmental Action Navy
CLP	Contract Laboratory Program
COC	Chemical of concern
CTO	Contract Task Order
DoD	United States Department of Defense
DQO	Data quality objective
DRMO	Defense Reutilization and Marketing Office
DVM	Data validation manager
EFANE	Engineering Field Activity Northeast
EP	Extraction Procedure
ER-M	Effects Range-Median
ER,N	Environmental Restoration, Navy
FOL	Field operations leader
FS	Feasibility Study
FWS	United States Fish and Wildlife Service
GIS	Geographical information system
GPS	Global Positioning System
HASP	Health and safety plan
HMW	High Molecular Weight
ICP	Inductively coupled plasma
IDL	Instrument detection limit
IDW	Investigative-derived waste
IMRG	Information Management Resource Group
IRCDQM	Installation Restoration Chemical Data Quality Manual
IRG	Interim Remediation Goal
IRP	Installation Restoration Program
JILF	Jamaica Island Landfill
Lab QA/QC Program	Laboratory Quality Assurance/Quality Control Program
LAN	Local Area Network
LCS	Laboratory control sample

LQAP	Laboratory Quality Assurance Plan
MDL	Method detection limit
MEDEP	Maine Department of Environmental Protection
MS	Matrix spike
MSD	Matrix spike duplicate
NAD	North American Datum
NAVFAC	Naval Facilities Engineering Command
NFESC	Naval Facilities Engineering Service Center
NOAA	National Oceanic and Atmospheric Administration
OU	Operable Unit
PAH	Polycyclic aromatic hydrocarbon
PARCC	Precision, accuracy, representativeness, comparability, and completeness
PCB	Polychlorinated biphenyl
PDF	Portable document file
PDS	Post-digestion spike
PES	Performance Evaluation Sample
PM	Project manager
PNS	Portsmouth Naval Shipyard
PPE	Personal protective equipment
PQL	Practical quantitation limit
PRG	Preliminary remediation goal
QA	Quality assurance
QAPP	Quality Assurance Project Plan
QC	Quality control
OSWER	Office of Solid Waste and Emergency Response
RAB	Restoration Advisory Board
RAO	Remedial action objective
RI	Remedial Investigation
ROD	Record of Decision
RPD	Relative percent difference
RPM	Remedial Project Manager
SDG	Sample delivery group
SIM	Selective ion monitoring
SMC	Sample management coordinator
SQL	Sample quantitation limit
SOP	Standard operating procedure
SOW	Statement of Work

SVOC	Semivolatile organic compound
TAL	Target Analyte List
TOC	Total organic carbon
TPH	Total petroleum hydrocarbons
TtNUS	Tetra Tech NUS, Inc.
USEPA	United States Environmental Protection Agency
USEPA-NE	United States Environmental Protection Agency Region I – New England
°C	degrees Celsius
%R	Percent recovery

EXECUTIVE SUMMARY

This Additional Scrutiny Additional Extent Investigation Quality Assurance Project Plan (QAPP) provides the basis and methods for conducting additional scrutiny at select interim offshore monitoring stations at Operable Unit (OU) 4 at Portsmouth Naval Shipyard (PNS), Kittery, Maine. Tetra Tech NUS, Inc., (TtNUS) prepared this QAPP for the United States Department of Navy Engineering Field Activity Northeast (EFANE), Naval Facilities Engineering Command (NAVFAC) under the Comprehensive Long-Term Environmental Action Navy (CLEAN) Contract Number N62472-03-D-0057, Contract Task Order (CTO) 023. This QAPP provides the basis and methods to obtain additional information to support the evaluation of the nature and extent of chemicals detected in the offshore areas of PNS. This additional scrutiny is being conducted as required by the interim offshore monitoring program. Under the OU4 interim offshore monitoring program (TtNUS, October 1999), concentrations of select chemicals of environmental significance are plotted over time to determine whether temporal concentration trends are changing and how they compare with Interim Remediation Goals (IRGs). Based on an evaluation of the monitoring data collected between September 1999 and August 2003 (Rounds 1 through 7), additional scrutiny was recommended for the following monitoring stations: MS-01, MS-03, MS-04, MS-05, MS-08, MS-09, MS-11, and MS-12 (TtNUS, November 2004). Two chemical groups [e.g., metals and polycyclic aromatic hydrocarbons (PAHs)] were identified as target analytes for this scrutiny. The objective of the additional scrutiny is to assess existing data and to collect and assess additional data at monitoring stations where concentration trend lines for chemicals are greater than IRGs and are projected to continue to exceed IRGs for the next 5 years or are increasing and projected to exceed IRGs within the next 5 years.

As discussed in the June 2004 Technical Memorandum for Additional Scrutiny at Monitoring Stations MS-05, MS-08, and MS-09 (included in Appendix B), additional scrutiny for MS-05, MS-08, and MS-09 includes sediment sampling to re-establish the trend line. This sampling will be conducted as part of Round 8 of the interim offshore monitoring program, which is scheduled for August 2005. Therefore, sampling to re-establish the trend line at MS-05, MS-08, and MS-09 is not discussed further in this QAPP. Re-establishing the trend line is the only additional scrutiny activity for MS-08; therefore, MS-08 is not discussed further in this QAPP. Additional scrutiny sampling for MS-05 and MS-09 is presented in this QAPP.

The additional scrutiny needed at monitoring stations MS-03 and MS-04 for PAHs will be evaluated as part of the planning for the Site 32 Phase 2 Remedial Investigation (RI) and is therefore not discussed in this QAPP. This QAPP presents the plan for additional scrutiny at monitoring stations MS-01, MS-05, MS-09, MS-11, and MS-12.

Additional scrutiny sampling and data evaluation activities are discussed in this QAPP. Sampling at monitoring stations MS-01, MS-05, MS-09, MS-11, and MS-12 and background locations include the following:

MS-01: MS-01 is located in the Back Channel, off shore of Site 34 and adjacent to the bridge leading to Gate No. 1. The following data will be collected as part additional scrutiny for MS-01 to determine whether an Installation Restoration Program (IRP) source is the primary source of PAHs and pesticides in sediment:

- Seven sediment samples in the offshore area around MS-01. All seven samples will be analyzed for pesticides and Total Petroleum Hydrocarbon (TPH). Based on the TPH results, four of the seven samples will be selected for additional forensics analysis including PAH, biomarker, and total organic carbon (TOC) analyses.

- Sediment from two catch basins near, but not in the immediate vicinity of Site 34 to represent "background" (i.e., non-Site 34) input to sediment from storm water runoff. One sample will be analyzed for forensics analysis and pesticides and the other sample will be analyzed for pesticides. [Also see the discussion of reference samples below.]

- Two composite soil samples at Site 34 where elevated PAH concentrations were noted. Both samples will be analyzed for TPH and based on the TPH results, one of the two samples will be selected for additional forensics analysis including PAH, biomarker, and TOC analyses.

MS-05: MS-05 is located in Jamaica Cove, adjacent to the wetland constructed as part of the remedy for OU3. Data will be collected to determine the extent of elevated levels of metal (copper, lead, and nickel) in sediment in Jamaica Cove. Data from Round 8 of the interim offshore monitoring program locations will also be used to determine the extent of contamination. The following data will be collected for MS-05:

- Fourteen sediment samples in the offshore area at MS-05. The samples will be analyzed in three phases for copper, lead, and nickel.

MS-09: MS-09 is located in Clark Cove, adjacent to OU3. Data will be collected to determine the extent of elevated chemicals (metals and PAHs) in sediment at MS-09. Data from Round 8 of the interim offshore monitoring program locations will also be used to determine the extent of contamination. The following data will be collected for MS-09:

- Six sediment samples in the offshore area at MS-09. The samples will be analyzed for copper, nickel, and PAHs.

MS-11: MS-11 is located in the Main Channel, off shore of OU2. Data will be collected to confirm whether eroding material at OU2 is the likely source of sediment contamination at MS-11. The following data will be collected for MS-11:

- Sediment from one catch basin that collects storm water runoff near a soil erosion area at OU2. The sample will be analyzed for copper, lead, and nickel.
-
- Two composite samples from soil erosional areas. The samples will be analyzed for copper, lead, and nickel.

MS-12: MS-12 is located in the dry docks area offshore of Site 10. The following data will be collected for MS-12 to determine whether an IRP source is the primary source of PAHs and lead in sediment:

- Fourteen sediment samples in the offshore area around MS-12. All samples will be analyzed for lead. Eight of the samples will be analyzed for TPH; two representing "background" conditions for MS-12 and six near MS-12. Based on the TPH results, one of the two "background" samples and three of the six MS-12 area samples will be selected for additional forensics analysis including PAH, biomarker, and TOC analyses. [Also, see the discussion of reference samples below.]

- Two sediment samples from the sediment within Building 178. Both samples will be analyzed for forensics parameters including TPH, PAH, biomarker, and TOC.

- Sediment samples from two catch basins onshore at Site 10; one sample will be analyzed for lead and PAHs and one sample will be analyzed for lead.

Reference Samples: Samples will be collected from locations at two of the reference stations sampled as part of the interim offshore monitoring program and near two storm water outfalls not associated with PNS. The following data will be collected to determine whether the sources of the PAHs between the PNS site samples and the reference samples are similar:

- Three sediment samples at two of the interim offshore monitoring program reference stations for TPH analysis. Based on the TPH results, two of the three samples will be selected for additional forensics analysis including PAH, biomarker, and TOC analyses.

- Sediment samples offshore of two storm water outfalls not associated with PNS (one located in Kittery, Maine and the other located in Portsmouth, New Hampshire). Both samples will be analyzed for TPH and based on the TPH results, one of the samples will be selected for additional forensics analysis including PAH, biomarker, and TOC analyses.

The data collected as part of the additional scrutiny activities will be presented in a data package and a report will be prepared to present the results of the data evaluation.

1.0 INTRODUCTION

This Additional Scrutiny Quality Assurance Project Plan (QAPP) provides the basis and methods for conducting additional scrutiny at select interim offshore monitoring stations at Operable Unit (OU) 4 at Portsmouth Naval Shipyard (PNS), Kittery, Maine.

1.1 OBJECTIVE AND SCOPE

Tetra Tech NUS, Inc. (TtNUS) prepared this QAPP for the United States Department of Navy, Engineering Field Activity Northeast (EFANE), Naval Facilities Engineering Command (NAVFAC) under the Comprehensive Long-Term Environmental Action Navy (CLEAN) Contract Number N62472-03-D-0057, Contract Task Order (CTO) 023. This QAPP provides the basis and methods to obtain additional information to support the evaluation of the nature and extent of chemicals detected in the offshore areas of PNS. This additional scrutiny is being conducted as required by the interim offshore monitoring program. Under the OU4 interim offshore monitoring program (TtNUS, October 1999), concentrations of select chemicals of environmental significance are plotted over time to determine whether temporal concentration trends are changing and how they compare with Interim Remediation Goals (IRGs). Based on an evaluation of the monitoring data collected between September 1999 and August 2003 (Rounds 1 through 7), additional scrutiny was recommended for the following monitoring stations: MS-01, MS-03, MS-04, MS-05, MS-08, MS-09, MS-11, and MS-12 (TtNUS, November 2004). Two chemical groups [e.g., metals and polycyclic aromatic hydrocarbons (PAHs)] were identified as target analytes for this scrutiny. The objective of the additional scrutiny is to assess existing data and to collect and assess additional data at monitoring stations where concentration trend lines for chemicals are greater than IRGs and are projected to continue to exceed IRGs for the next 5 years or are increasing and projected to exceed IRGs within the next 5 years.

As discussed in the June 2004 Technical Memorandum for Additional Scrutiny at Monitoring Stations MS-05, MS-08, and MS-09 (included in Appendix B), additional scrutiny for MS-05, MS-08, and MS-09 includes sediment sampling to re-establish the trend line. This sampling will be conducted as part of Round 8 of the interim offshore monitoring program, which is scheduled for August 2005. Therefore, sampling to re-establish the trend line at MS-05, MS-08, and MS-09 is not discussed further in this QAPP. Re-establishing the trend line is the only additional scrutiny activity for MS-08; therefore, MS-08 is not discussed further in this QAPP. Additional scrutiny sampling for MS-05 and MS-09 is presented in this QAPP.

The additional scrutiny needed at monitoring stations MS-03 and MS-04 for PAHs will be evaluated as part of the planning for the Site 32 Phase 2 Remedial Investigation (RI) and is therefore not discussed in

this QAPP. This QAPP presents the plan for additional scrutiny at monitoring stations MS-01, MS-05, MS-09, MS-11, and MS-12.

1.2 REPORT ORGANIZATION AND DOCUMENT CONTROL

1.2.1 Additional Scrutiny QAPP Contents

This Additional Scrutiny QAPP consists of the following sections:

- Section 1.0 is this introduction and the background information used to support the basis and data quality objectives (DQOs) for the Additional Scrutiny program.
- Section 2.0 presents the DQOs guiding the data collection and evaluation necessary to make decisions regarding the Additional Scrutiny.
- Section 3.0 describes the project organization and responsibilities.
- Section 4.0 describes the requirements for the sampling of environmental media and the maintenance of field documentation.
- Section 5.0 describes the fixed-base laboratory analytical plan for the Additional Scrutiny.
- Section 6.0 provides the requirements for management and quality assessment of the fixed-base laboratory data.
- Appendix A provides information supporting the discussions in Section 1.0.
- Appendix B includes the Additional Scrutiny Technical Memoranda, the Analytical Methods Technical Memorandum, and responses to comments associated with the memoranda.
- Appendix C provides standard operating procedures (SOPs) and field forms for sampling.
- Appendix D presents the PAH forensics sample analysis QAPP.
- Appendix E provides the responses to comments on the QAPP, conference call notes, and meeting minutes.

1.2.2 USEPA-NE QAPP Worksh t No. 2

The United States Environmental Protection Agency (USEPA) Region 1 - New England (USEPA-NE) QAPP guidance (USEPA, October 1999) requires inclusion of Worksheet No. 2 to provide introductory information, to identify key project participants, to document previous site work, and to identify the USEPA program for which the current project is being performed. USEPA-NE QAPP Worksheet No. 2 for the Additional Scrutiny QAPP also includes a crosswalk to the elements of the QAPP per the guidance. The worksheet is provided at the end of Section 1.0.

1.2.3 Document Control

Document control procedures are used to identify the most current version of the Additional Scrutiny QAPP and to help ensure that only the most current version of the QAPP is used by project participants. To meet this goal, text, tables, and figures in the final QAPP will include a header indicating the document name, revision number, and date. The footer indicates the page number within the section. Revision 0 with the month and year will be used as part of the header for the draft, draft final and final versions. Any revisions made after submittal of the final document will be indicated with an appropriate sequential revision number and date.

A document control numbering system will not be used for this QAPP because this project has a distinct PNS distribution list. The plan and any revisions, addenda, or amendments will be provided in accordance with the document distribution list. The PNS distribution list includes the USEPA, Maine Department of Environmental Protection (MEDEP), Navy, Natural Resource Trustees, and Restoration Advisory Board (RAB) members. The cover letter accompanying the document indicates the distribution list and number of copies (in the case of multiple copies only). The distribution list for the QAPP is summarized in Table 1-1. Each person listed in Table 1-1 will receive a copy of this Revision 0 plan. Any subsequent revisions will be provided to the most recent PNS distribution list at the time of the revision.

Table 1-2 provides an example of the project personnel sign-off sheet that will be signed by personnel working on the project. A signature on this form indicates the person has read this QAPP and is familiar with the tasks to be performed. The completed sign-off sheet will be maintained in the TtNUS project file.

1.3 FACILITY BACKGROUND INFORMATION

This section presents facility information and a summary of the interim offshore monitoring program. Specific information regarding monitoring stations included in the additional scrutiny investigation is provided in Sections 1.4 through 1.7.

1.3.1 Facility Location and Description

PNS is a military facility with restricted access located on an island in the Piscataqua River, as shown on Figure 1-1. PNS is referred to on National Oceanic and Atmospheric Administration (NOAA) nautical charts as Seavey Island, with the eastern tip given the name Jamaica Island. Attached by a rock causeway is Clark's Island. The Piscataqua River is a tidal estuary that forms the southern boundary between Maine and New Hampshire. PNS is located in Kittery, Maine, north of Portsmouth, New Hampshire, at the mouth of the Great Bay Estuary (commonly referred to as Portsmouth Harbor).

The Piscataqua River is part of the tidal Great Bay Estuary, and in the vicinity of PNS, the water is predominantly saline (salinities greater than 20 parts per thousand). The mean tidal range in the vicinity of PNS is approximately 8 feet, and average tidal currents (ebb and flood) are generally strong (around 3 to 4 knots). The water is not used for human consumption. The back channel is approximately 20 feet deep (mean low water) and is generally used for recreational boating (TtNUS, October 1999). Some commercial fishing (lobstering) may also occur in portions of the back channel.

1.3.2 Facility History and Background

PNS is engaged in the conversion, overhaul, and repair of submarines for the Navy. The long history of shipbuilding in Portsmouth Harbor dates back to 1690, when the first warship launched in North America, the Falkland, was built. PNS was established as a government facility in 1800, and it served as a repair and building facility for ships during the Civil War. The first government-built submarine was designed and constructed at PNS during World War I. A large number of submarines have been designed, constructed, and repaired at this facility since 1917. PNS continues to service submarines as its primary military focus.

1.3.3 Summary of Interim Offshore Monitoring Program

In May 1999, an Interim Record of Decision (ROD) for OU4 (Navy, May 1999) was signed requiring the Navy to conduct monitoring in the offshore area of PNS in the interim period before completion of the offshore Feasibility Study (FS) and implementation of the final remedy for OU4. Data collected as a part of the monitoring program provides the information necessary to determine whether the remedial action objectives (RAOs) for this interim period are being met. These interim RAOs were developed so that the protection of ecological offshore communities can be ensured by the identification of exposure to chemicals of concern (COCs) at concentrations greater than acceptable levels.

The Interim Offshore Monitoring Plan (TtNUS, October 1999) provides the methodology for the development of these acceptable exposure levels. These levels provide a basis of comparison for the

overall chemical trends of the COCs during the interim period and are referred to as IRGs. The IRGs were developed for the chemicals potentially causing the most offshore impact, which are referred to as the limiting COCs. The IRGs were developed using the sediment-based preliminary remediation goals (PRGs) developed for OU4 (TtNUS, November 2001) for the following chemicals:

Parameter	IRG (dry weight)
Copper	486 mg/kg
Nickel	124 mg/kg
Acenaphthylene	210 µg/kg
Anthracene	1,236 µg/kg
Fluorene	500 µg/kg
High Molecular Weight (HMW) PAHs	13,057 µg/kg

Although pesticides were not identified as COCs for OU4; PRGs were developed for endosulfan II (3.95 µg/kg), trans-nonachlor (3.99 µg/kg), and 4,4'-DDT (66.4 µg/kg). The PRGs developed for pesticides are not used as IRGs because they were not identified as COCs for OU4; however, the PRGs are considered when evaluating pesticides data. [Lead was not identified as a limiting COC, so a PRG was not developed. Lead is a primary COC for several onshore sites; therefore, the Effects Range-Median (ER-M) value (Long et al., 1995) was used for screening sediment lead data.]

The interim offshore monitoring sampling program is presented in the Interim Offshore Monitoring Plan (TtNUS, October 1999), and modifications based on the Baseline Report (TtNUS, July 2002) were implemented after Round 5. In summary, the sampling investigation consists of collecting samples at 14 monitoring stations (MS-01 through MS-14) adjacent to PNS and four reference stations (RS-01 through RS-04) in the Piscataqua River. Figures 1-2 and 1-3 present the overall layout of the monitoring and reference stations, respectively.

At each monitoring station, three sediment samples (with the exception of MS-11), one to three mussel samples, and one juvenile lobster sample (Rounds 1 through 5 only) were collected during each monitoring event. Four sediment samples, two mussel samples, and one juvenile lobster sample (Rounds 1 through 5 only) were collected at each reference station. For this report, "Loc" designates the sediment sampling location for that station. For example, MS-01, Loc. 3 is location 3 at monitoring station MS-01.

Sediment and mussel samples were collected during Rounds 1 through 7. Lobster samples were collected during Rounds 1 through 5 and sediment porewater samples were collected during Round 2.

The first seven rounds of sampling were conducted between September 1999 and August 2003 as follows:

- Round 1 - September 7 through 11, 1999
- Round 2 - May 2 through 7 and May 23, 2000
- Round 3 - August 27 through 30, 2000
- Round 4 - May 5 through 9, 2001
- Round 5 - August 18 through 22, 2001
- Round 6 - August 10 through 15, 2002
- Round 7 - August 9 through 13, 2003

The data from the first seven rounds was evaluated and documented in the Rounds 1 through 7 Interim Offshore Monitoring Program Report (Rounds 1 through 7 Report) (TtNUS, November 2004). The main objective of the Rounds 1 through 7 Report was to determine the appropriate frequency of monitoring for each monitoring station for the next 5 years and to determine whether additional scrutiny was recommended at any monitoring station. The evaluation also included recommendations for other modifications to the monitoring program.

The following table presents a summary of the recommendations for sampling frequency/need for additional scrutiny at each monitoring station, as presented in the Rounds 1 through 7 Report (TtNUS, November 2004):

Monitoring Station	Sampling Frequency			Recommended for Additional Scrutiny
	Round 8 (Aug 2005)	Round 9 (Aug 2007)	Round 10 (Aug 2008)	
MS-01			X	Yes
MS-02			X	No
MS-03			X	Yes(1)
MS-04			X	Yes(1)
MS-05	X	X	X	Yes
MS-06			X	No
MS-07			X	No
MS-08	X	X	X	Yes(2)
MS-09	X	X	X	Yes
MS-10	X	X	X	No
MS-11			X	Yes
MS-12			X	Yes
MS-13	X	X	X	No
MS-14	X	X	X	No

Monitoring Station	Sampling Frequency			Recommended for Additional Scrutiny
	Round 8 (Aug 2005)	Round 9 (Aug 2007)	Round 10 (Aug 2008)	
Reference Stations	X	X	X	Not applicable

1 - Additional scrutiny was conducted for copper and nickel at these stations as part of the Site 32 RI. PAHs will be evaluated in the planning for the Phase 2 RI for Site 32 to determine any additional scrutiny required for these chemicals.

2 - As presented in Section 1.1, the additional scrutiny for MS-08 (re-establishing the trend line) will be conducted as part of the interim offshore monitoring program and therefore MS-08 is not included in this QAPP.

1.4 MONITORING STATION MS-01

1.4.1 Description of Monitoring Station

MS-01 is located in the back channel of the Piscataqua River, offshore of Site 34 (former Oil Gasification Plant) (See Figure 1-4). Three sediment locations are sampled at MS-01 as part of the Interim Offshore Monitoring Program: MS-01, Locs. 1 and 3 are subtidal and MS-01, Loc. 2 is intertidal. The intertidal area is relatively narrow, with generally 20 to 40 feet between mean high and mean low tide elevations. This monitoring station is located in an area where the width of the channel decreases and the water velocity is very fast during the incoming and outgoing tides. As a result, the average silt content in the sediment at this station is less than 9 percent, while the average sand content is greater than 80 percent (TtNUS, November 2004). The greatest percentage of silt is found in the intertidal location.

It was difficult to collect sediment samples from subtidal locations during several of the rounds because of the strong current and rocky nature of the river bottom. During sample collection, especially at MS-01, Loc. 3, the boat had to be repositioned several times to obtain a full sediment grab sample. Biota present along the shoreline included mussels, snails, fucus, and ascophyllum. Organisms such as clam worms, red worms, snails, and crabs were found in the sediment samples from this monitoring station. No seeps were observed at this station during offshore sampling events.

1.4.2 Summary of Interim Offshore Monitoring Program Data

As presented in the Rounds 1 through 7 Report (TtNUS, November 2004), concentrations of PAHs were greater than IRGs and concentrations of 4,4'-DDT were greater than the PRG in several sediment samples; concentrations of metals were less than IRGs. For these reasons, additional scrutiny was recommended for PAHs and 4,4'-DDT at MS-01.

Appendix A-1 presents the concentration trend plots from Rounds 1 through 7 for PAHs and 4,4'-DDT at MS-01. As can be seen from the trend plots, the intertidal location generally had the lowest PAH levels and had the fewest number of samples with concentrations that exceeded IRGs. Also, the trend lines show an upward trend over the seven rounds. However, the slope of the trend lines appears to be biased by low PAH concentrations during Round 1 and high concentrations of PAHs at MS-01, Loc. 1 during Round 7. Additional data collection as part of the interim offshore monitoring program will help to better define the concentration trends.

Concentrations of 4,4'-DDT exceeded its PRG at MS-01, Loc. 2 during all rounds, and at MS-01, Loc. 3 during Rounds 1 and 6. The concentrations of 4,4'-DDT were much greater at MS-01, Loc. 3 during those two rounds than they were at MS-01, Loc. 2 during any round. However, during Round 6, 4,4'-DDT was detected at a concentration of 22.6 µg/kg in the original sample but was detected at a concentration of 1,613 µg/kg in the duplicate.

1.4.3 Potential PNS Sources of Contamination

The primary COCs at MS-01 are PAHs and 4,4'-DDT, a pesticide. Therefore, this section focuses on potential onshore sources of PAHs and pesticides to the sediment at MS-01 and discusses potential Installation Restoration Program (IRP) sources and potential non-IRP sources separately.

1.4.3.1 IRP Sources

Site 34 (OU9) is located adjacent to MS-01. Building 62 (built in the late 1800s) and its more recent annex (built in the 1940s) are the most prominent features related to the use of Site 34. The following is a brief summary of the site features, potential sources of contamination, and sample results from Site 34. See the Site Screening Investigation Report for Site 34 (TtNUS, August 2004) for more details.

Site 34 is located north of Smoot Street, near the northern shoreline of PNS. Figure 1-4 shows the layout of the site (in the vicinity of Building 62 and annex) and nearby features. The southern side of Buildings 62 and 62-A are on Smoot Street, which is at a higher elevation than the paved roadway on the northern side. The land on the northern side of Building 62 slopes gently towards the roadway and then slopes steeply to the water's edge at the back channel of the Piscataqua River. Access to the shoreline from the site is difficult because of the rapid change in terrain. North of the paved roadway, there is a narrow, flat, vegetated strip (approximately 2 to 5 feet wide) before the ground surface forms a steep bank near the shoreline of the back channel of the Piscataqua River. On the water-side slope of this bank, the ground surface is irregular with bedrock outcrops and scrub vegetation such that it is not easily accessible by foot.

Potential environmental concerns associated with Site 34 operation are associated with the generation of ash and tar and management of pesticides. Tar, generated and contained in a pit within Building 62 (from 1870s to early 1900s), is not in contact with groundwater or surface water runoff; therefore, it is not a likely source of contamination to the offshore. For this reason, tar associated with Site 34 operations is not discussed further in this QAPP.

Coal (fuel) combustion during the oil gasification process led to the generation of ash from 1870s to early 1900s, and coal (fuel) combustion during the blacksmith operation also led to the generation of ash from 1915 to 1930. Ash from these operations (and potentially including ash from a building fire in 1919) appears to have been deposited primarily adjacent to the northern wall of Building 62; however it has been found at other locations around Buildings 62 and 62-A and adjacent to Building 63, which is located east of Building 62. The Navy conducted a site screening investigation in 2003 (TtNUS, August 2004) and an ash extent investigation in 2004 (TtNUS, February 2004). The ash is intermixed with varying fractions of soil and is covered with vegetation (i.e., grass and small trees) adjacent to the northern walls of the buildings or pavement under the parking area adjacent to the southern walls of the buildings. North of the buildings, ash is also present under a narrow paved roadway overlying a former railroad bed oriented parallel to the shoreline.

Potential migration mechanisms for PAHs from Site 34 to the offshore area include erosion of PAH-contaminated soil and ash from the area near Building 62 (and adjacent buildings) into the offshore area either by direct overland flow to the river or by overland flow into the storm water system and then into the river (see Figure 1-4). Surface soil along the shoreline also could erode into the offshore area by direct overland flow, and the soil located along the slope of the bank could erode directly into the offshore area during periods of extremely high tide.

Pesticide storage inside Building 62 and possibly rinsing of equipment and overalls was conducted from approximately the 1960s to 1985 at the small (approximately 10-foot by 12-foot) wash pad area located adjacent to the southern wall of Building 62. However, information from the Initial Assessment Study (Weston, June 1983) indicates that pesticide management at PNS since the 1960s was carefully managed and that standard practices included triple rinsing all sprayers, empty cans, and containers and reusing the rinse water to dilute the next batch of pesticides. Pesticides stored in the building included several pesticides/insecticides/herbicides such as Diazinon, Dursban, Baygon, Malathion, Bromacil, Biotrol, Carbaryl, and Avitrol (TtNUS, August 2004).

Drains within and next to the abandoned wash pad on the southern side of Building 62 connect to Outfall 49. This outfall, which discharges to the Piscataqua River, is apparently not connected to the other storm water drains in the paved area south of Buildings 62 and 63 (see Figure 1-4). The drain likely collects

runoff from the parking lot south of Building 62. The outlet of Outfall 49 is in the intertidal zone offshore of Site 34 and is only exposed when tides are close to low tide. This may have been a previous pathway of pesticide rinse waters to the offshore. If 4,4'-DDT had been managed at the building, this would have been the primary migration pathway from the site to the offshore area. However, pesticides are no longer managed in this area, so this migration pathway is no longer complete.

Figures A-1 through A-6 in Appendix A-1 present the PAH concentrations for the following:

- Surface soil samples collected in the vegetated area at Site 34 because soil from this area could erode into the offshore area by direct overland flow to the river.
- Maximum total PAH concentrations in surface/subsurface soil samples located along the shoreline because the soil could erode into the offshore area either by direct overland flow or directly into the offshore area during periods of extremely high tide.
- Offshore sediment samples collected as part of the interim offshore monitoring program.
- Other sediment samples collected in the offshore area.

The soil sample locations are color coded as depicted in the legend of each figure, with blue dots representing locations with the lowest PAH concentrations and red dots representing locations with the greatest concentrations. Concentrations for sediment samples are shown in the tags of Figures A-1 through A-6 in Appendix A-1. The greatest PAH concentrations in soil samples are generally located in the area closest to Building 62 (where ash has been observed), although elevated concentrations were present in soil samples collected closest to the shoreline. PAH concentrations in sediment samples collected as part of the interim offshore monitoring program are generally less than the greatest concentrations in the soil samples. PAH concentrations in the two offshore sediment samples collected as part of another investigation are similar to concentrations in the other offshore sediment samples.

1.4.3.2 Non-IRP Sources

There are several potential onshore non-IRP sources of PAHs and pesticides to the offshore sediment at MS-01.

Based on the results of the SSI investigation, pesticides in soil in the vicinity of Site 34 are not considered to be from an IRP source. 4,4'-DDT concentrations in soil samples are indicative of the general historical spraying of pesticides at the shipyard and not associated with the management of pesticides at Building 62 (TtNUS, August 2004). The pesticides in soil are considered a non-IRP source to the offshore. The

only current migration pathways for onshore pesticides to reach the offshore area is similar to that described above for PAHs: direct overland flow, overland flow to the storm water system, and erosion directly into the offshore area during periods of extremely high tide.

Figure A-7 in Appendix A-1 presents 4,4'-DDT concentrations for the following:

- Surface soil samples collected in the vegetated area at Site 34 because soil from this area could erode into the offshore area by direct overland flow to the river.

- Maximum 4,4'-DDT concentrations in surface/subsurface soil samples located along the shoreline because the soil could erode into the offshore area either by direct overland flow or directly into the offshore area during periods of extremely high tide.

- Offshore sediment samples collected as part of the interim offshore monitoring program.

- Other sediment samples collected in the offshore area and in the catch basin next to the abandoned wash pad at 34-18.

The soil sample locations are color coded as depicted in the legend of Figure A-7, with blue dots representing locations with the lowest 4,4'-DDT concentrations and red dots representing locations with the greatest concentrations. Concentrations for sediment samples are shown in the tags of Figure A-7.

The greatest 4,4'-DDT concentration was in a soil sample collected closest to the shoreline, at location 34-03 (see Figure A-7). As discussed above, 4,4'-DDT concentrations in soil samples are likely the result of the application of pesticides during typical spraying activities at the shipyard and not the result of the management of pesticides at Building 62. 4,4'-DDT concentrations in sediment samples collected as part of the interim offshore monitoring program are less than the greatest concentration in the soil sample. 4,4'-DDT concentrations in offshore sediment samples collected closest to the outfall from the abandoned wash pad area are relatively low and are much lower than the 4,4'-DDT concentration of 600 µg/kg in the catch basin. The sediment in the catch basin contained much debris (e.g., cigarette butts, plastic, hair, insects, twigs, etc.) indicative of surface water runoff. Therefore, pesticide concentrations in the sediment are likely from surface water runoff from soil or from erosion of soil rather than from the potential use of the wash pad [which is connected to outfall (OF)-49] for rinsing activities as part of the pesticide management.

The area surrounding Site 34 is almost entirely paved, with vehicles parked throughout the area. Two storm water outfalls (OF-49 and OF-50) discharge in the middle of MS-01, and two other outfalls (OF-48

and OF-51) discharge immediately adjacent to MS-01. Therefore, PAHs related to vehicles (i.e., oil leaks, combustion products, etc.) are also a source of PAHs to the offshore.

1.4.4 Non-PNS Sources of Contamination

There are several potential non-PNS sources of PAHs to offshore sediment at MS-01. Petroleum products (such as fuel oil, diesel, etc.) and the incomplete combustion products of fuel oils and diesel from industrial areas outside the shipyard and from parking lots can be sources of PAHs. These PAHs could migrate to the offshore via storm sewers outside of the shipyard. Also, PAHs related to boat traffic in the back channel are a potential source of PAHs to the offshore area.

1.5 MONITORING STATIONS MS-05 AND MS-09

1.5.1 Description of Monitoring Stations

MS-05 and MS-09 are located in the offshore area of OU3. Monitoring station MS-05 is located in Jamaica Cove and MS-09 is located in Clark Cove (see Figure 1-5).

As part of the remedy for OU3, the Navy completed the excavation and consolidation of contaminated soil/waste in the area adjacent to Jamaica Cove in September 2002 and completed the construction of wetlands in June 2003. Other activities for the OU3 remedy began in spring 2003, including construction of shoreline erosion controls in Clark Cove and site compaction and grading, and construction of drainage systems, followed by placement of geosynthetics on the northern portion of OU3. In the 2004 construction season, the geosynthethic materials were placed on the southern portion of OU3, the concrete wearing surface was placed on the boat storage area, the upper revetment was constructed along Clark Cove, landscaping plantings were installed, and topsoil was placed for construction of ballfields. Additionally in 2004, an area of waste was identified in Clark Cove outside the revetment, near MS-08. The area was excavated and the waste was placed under the geosynthetic material. The excavated area was backfilled with stone and silty sand.

During OU3 construction activities, turbidity curtains were used in Jamaica Cove and Clark Cove to minimize the size of the area in each cove potentially impacted by eroding soil via overland runoff. Therefore, chemical concentrations are expected to be greater in sediment within the turbidity curtain. The locations of the curtains were not surveyed, but the approximate location of the curtain in Jamaica Cove was determined using photographs of the curtain when it was deployed and aerial photographs (see Appendix A-2). The photographs were not at an adequate angle to determine locations of the turbidity curtains with respect to the sediment sample locations in Clark Cove (by MS-09). However, it is

thought that the turbidity curtain in Clark Cove was approximately 30 to 40 feet from the edge of the shoreline at MS-09.

Monitoring station MS-05 is adjacent to the wetland constructed as part of the remedy for OU3 (see Figure 1-5). Based on the approximate location of the turbidity curtain in Jamaica Cove, one of the three sample locations at MS-05 (MS-05, Loc. 1) was within the turbidity curtain; the other two sample locations at this station were outside of the turbidity curtain (see Figure 1-5). Three sediment locations are sampled at MS-05 as part of the interim offshore monitoring program; MS-05, Locs. 1 and 3 are intertidal and MS-01, Loc. 2 is subtidal. The intertidal area at MS-05 is mudflat and provides habitat for an abundance of biota including mussels, snails, worms, and seaweed. The subtidal location at monitoring station MS-05 also provides habitat for a variety of biota including algae, eelgrass, red worms, clam worms, snails, and other isopods. No seeps at this monitoring station originate from OU3 and create a furrow in the sediment above mid-tide.

Monitoring station MS-09 is in Clark Cove. Three sediment locations are sampled at MS-09 as part of the interim offshore monitoring program. MS-09, Locs. 1 and 2 were intertidal during Rounds 1 through 6. As a result of the OU3 remedial action construction activities, the intertidal sediment, which consisted of a very small area that was only exposed at very low tide, is under rip-rap. Therefore, because there is no intertidal sediment in this area, Locs. 1 and 2 were moved slightly offshore to the subtidal area. MS-09, Loc. 3 is also subtidal. It is likely that all three sediment locations were within the turbidity curtain during OU3 construction activities.

The sediment at MS-09 is generally dark and black sandy silt with some clay. The sediment is typical of "mucky" conditions and therefore provides habitat to benthic organisms that are tolerant of low dissolved oxygen concentrations (i.e., worms). After construction activities were complete in 2004, no seeps have been observed at MS-09.

1.5.2 Summary of Interim Offshore Monitoring Data

As presented in the Rounds 1 through 7 report (TtNUS, November 2004), concentrations of metals were greater than their IRGs at MS-05 and MS-09 during several of the rounds, and concentrations of fluorene and HMW PAHs were greater than their IRGs at MS-09 during Round 7 only. Concentrations of 4,4-DDT were greater that the PRG at MS-09 during several rounds.

Appendix A-2 presents the concentration trend plots from Rounds 1 through 7 for MS-05 and MS-09 for selected COCs. As discussed below, there was a sharp increase in chemical concentrations after Round 5 at MS-05 and after Round 6 at MS-09.

The conclusion that MS-05, Loc. 1 was within the turbidity curtain and the other two sample locations at MS-05 were outside of the turbidity curtain (see Figure 1-5) is supported by analytical data. The concentrations of metals were greater at MS-05, Loc. 1 in Round 6 than previous rounds, and the concentrations were still elevated in Round 7 (see Appendix A-2). The concentrations of chemicals did not increase during Rounds 6 or 7 at the other two locations. Copper was the only chemical detected at concentrations greater than the IRG; the levels of PAHs and nickel in the sediment were less than IRGs. Lead was detected at concentrations greater than the ER-M during Round 7 at MS-05.

Concentrations of metals and organic chemicals were greater at MS-09 in Round 7 than previous rounds, after the majority of the construction activities related to OU3 in this area occurred (see Appendix A-2). It is difficult to draw any meaningful data trends because the OU3 construction activities disrupted the trend lines and the two intertidal locations at MS-09 were moved to the subtidal area during Round 7. However, at MS-09, the concentrations of PAHs were generally greater in the subtidal sample, but the concentrations of metals were greater in the intertidal samples.

1.5.3 Potential PNS Sources of Contamination

The primary COCs at MS-05 are metals (copper, lead, and nickel) and the primary COCs at MS-09 are metals and organic chemicals. Therefore, this section focuses on potential onshore sources of metals and organic chemicals to the sediment at MS-05 and MS-09 and discusses potential IRP sources and potential non-IRP sources separately.

1.5.3.1 IRP Sources

OU3 is the only IRP source upgradient of MS-05 and MS-09 and is therefore the only known IRP contaminant source that may potentially impact the sediment at MS-05 and MS-09. Monitoring stations MS-05 and MS-09 are located adjacent to OU3, which is approximately 22 acres in size and consists of the soil (including landfill material) and groundwater within the Jamaica Island Landfill (JILF) boundary. The layout of OU3 is shown on Figure 1-5. This figure reflects the new boundary of the landfill and the land uses based on the remedial design (US Army, November 2002). A recent aerial photograph of the area is included in Appendix A.2. Land uses at OU3 include vehicle parking, equipment storage, and recreational areas, with asphalt or vegetation as the final cover layer over the landfill cap depending on the specific planned use of the area. OU3 consists of the following three sites:

- Site 8 - the JILF. The Navy used the JILF, which previously consisted of tidal mudflats, as a disposal area from 1945 to 1978 for general refuse, trash, construction rubble, and various industrial wastes. The boundary of OU3 is defined by the boundary of the landfill.

- Site 9 - the Former Mercury Burial Sites (MBI and MBII). Mercury burial vaults were placed in two locations within the landfill in the 1970s and then removed (intact) and disposed off site in the 1990s/early 2000. There is no indication that mercury from the vaults has contaminated surrounding soil or groundwater.

- Site 11 - the Former Waste Oil Tanks Nos. 6 and 7. The two underground storage tanks at Site 11 were used from 1943 to 1989. The waste oil tanks were removed intact and surrounding soil was removed in 1989. Soil contamination remaining in the vicinity of Site 11 appears to be landfill material mixed with petroleum materials that may have originated from spills during filling of the former tanks.

A more detailed description of OU3 can be found in Section 1.0 of the Feasibility Study Report for Operable Unit 3 (TtNUS, November 2000).

As part of the OU3 remedy, a cap was placed over the landfill material, after which migration of contamination from infiltration of runoff through unsaturated soils to the saturated zone is no longer a significant potential migration mechanism. Shoreline erosion controls were constructed so that soil erosion from OU3 to the offshore is not a current migration pathway of concern. However, during OU3 construction activities, contaminated soil likely eroded into the offshore area, as discussed above. No construction activities that may have affected chemical concentrations in Jamaica Cove sediment occurred after Round 7.

Chemicals in OU3 landfill material could migrate from the landfill to the offshore area via the following mechanisms:

- Groundwater transport occurs from areas upgradient of OU3 through the saturated zone of the landfill exiting in the intertidal zone downgradient of the landfill (i.e., in Jamaica and Clark Coves).

- Groundwater exiting the landfill in the intertidal zone passes through sediment and then mixes with river water or exits as seeps and then mixes with river water.

- Saline river water enters portions of the landfill along the shorelines of Jamaica and Clark Coves during high tide and mixes with groundwater before exiting the landfill in the intertidal zone during low tide.

1.5.3.2 Non-IRP Sources

The primary onshore non-IRP source of chemicals to the offshore sediment in Clark Cove and Jamaica Cove is storm water runoff, which may contain organic chemicals such as metals and PAHs related to vehicles (i.e., oil leaks, combustion products, etc.) or from the asphalt in paved areas.

1.5.4 Non-PNS Sources of Contamination

There are several potential offshore non-PNS sources of metals and PAHs to the offshore sediment in Clark Cove and Jamaica Cove. Petroleum products (such as fuel oil, tar, diesel, etc.) and the incomplete combustion products of fuel oils and diesel from industrial areas outside the shipyard and from parking lots and non-PNS boat traffic can be sources of metals and PAHs. These metals and PAHs could migrate to the offshore via storm sewers outside of the shipyard. Also, metals and PAHs related to boat traffic, especially in Clark Cove, where numerous boats are docked and often refueled, may be a significant source of metals and PAHs in Clark Cove.

1.6 MONITORING STATION MS-11

1.6.1 Description of Monitoring Station

This monitoring station is located in the main channel of the Piscataqua River, just offshore of OU2 (Sites 6 and 29). Three sampling locations are included within MS-11, as shown on Figure 1-6. During the interim offshore monitoring program, sediment has been consistently available at one location (MS-11, Loc. 3), which is in a small depositional intertidal area east of the OU2 shoreline. During the first round of monitoring, a small amount of sediment (eroded soil) was found at another location (MS-11, Loc. 2); however, this location is within the area addressed by the emergency removal action (shoreline erosion controls) and subsequently there has been no sediment or eroded soil at this location.

Only limited amounts of biota have been observed at MS-11. Mussels were not collected at two of the locations during the fifth round because only small mussels (much smaller than the targeted sampling size) were present. Mussels of the appropriate size had repopulated the area by the sixth monitoring round. Mud snails were noted at MS-11, Loc. 1 during Round 2, and green crabs, periwinkles, and urchins were noted at MS-11, Loc. 3 during Rounds 6 and 7.

1.6.2 Summary of Interim Offshore Monitoring Program

As presented in the Rounds 1 through 7 report (TtNUS, November 2004), additional scrutiny was recommended at MS-11 because concentrations of metals exceed their IRGs and because the contaminant concentration trend lines for offshore sediment indicate that concentrations are increasing.

Also, the concentrations of lead exceeded the ER-M at this station, and the trend lines indicate that the concentrations are increasing. Sediment is only present at one of the three station locations, at MS-11, Loc. 3; at the other two locations, mussel data along with biota-sediment accumulation factors (BSAFs) are used to estimate sediment concentrations for comparisons to IRGs. See Appendix A-3 for the concentration trend plots for copper, nickel, and lead and MS-11.

1.6.3 Potential PNS Sources of Contamination

1.6.3.1 IRP Sources

OU2 is the only known IRP source that may potentially impact the sediment at MS-11. OU2 consists of Site 6 [Defense Reutilization and Marketing Office (DRMO)] and Site 29 (Teepee Incinerator Site). Figure 1-6 shows the locations of Sites 6 and 29.

Site 6, which is approximately 2 acres in size, was established in 1920 and has served multiple purposes including a stone crusher facility and as a temporary storage area from approximately 1960 to the present. The site consisted of several old, wooden stables that served as temporary storage areas for a variety of materials and scrap metals prior to off-site recycling, disposal, or sale.

The major hazardous materials of concern at Site 6 are the lead battery cell plates that were stockpiled on uncovered pallets. Nickel-cadmium batteries were stored in the same manner. Open storage of batteries and other materials that could cause contaminants to be leached or otherwise released by pathways such as infiltration or runoff was terminated in approximately 1983. In 1993, interim corrective measures at Site 6 included the capping and paving of sections of the site, installation of storm water controls, and installation of a new concrete curb.

Most of Site 29 is situated on filled land on the southern side of Seavey Island directly bordering the Piscataqua River and includes the area surrounding Buildings 298 and 310 and the former location of Building 314 as illustrated on Figure 1-6. The site encompasses a former industrial incinerator (Teepee Incinerator) and a waste disposal area. The first reported activity at Site 29 began in 1918 with open burning of shipyard refuse until the construction of the Teepee Incinerator at the site in 1965. The incinerator ceased operations in 1975 (TtNUS, March 2000). The site is currently used as an occupational area; hazardous chemicals are not used as part of any operations at the site. The following bullets summarize the potential onshore sources of contamination to the offshore area:

- The open burning area was reportedly used for burning and as a dumping area for residual waste (i.e., paper, wood, and rubbish). Approximately 75,000 cubic yards of shipyard solid waste were burned annually (TtNUS, March 2000).

- The Teepee Incinerator was used primarily for disposal of wood, paper, and rubbish with occasional burning of cans of paint and solvents. It was reported in 1971 that approximately 1,150 cubic yards of combustible waste were burned a week at the incinerator.

- Ash from the incinerator was deposited south of the incinerator until 1971 when the residue began to be landfilled in the JILF (at OU3) and the Kittery municipal landfill.

The OU2 shoreline is steeply sloped and includes shoreline protection or erosion control measures over most of its length (see Figure 1-6). Asphalt covers most of the western portion of Site 6, and a cap (installed as an interim measure) consisting of crushed stone aggregate choked with cement overlying a clay-lined geotextile covers most of the eastern portion of Site 6. The ground surface at Site 29 consists of grass, concrete and asphalt, as well as two buildings (Building 298 and 310). The Site 6 shoreline erosion controls consist of a rock riprap revetment system installed in 1999 that extends along 630 feet of the shoreline from just west of Site 6 to the southern corner of Building 298. An approximate 300-foot long, 12-foot-high seawall runs along the shoreline from just east of Building 298 to the end of the point where the coastline angles to the southeast. The seawall acts as a retaining wall separating the fill areas from the shoreline. The seawall appears to be constructed of base layers of granite stone blocks upon which a concrete wall was poured. An approximate 70-foot segment of the Site 29 shoreline, from the eastern end of the Site 6 stabilized shoreline to the western end of the seawall, is without shoreline protection.

Periodic shoreline inspections are conducted at OU2, and in the summer of 1999, erosion was discovered along the shoreline of the Piscataqua River adjacent to Site 6. The existing embankment rock had sloughed, exposing lead-contaminated soil from the site. An emergency removal action under Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) (including shoreline erosion controls) was implemented to prevent potential exposure to the eroding soil. Details of the removal action are presented in the report titled Final Action Memorandum for Site 6 (FWENC, June 2001).

Recent observation of the OU2 shoreline shows that, overall, the erosion controls in place appear to be in reasonably good condition. However, two areas of over-steepened riprap along Site 6 (at the apparent high tide zone) and some damage to the western section of the seawall were observed. Approximately 200 feet east of the western end of the Site 6 shoreline protection system, an area was observed where some of the surface rock had moved down the slope. Approximately 50 feet east of this location, an area was observed where more of the surface rock had moved down the slope exposing a 3-foot-diameter area of geotextile. Appendix A-3 provides the MS-11 shoreline evaluation memorandum.

The western section of the seawall appears to be structurally distressed at its endpoint adjacent to Building 298. Erosion of the bank beyond the end of the wall has extended behind the end of the wall where a few of the blocks at the base of the wall have become dislodged. Pieces of metal debris were observed in the soil that was eroding in this area. One displaced block of the wall was observed on the rocky shoreline below. The blocks forming the eastern two-thirds of the wall appear reasonably tightly situated with little evidence of significant displacement. Finally, metal debris was observed on the surface in the wooded area along the eastern section of the wall. It is not known if the debris is surficial or if it extends to the subsurface. Soil from this area may be eroding to the offshore sediment at MS-11, Loc. 3 because this onshore area is immediately adjacent to that monitoring station location (See Figure 1-6).

The analytical data are consistent with the previous activities conducted at Site 29 in the area east of Building 298 (incinerator and waste disposal areas) and suggest DRMO activities or impact from DRMO activities in the area west of Building 298. In the former incinerator area, contaminant concentrations tend to be greater in surface soil than subsurface soil, and elevated levels of dioxin/furans, polychlorinated biphenyls (PCBs), PAHs, and metals were detected in this area. The concentrations of chemicals in this area are less than the concentrations detected in the waste disposal area (in subsurface soil). In the waste disposal area, concentrations tend to be greater in subsurface soil than surface soil, and the main chemicals are semivolatile organic compounds (SVOCs), PCBs, dioxin/furans, and metals. The maximum detections of these chemicals at Site 29 occur in subsurface soil samples collected within the waste disposal area. West of Building 298, concentrations of chemicals (PAHs, dioxins/furans, and metals) were generally less than concentrations observed east of the building. However, the higher concentrations of lead (and antimony) in surface soil samples nearest Site 6 (on the northwestern and southwestern sides of Building 298) are likely from DRMO operations.

Figure 1-6 presents the concentrations of copper, lead, and nickel in soil samples collected along the shoreline at Site 29. The concentrations in soil in this area may be indicative of the concentrations in soil along the shoreline that is eroding into the offshore area. Concentrations of copper, lead, and nickel are greater than 1,000 mg/kg in several samples, although the greatest concentrations are in samples that are deep [i.e., greater than 20 feet below ground surface (bgs)].

Figure 1-6 presents the potential migration pathways for onshore and offshore chemicals to be deposited at MS-11. Shoreline erosion is a current and future potential migration pathway for OU2. As described above, the shoreline along OU2 is generally steep and although there are erosion controls along most of the OU2 shoreline, there are some areas where soil along the shore is apparently eroding directly into the offshore area. Also, eroded soil may discharge to the offshore area through storm water outfalls. OU2 is located along the main channel of the Piscataqua River where the river flow is very swift, so most of the

eroding soil will be dispersed rapidly. The only intertidal sediment in the area is at MS-11, Loc. 3, and because of its location along a bend in the shoreline, eroded soil may be deposited in this area. Based on groundwater concentrations, contaminant fate and transport results, and modeling, migration of contamination through groundwater to the offshore is not considered a significant current or future pathway.

1.6.3.2 Non-IRP Sources

There are a few potential onshore non-IRP sources that may contribute contamination to the offshore area by MS-11, Loc. 3. Several outfalls are located along the OU2 shoreline that may drain surface runoff not associated with OU2. Outfall OF-78 (located east of OU2) discharges to the offshore area immediately adjacent to MS-11, Loc. 3 and could be a source of metals in the area, although there are no known sources of metals in the drainage area of this outfall. Also, based on the relatively high concentrations of metals in the sediment samples collected from MS-11, Loc. 3, it is not likely that a non-IRP site is a significant source of metals to the offshore area compared to soil erosion from OU2.

1.6.4 Non-PNS Sources of Contamination

Although it is possible that offshore sources of contamination, such as urban runoff and boat traffic, may contribute some contamination to the sediment at MS-11, based on the elevated levels of metals at this location, it is not likely that offshore sources represent a significant percentage of the metals contamination at this location compared to soil erosion from OU2.

1.7 MONITORING STATION MS-12

1.7.1 Description of Monitoring Station

MS-12 is located in a depositional area in the dry docks area offshore of Site 10 and Building 178 (see Figure 1-7). Three sediment locations are sampled at MS-12 as part of the Interim Offshore Monitoring Program; MS-12, Locs. 2 and 3 are subtidal and MS-12, Loc. 1 is intertidal. The intertidal sample is collected within a few feet south of Building 178. The subtidal locations are within a large eelgrass bed, and it was difficult during some rounds to collect sediment samples because the eelgrass prevented the sampling device from closing completely.

A large amount of biota was reported at MS-12 during the first seven sampling rounds; mussels, snails, starfish, periwinkles, eelgrass, clam worms, and red worms were found in the sediment samples from this monitoring station.

1.7.2 Summary of Interim Offshore Monitoring Program Data

As presented in the Rounds 1 through 7 report (TtNUS, November 2004), concentrations of PAHs were greater than IRGs and concentrations of lead were greater than the ER-M value in several sediment samples. For these reasons, additional scrutiny was recommended for PAHs and lead at MS-12.

Appendix A-4 presents the concentration trend plots from the Rounds 1 through 7 report for PAHs and lead at MS-12.

Concentrations of PAHs exceeded their PRGs in all rounds at one or more locations. MS-12, Loc. 1, in the intertidal area, had the greatest concentrations of PAHs and lead, and of the two subtidal samples, MS-12, Loc 2. generally had greater concentrations of PAHs while MS-12, Loc. 3 generally had greater concentrations of lead.

Concentrations of lead exceeded its ER-M in all rounds except Round 1 at one or more locations. Typically the lead concentrations at MS-12, Loc. 1 (in the intertidal area) exceeded the ER-M, whereas those at MS-12, Loc. 2 and MS-12, Loc. 3 (both of which are in the subtidal eelgrass beds) typically did not exceed the ER-M.

1.7.3 Potential PNS Sources of Contamination

The primary COCs at MS-12 are PAHs and lead. Therefore, this section focuses on potential onshore sources of PAHs and lead to the sediment at MS-12 and discusses potential IRP sources and potential non-IRP sources separately.

1.7.3.1 IRP Sources

Site 10, the former Battery Acid Tank No. 24, is the only known IRP site in the general area of MS-12. Site 10 is located on a small peninsula in the Controlled Industrial Area (CIA) near the southern shore of PNS (see Figure 1-7). Historical land use at Site 10 was industrial. Current uses include office space inside the building and some minor battery recharging work that does not generate chemical waste. The grounds surrounding Building 238 and spanning Site 10 are covered by asphalt. The Site 10 shoreline along the Piscataqua River is bounded by a quay wall of granite blocks.

Building 238 was constructed in 1955. Lead-acid battery recharging operations were conducted within the building. Sulfuric acid, used for the recharging operations, was stored in large tanks inside Building 238. Large lead-acid storage batteries were drained inside Building 238 from 1974 to 1984, and the acidic discharges were directed into the lead-acid drain pipeline, of unknown composition but probably

cast iron or steel. The acidic discharge flowed through a drain line through the floor of the building and out to an underground storage tank (Battery Acid Tank No. 24) of 9,680-gallon capacity.

The tank, which was located approximately 40 feet south of Building 238, was operational from 1974 to 1984. Chemicals discharged into the tank would have included sulfuric acid, lead, and other metals. A leak was discovered in the tank in 1984, and the tank was removed in 1986. Removal of the tank in 1986 revealed a 2-inch-diameter hole in the tank bottom. A three-aliquot composite subsurface soil sample was collected during tank removal and analyzed for Extraction Procedure (EP) Toxic metals and nickel. The data indicated no exceedance of hazardous waste criteria for these metals. The MEDEP did not require a clean-up action at the time of the tank removal.

Currently, migration of contaminants via groundwater in the fill may be the only potential migration pathway at Site 10. The groundwater in the fill is strongly affected by the daily tidal cycle. A large volume of river water is introduced through the quay wall into the site during the incoming tide, and during the outgoing tide, the displaced water returns to near pre-displaced conditions. Because there is also a net flow of groundwater from the island interior towards the river, there is a slow, net migration toward the river with each complete tidal cycle. Based on the results from site investigations, lead contamination does not appear to be migrating in the groundwater at detectable concentrations (i.e., measurable with routine analytical methods). Compared to lead concentrations in subsurface soil where site wells are screened, concentrations of lead detected in groundwater are several orders of magnitude lower, indicating that dissolution of lead is minor. Therefore, even though groundwater flux is high in the fill material at the site, the data indicate that lead contamination is not migrating in the groundwater at concentrations of concern.

The most likely contaminant release pathway was direct point-source releases to surface and subsurface soils from the acid lead drain line, leaking tank, and operational spills. There appear to be no lead migration pathways in either the soil or groundwater at the site.

1.7.3.2 Non-IRP Sources

Potential non-IRP sources of lead and PAHs (such as parking lot and road runoff, river traffic, etc.) may be contributing to the contamination at MS-12 via storm sewer discharges and overland runoff. It can be seen from Figure 1-7 that almost the entire onshore area surrounding MS-12 is paved or covered with buildings, and there are a few storm water outfalls in the area.

MS-12 is located adjacent to Building 178, a one-story 178,000-square-foot building. The floor in the southern portion of the building (closest to the water) is concrete, but the floor in the northern part of the building is concrete covered with creosote-treated wood blocks (Malcolm Pirnie, November 1998).

However, because the wood floor is not covered with water, it is not likely a significant source of PAHs to the offshore area.

Building 178 is currently used as a storage area for items including wooden pallets, large cable coils, drums containing silica sand sealant and blasting materials, and several compressed gas cylinders (Malcolm Pirnie, November 1998).

From 1944 until 1970, the primary operation in Building 178 involved the construction of submarines (Malcolm Pirnie, November 1998). The operations included welding, spray-painting, lead-working (melting, cutting, etc.), metal cleaning/polishing, and sand blasting. After 1970, the activities shifted to maintaining and repairing naval vessels. It is possible that the operations in the building resulted in the release of lead and/or PAHs to the offshore area. However, the only documented release was a 0.5-gallon spill of non-oil based paint to the Piscataqua River (Malcolm Pirnie, November 1998). [The Navy does not currently consider the operations inside Building 178 to be an IRP source because it would be a release from within a building, which is not eligible for Environmental Restoration, Navy (ER,N) funds. However, further evaluation will be performed to determine whether a release from within a building is eligible for ER,N funds when appropriate.]

1.7.4 Non-PNS Sources of Contamination

There are several potential non-PNS sources of PAHs to the offshore sediment at MS-12. Petroleum products (such as fuel oil, tar, diesel, etc.) and the incomplete combustion products of fuel oils and diesel from industrial areas outside the shipyard and from parking lots can be sources of lead and PAHs. These chemicals could migrate to the offshore via storm sewers outside of the shipyard. Also, PAHs related to boat traffic in the river are a potential source of PAHs to the offshore area at MS-12.

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USEPA-NE QAPP Worksheet #2 - Rev. 0

Site Name/Project Name: Additional Scrutiny Investigation
Site Location: Portsmouth Naval Shipyard (PNS), Kittery, Maine
Site Number/Code: Offshore
Operable Unit: OU4

Contractor Name: Tetra Tech NUS, Inc. (TtNUS)
Contract Task Order Number: 023
Contract Title: Navy Comprehensive Long-term Environmental Action Navy (CLEAN) Program

1. **Identify Guidance used to prepare QAPP:**

   Region I, USEPA-NE Compendium QAPP Guidance, Attachment and/or other:

   ***Region 1 USEPA**-New England Compendium of Quality Assurance Project Plan Guidance, October 1999, Final.*

2. **Identify USEPA Program:** *Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)*

3. **Identify approval entity: USEPA-NE or State:** *USEPA-NE*

   or other entity:

4. **Indicate whether the QAPP is a generic program QAPP or a project specific QAPP:** *Project Specific*

5. **List dates scoping meetings were held:** *Scoping meetings were held between the Navy (EFANE/PNS) and TtNUS in 2004 and 2005 and regulatory and RAB input was provided by review and comment as discussed in Section 2.1.*

6. **List dates and titles of QAPP documents written for previous site work, if applicable:**

   References to previous investigations are provided in the background discussions in Sections 1.3 through 1.7.

7. **List organizational partners (stakeholders) and connection with USEPA and/or State:**
   MEDEP; Natural Resources Trustees; PNS RAB

8. **List data users:** *The Navy will use the data to support evaluation of the nature and/or extent of chemicals observed in the offshore areas of PNS. The USEPA, MEDEP, Natural Resources Trustees, and RAB will review the documents prepared for OU4.*

9. **If any required QAPP Elements (1-20), Worksheets and/or Required Information are not applicable to the project, then circle the omitted QAPP Elements, Worksheets, and Required Information on the attached Table. Provide an explanation for their exclusion below:**

   The information needed for the worksheets was directly filled into the tables of relevant QAPP sections; therefore, except for this work sheet (Worksheet No. 2), worksheets are not included in the QAPP.

USEPA-NE QAPP Worksh t #2 (Continu d)

REQUIRED USEPA QA/R-5 ELEMENTS	QAPP CORRESPONDING SECTION	REQUIRED USEPA-NE QAPP ELEMENT(S) and CORRESPONDING USEPA-NE QAPP SECTION(S)	USEPA-NE QAPP Worksheet #	REQUIRED INFORMATION
		Project Management and Objectives		
A1	Title and Signature page	1.0 Title and Approval Page	1	- Title and Approval Page
A2	1.2 Begin. of Document 1.2.3 1.2.3 1.2.2	2.0 Table of Contents and Document Format 2.1 Table of Contents 2.2 Document Control Format 2.3 Document Control Numbering System 2.4 USEPA-NE QAPP Worksheet #2	2	- Table of Contents - USEPA-NE QAPP Worksheet
A3	1.2.3	3.0 Distribution List and Project Personnel Sign-off Sheet	3 4	- Distribution List - Project Personnel Sign-off Sheet
A4; A8	3.0 3.1 3.2 3.2.1 3.3 3.4	4.0 Project Organization 4.1 Project Organizational Chart 4.2 Communication Pathways 4.2.1 Modifications to Approved QAPP 4.3 Personnel Responsibilities and Qualifications 4.4 Special Training Requirements/ Certification	5a 5b 6 7	- Organizational Chart - Communication Pathways - Personnel Responsibilities and Qualifications Table - Special Personnel Training Requirements Table
A5	2.1 2.1 1.3,1.4, 1.5,1.6, 1.7	5.0 Project Planning/Project Definition 5.1 Project Planning Meetings 5.2 Problem Definition/Site History and Background	8a 8b	- Project Planning Meeting Documentation - Project Scoping Meeting Attendance Sheet with Agenda - Problem Definition/Site History and Background - USEPA-NE DQO Summary Form - Site Maps (historical and present)

USEPA-NE QAPP Worksh et #2 (Continued)

REQUIRED USEPA QA/R-5 ELEMENTS	QAPP CORRESPONDING SECTION	REQUIRED USEPA-NE QAPP ELEMENT(S) and CORRESPONDING USEPA-NE QAPP SECTION(S)	USEPA-NE QAPP Worksheet #	REQUIRED INFORMATION
Project Management and Objectives (Continued)				
A6	2.0 2.2 through 2.6, 4.6, 5.1 3.7	6.0 Project Description and Schedule 6.1 Project Overview 6.2 Project Schedule	9a 9b 9c 9d 10	- Project Description - Contaminants of Concern and Other Target Analytes Table - Field and Quality Control Sample Summary Table - Analytical Support Laboratories - System Designs - Project Schedule Timeline, Products, and Deliverable table
A7	2.0, 5.0, 6.0 2.2 through 2.6 6.3	7.0 Project Quality Objectives and Measurement Performance Criteria 7.1 Project Quality Objectives 7.2 Measurement Performance Criteria	11 11	- Measurement Performance Criteria - Concentration Levels
Measurement/Data Acquisition				
B1	4.0 2.2 through 2.6 and 4.0	8.0 Sampling Process Design 8.1 Sampling Design Rationale	12a 12b	- Sampling Rationale - Sampling Locations, Sampling and Analytical Method/SOP Requirements Table - Sample Location Map
B2, B6, B7, B8	4.0 4.0 4.11 4.8 NA 4.12 4.12	9.0 Sampling Procedures and Requirements 9.1 Sampling Procedures 9.2 Sampling SOP Modifications 9.3 Cleaning and Decontamination of Equipment/Sample Containers 9.4 Field Equipment Calibration 9.5 Field Equipment Maintenance, Testing and Inspection Requirements 9.6 Inspection and Acceptance Requirements for Supplies/Sample Containers	13 12b 14 15	- Sampling SOPs - Project Sampling SOP Reference Table - Sampling Container, Volumes and Preservation Table - Sampling Equipment Calibration Table - Cleaning and Decontamination SOPs - Field Equipment Maintenance, Testing and Inspection Table

USEPA-NE QAPP Worksheet #2 (Continued)

REQUIRED USEPA QA/R-5 ELEMENTS	QAPP CORRESPONDING SECTION	REQUIRED USEPA-NE QAPP ELEMENT(S) and CORRESPONDING USEPA-NE QAPP SECTION(S)	USEPA-NE QAPP Worksheet #	REQUIRED INFORMATION
		Measurement/Data Acquisition (Continued)		
B3	4.7 4.10 4.10 4.10 4.7 4.7	10.0 Sample Handling, Tracking, and Custody Requirements 10.1 Sample Collection Documentation 10.1.1 Field Notes 10.1.2 Field Documentation Management System 10.2 Sample Handling and Tracking System 10.3 Sample Custody	16	- Sample Handling, Tracking and Custody SOPs - Sample Handling Flow Diagram - Sample Container Label (Sample Tag) - Chain-of-Custody Form and Seal
B4, B6, B7, B8	NA 4.12 4.12	11.0 Field Analytical Method Requirements 11.1 Field Analytical Methods and SOPs 11.2 Field Analytical Method/ SOP Modifications 11.3 Field Analytical Instrument Calibration 11.4 Field Analytical Instrument/ Equipment Maintenance, Testing and Inspection Requirements 11.5 Field Analytical Inspection and Acceptance Requirements for Supplies	17 18 19	- Field Analytical Methods/SOPs - Field Analytical Method/SOP Reference Table - Field Analytical Instrument Calibration Table - Field Analytical Instrument/ Equipment Maintenance, Testing and Inspection Table

USEPA-NE QAPP Worksh t #2 (Continued)

REQUIRED USEPA QA/R-5 ELEMENTS	QAPP CORRESPONDING SECTION	REQUIRED USEPA-NE QAPP ELEMENT(S) and CORRESPONDING USEPA-NE QAPP SECTION(S)	USEPA-NE QAPP Worksheet #	REQUIRED INFORMATION
		Measurement/Data Acquisition (Continued)		
B4, B6, B7, B8	5.0 5.2 5.2 5.3 5.3, 5.4 5.5	12.0 Fixed Laboratory Analytical Method Requirements 12.1 Fixed Laboratory Analytical Methods and SOPs 12.2 Fixed Laboratory Analytical Method/SOP Modifications 12.3 Fixed Laboratory Instrument Calibration 12.4 Fixed Laboratory Instrument/ Equipment Maintenance, Testing and Inspection Requirements 12.5 Fixed Laboratory Inspection and Acceptance Requirements for Supplies	20 21	- Fixed Laboratory Analytical Methods/SOPs - Fixed Laboratory Analytical Method/SOP Reference Table - Fixed Laboratory Instrument Maintenance and Calibration Table
B5	4.6 4.6 4.6, 5.4 NA 5.4	13.0 Quality Control Requirements 13.1 Sampling Quality Control 13.2 Analytical Fixed Laboratory Quality Control 13.2.1 Field Analytical QC 13.2.2 Fixed Laboratory QC	22a 22b 23a 23b 24a 24b	**Sampling** - Field Sampling QC Table - Field Sampling QC Table cont. **Analytical** - Field Analytical QC Sample Table - Field Analytical QC Sample Table cont. - Fixed Laboratory Analytical QC Sample Table - Fixed Laboratory Analytical QC Sample Table cont.
B9	NA	14.0 Data Acquisition Requirements	25	- Non-Direct Measurements Criteria and Limitations Table

USEPA-NE QAPP Worksh t #2 (Continued)

REQUIRED USEPA QA/R-5 ELEMENTS	QAPP CORRESPONDING SECTION	REQUIRED USEPA-NE QAPP ELEMENT(S) and CORRESPONDING USEPA-NE QAPP SECTION(S)	USEPA-NE QAPP Worksheet #	REQUIRED INFORMATION
Measurement/Data Acquisition (Continued)				
A10, B10	6.1 6.1.1 6.1.2 6.1.3 6.1.4 6.1.5 6.1.6	15.0 Documentation, Records, and Data Management 15.1 Project Documentation and Records 15.2 Field Analysis Data Package Deliverables 15.3 Fixed Laboratory Data Package Deliverables 15.4 Data Reporting Formats 15.5 Data Handling and Management 15.6 Data Tracking and Control	26	- Project Documentation and Records Table - Data Management SOPs
Assessment/Oversight				
C1	3.5 3.5.1 3.5.2 3.5.3	16.0 Assessments and Response Actions 16.1 Planned Assessments 16.2 Assessment Findings and Corrective Action Responses 16.3 Additional QAPP Non-Conformances	27a 27b 27c	- Assessment and Response Actions - Project Assessment Table - Project Assessment Plan - Audit Checklists
C2	3.6	17.0 QA Management Reports	28	- QA Management Reports Table
Data Validation and Usability				
D1	6.2	18.0 Verification and Validation Requirements		- Validation Criteria Documents
D2	6.2	19.0 Verification and Validation Procedures	29a 29b 29c	- Data Evaluation Process - Data Validation Summary Table - Data Validation Modifications
D3	6.3	20.0 Data Usability/Reconciliation with Project Quality Objectives	30	- Data Usability Assessment

TABLE 1-1

DISTRIBUTION LIST
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

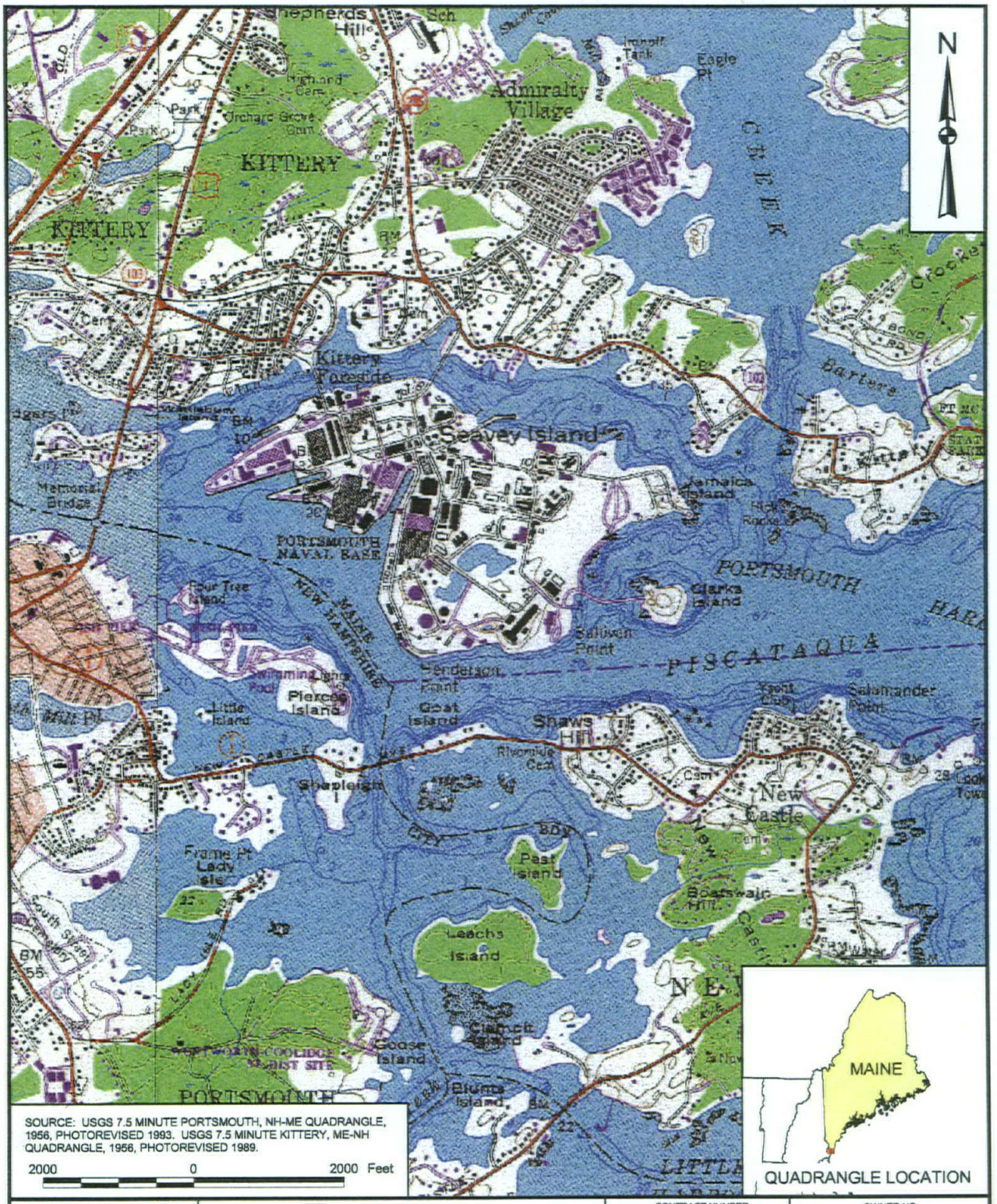
QAPP Recipients	Title	Organization	Telephone Number
Mr. Matthew Audet	USEPA Remedial Project Manager (RPM)	USEPA Region 1	617-918-1449
Mr. Iver McLeod	MEDEP RPM	Maine Department of Environmental Protection	207-287-8010
Mr. Fred Evans	Navy RPM	EFANE, Navy	610-595-0567 ext. 159
Ms. Marty Raymond	PNS IRP Manager	Portsmouth Naval Shipyard	207-438-2536
Ms. Deborah Cohen	TtNUS PNS Facility Coordinator	Tetra Tech NUS, Inc., Pittsburgh, PA	Contact Fred Evans
Mr. Aaron Bernhardt	TtNUS Project Manager (PM)/ Technical Lead	Tetra Tech NUS, Inc., Pittsburgh, PA	Contact Fred Evans
Ms. Kelly Carper	TtNUS Quality Assurance (QA) Officer	Tetra Tech NUS, Inc., Pittsburgh, PA	Contact Fred Evans

Note: All people on the PNS distribution list (including the Natural Resources Trustees and RAB) will receive copies of the QAPP and all updates to the QAPP. A complete distribution list is available from the Navy and can be provided on request. The TtNUS PM will be responsible for distribution of copies of the QAPP and all updates to the QAPP to TtNUS project personnel, including the field operations leader (FOL).

TABLE 1-2

EXAMPLE PROJECT PERSONNEL SIGN-OFF SHEET
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Project P rsonnel	Title	Signature	Date QAPP Read	QAPP Acceptable As Written
Deborah Cohen	TtNUS Facility Coordinator			
Aaron Bernhardt	TtNUS Project Manager/Technical Lead			
Kelly Carper	TtNUS QA Officer			
Doug Schloer	TtNUS Lead Chemist			
Joseph Samchuck	TtNUS Data Validation Supervisor			



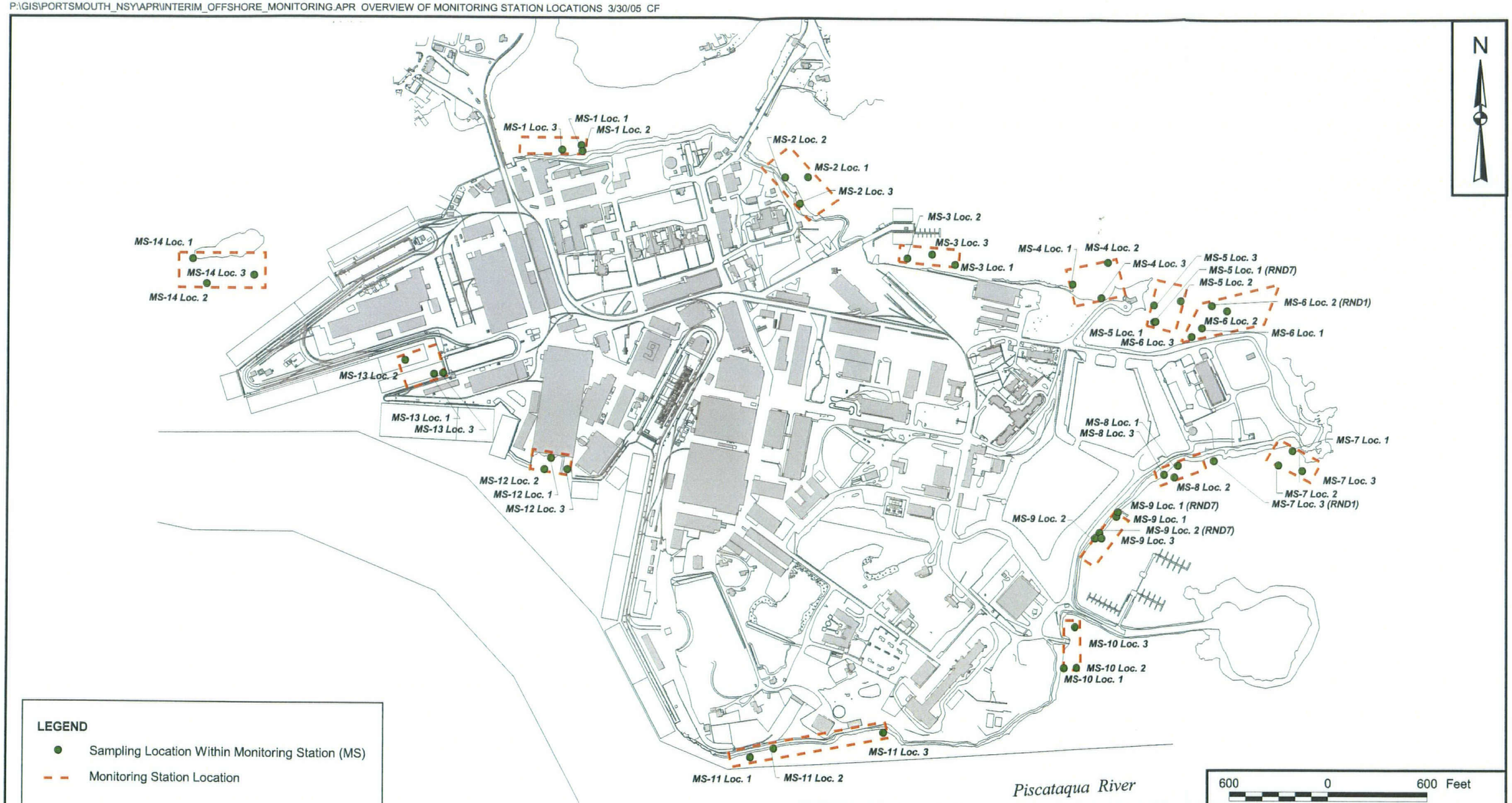
SOURCE: USGS 7.5 MINUTE PORTSMOUTH, NH-ME QUADRANGLE, 1956, PHOTOREVISED 1993. USGS 7.5 MINUTE KITTERY, ME-NH QUADRANGLE, 1956, PHOTOREVISED 1989.

2000 0 2000 Feet

DRAWN BY J. LAMEY — DATE 12/29/03	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NO. CTO 023
CHECKED BY A. BERNHARDT — DATE 3/29/05	PORTSMOUTH NAVAL SHIPYARD VICINITY MAP ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY AMB	DATE 9-12-05
COST/SCHEDULE-AREA		APPROVED BY —	DATE —
SCALE AS NOTED		DRAWING NO. FIGURE 1 - 1	REV 0

P:/GIS/PORTSMOUTH_NSY/APR/INTERIM_MONITORING_REPORT.APR VICINITY LAYOUT 3/29/05 CF

P:\GIS\PORTSMOUTH_NSY\APR\INTERIM_OFFSHORE_MONITORING.APR OVERVIEW OF MONITORING STATION LOCATIONS 3/30/05 CF

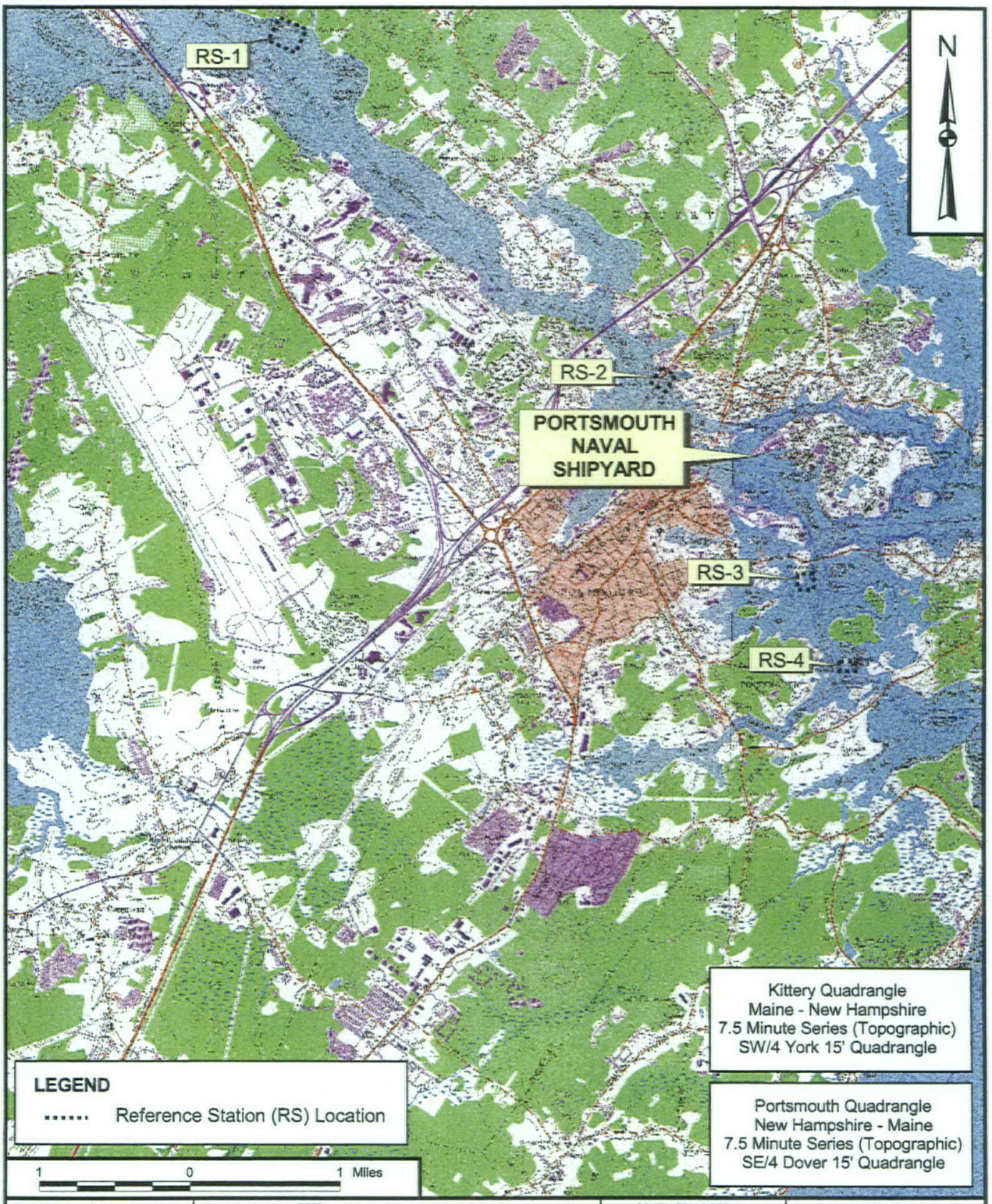


LEGEND

- ● Sampling Location Within Monitoring Station (MS)
- - - Monitoring Station Location

Note: This figure and all other figures show sample locations for data that were evaluated as part of this report. The locations with (RND1) and (RND7) indicates the locations of those stations during that round.

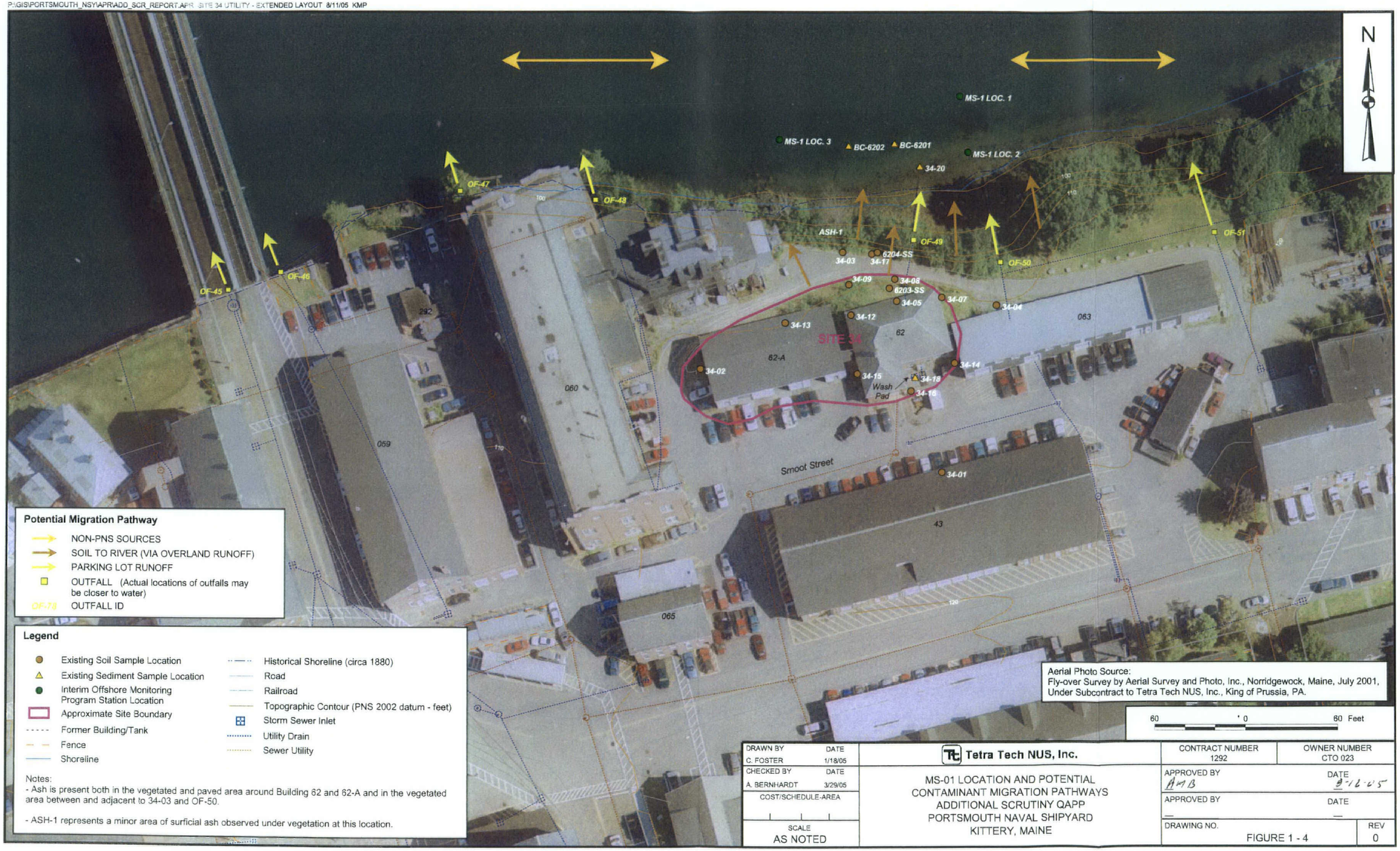
DRAWN BY J. LAMEY	DATE 4/20/04	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292 / OWNER NUMBER CTO 023
CHECKED BY A. BERNHARDT	DATE 3/24/05	OVERVIEW OF MONITORING STATION LOCATIONS FOR THE INTERIM OFFSHORE MONITORING PROGRAM ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY AMB / DATE 8-12-05
COST/SCHEDULE-AREA			APPROVED BY — / DATE —
SCALE AS NOTED			DRAWING NO. FIGURE 1 - 2 / REV 0



DRAWN BY J. LAMEY DATE 4/27/04	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NO. CTO 023
CHECKED BY A. BERNHARDT DATE 3/24/05	OVERVIEW OF REFERENCE STATION LOCATIONS FOR THE INTERIM OFFSHORE MONITORING PROGRAM ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY — DATE —	
COST/SCHEDULE-AREA		APPROVED BY — DATE —	
SCALE AS NOTED		DRAWING NO. FIGURE 1 - 3	REV 0

P:\GIS\PORTSMOUTH_NSY\APR\INTERIM_OFFSHORE_MONITORING.APR OVERVIEW OF REFERENCE STATION LOCATIONS 3/24/05 CF

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR SITE 34 UTILITY - EXTENDED LAYOUT 8/11/05 KMP



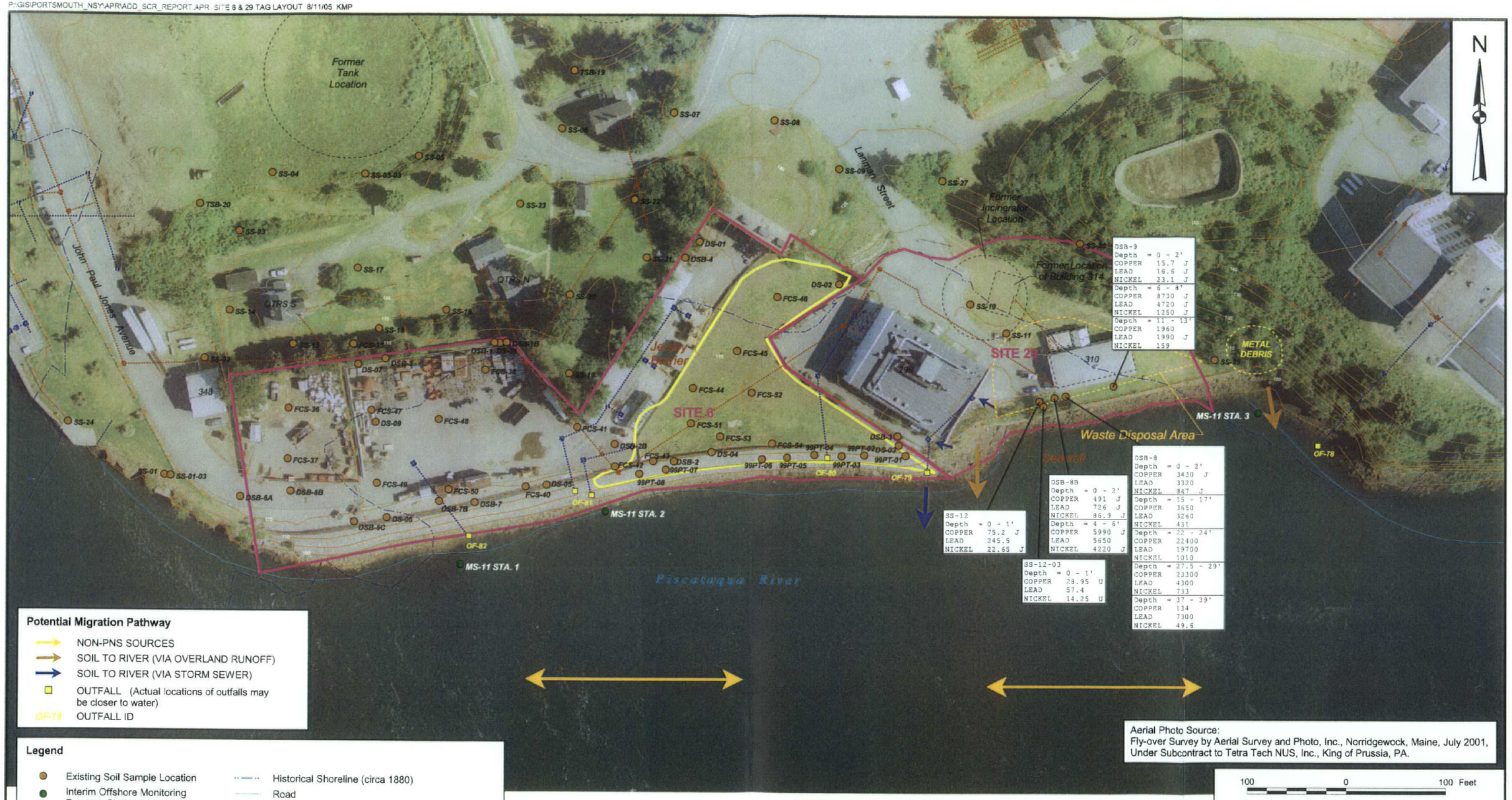
DRAWN BY	DATE	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
C. FOSTER	1/18/05			
CHECKED BY	DATE	MS-01 LOCATION AND POTENTIAL CONTAMINANT MIGRATION PATHWAYS ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY AMB	DATE 8-12-05
A. BERNHARDT	3/29/05		APPROVED BY —	DATE —
COST/SCHEDULE-AREA			DRAWING NO. FIGURE 1 - 4	REV 0
SCALE AS NOTED				

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR TURBIDITY CURTAIN LAYOUT 8/11/05 KMP

Aerial Photo Source:
Fly-over Survey by Aerial Survey and Photo, Inc., Norridgewock, Maine, July 2001, Under Subcontract to Tetra Tech NUS, Inc., King of Prussia, PA.

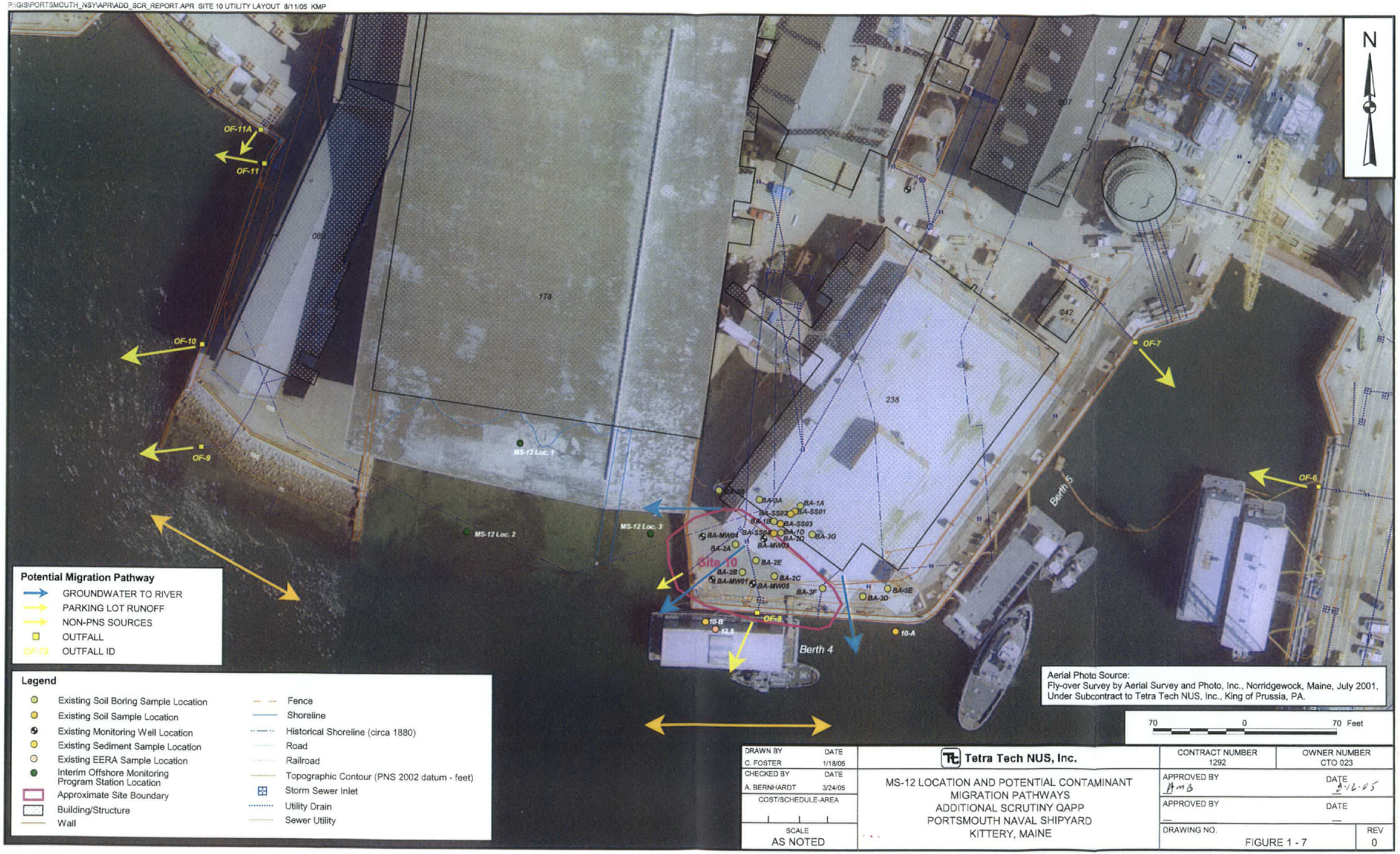
DRAWN BY C. FOSTER DATE 01/27/05	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
CHECKED BY A. BERNHARDT DATE 03/29/05	MS-05, MS-08, AND MS-09 LOCATIONS ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY AMB	DATE 8-12-05
COST/SCHEDULE-AREA		APPROVED BY	DATE
SCALE AS NOTED		DRAWING NO. FIGURE 1 - 5	REV 0

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR SITE 8 & 29 TAG LAYOUT 8/11/05 KMP



DRAWN BY	DATE	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
C.FOSTER	1/31/04			
CHECKED BY A. BERNHARDT	DATE 3/29/05	MS-11 LOCATION AND POTENTIAL CONTAMINANT MIGRATION PATHWAYS ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY AMB	DATE 8-16-05
COST/SCHEDULE-AREA			APPROVED BY —	DATE —
SCALE AS NOTED			DRAWING NO. FIGURE 1-6	REV 0

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR SITE 10 UTILITY LAYOUT 8/11/05 KMP



DRAWN BY	DATE	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
C. FOSTER	1/18/05	MS-12 LOCATION AND POTENTIAL CONTAMINANT MIGRATION PATHWAYS ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY AMB	DATE 8-16-05
CHECKED BY	DATE		APPROVED BY —	DATE —
A. BERNHARDT	3/24/05		DRAWING NO. FIGURE 1 - 7	REV 0
COST/SCHEDULE-AREA				
SCALE AS NOTED				

2.0 DATA QUALITY OBJECTIVES

This section summarizes the project DQOs developed in accordance with USEPA Guidance for the DQO Process, commonly known as QA/G-4 (USEPA, August 2000). The following discussion provides information on the project planning conducted to develop the DQOs. The project definition, the project quality objectives, and the measurement performance criteria are identified based on the DQOs and provided in this QAPP. The USEPA Region I QAPP guidance (USEPA, October 1999) provides worksheets to be completed during DQO planning meetings; however, the worksheets were not used because the information needed for the worksheets is included in the relevant sections of this plan. The DQOs were developed separately for each monitoring station because each station has specific characteristics and data needs.

2.1 PROJECT PLANNING MEETINGS

The Navy submitted two technical memoranda describing the additional scrutiny proposed at monitoring stations MS-01, MS-05, MS-08, MS-09, MS-11, and MS-12. The Navy received regulator comments on the memoranda and prepared response to comment documents. The technical memoranda and the responses to comments are included in Appendix B.

The technical memoranda were used as the starting point for the DQOs. During development of the DQOs (and based on some of the regulator comments), it was determined that some of the data and/or evaluations proposed in the technical memoranda would not provide useful information for making decisions at the monitoring stations. Therefore, some of the items presented in the technical memoranda are not included in the DQOs. Furthermore, it was determined that additional data and/or evaluations that were not proposed in the technical memoranda may provide useful information for making decisions at the monitoring stations, so these items are presented in the DQOs.

The Navy prepared a technical memorandum comparing the analytical methods used in the interim offshore monitoring program to standard USEPA analytical methods to determine whether USEPA analytical methods could be used for future rounds of sampling without compromising data usability. The memorandum was submitted to the regulators and RAB, and regulator comments were received. The memorandum and responses to comments are included in Appendix B. The recommendations from the memorandum are summarized as follows:

- Use NOAA analytical methods for metals analysis of sediment samples at the monitoring and reference stations as part of the Interim Offshore Monitoring Program stations for data that will be

used for chemical trend plots. USEPA analytical methods will be considered for sediment samples that will not be included in the trend plots (i.e., extent samples).

- Use USEPA analytical methods for metals analysis of mussel samples at the monitoring and reference stations as part of the interim offshore monitoring program.

- Use USEPA analytical methods for organic chemical analysis of sediment and mussel samples at the monitoring and reference stations as part of the interim offshore monitoring program provided that the detection limits are low enough to meet project objectives.

- Remove chlorpyrifos, pentachloroanisole, pentachlorobenzene, 1,2,3,4-tetrachlorobenzene, and 1,2,4,5-tetrachlorobenzene from the parameter list for future interim offshore monitoring program sampling rounds.

Based on these recommendations, USEPA methods (with some modifications for the PAH forensics analysis) will be used for chemical analysis of all samples collected for the additional scrutiny. Section 5.0 and Appendix D (the PAH Forensics Sample Analysis QAPP) presents the analytical methods that will be used for chemical analysis.

As part of developing the Additional Scrutiny QAPP, the Navy held two conference calls and one technical meeting with regulators as follows:

- Conference call between the Navy, TtNUS, NOAA, and the United States Fish and Wildlife Service (FWS) on November 9, 2004 to discuss the prioritization of the additional scrutiny under OU4.

- Conference call between the Navy, TtNUS, USEPA, MEDEP, and the FWS on May 5, 2005 to discuss initial comments during the review of the draft QAPP before receipt of comments.

- Technical meeting on June 14, 2005 to conduct a site visit and resolve MEDEP comments on the draft QAPP.

The conference call notes, meeting minutes, and responses to comments on the QAPP are provided in Appendix E.

2.2 MONITORING STATION MS-01

As discussed in Section 1.4, this monitoring station is located in the Back Channel, offshore of Site 34 and adjacent to the bridge leading to Gate No. 1 (see Figure 1-4). Additional scrutiny was recommended for this station because concentrations of PAHs exceeded their respective IRGs, and the trend lines indicated that concentrations are increasing. Also, the concentrations of 4,4'-DDT exceeded the PRG at MS-01 and is projected to exceed the PRG for the next 5 years.

2.2.1 Problem Statement

Unacceptable levels of PAHs and 4,4'-DDT are present in sediment at MS-01, but the source of the PAHs and 4,4'-DDT in the sediment is not known. The Navy needs to identify whether an IRP source is the primary source of PAHs and 4,4'-DDT in the sediment to justify an action or further evaluations of this area under the Navy's IRP.

The potential IRP sources for PAHs and/or 4,4'-DDT at MS-01 include the following:

- Erosion of soil containing high levels of PAHs related to ash from operations at Site 34.
- Historical discharges to outfall (OF-49) from pesticide rinsing activities at Site 34.

The potential non-IRP sources for PAHs and/or 4,4'-DDT at MS-01 include the following:

- Erosion of soil containing 4,4'-DDT from historical spraying activities in the area.
- Storm water runoff containing PAHs from onshore areas that are not related to ash at Site 34.
- Non-PNS sources such as urban runoff, boat traffic, etc.

2.2.2 Decision Statements

Based on the problem statement, a study question and decision statement for PAHs and a study question and decision statement for pesticides were developed.

Study Question No. 1: Is eroding soil at Site 34 a primary source of PAHs in sediment at MS-01?

Decision Statement No. 1: Determine whether Site 34 is a primary source of PAHs at MS-01:

- If it is either clearly a primary source, or if it may be a primary source, evaluate source control for offshore migration as part of the RI/removal actions conducted for Site 34 (soil and ash) or OU4 (sediment) and further refine ecological risks in the offshore area as part of OU4.

- If it is clearly not a primary source, do not evaluate source control for offshore migration or further refine ecological risks in the offshore area and consider modifying the interim offshore monitoring program.

Study Question No. 2: Were operations associated with Site 34 (i.e., potential rinsing activities at the wash pad) a past source of 4,4'-DDT in the sediment at MS-01?

Decision Statement No. 2: Determine whether past pesticide rinsing operations associated with Site 34 were a primary source of 4,4'-DDT in sediment at MS-01?

- If they were clearly a primary source, consider a removal action for OU4 and/or consider further refining ecological risk estimates in the offshore area as part of OU4.

- If it cannot be determined past rinsing operations associated with Site 34 were a primary source, hold discussions with the regulators and consider modifying the interim offshore monitoring program to reflect the importance of Site 34 as a potential offshore contaminant source of 4,4'-DDT to MS-01.

- If they were clearly not a source, do not consider a removal action for OU4 or further refine ecological risk estimates in the offshore area as part of OU4 and consider modifying the interim offshore monitoring program to reflect the importance of Site 34 as a potential offshore contaminant source of 4,4'-DDT to MS-01.

2.2.3 Decision Inputs

The following data and evaluations are needed to determine whether soil at Site 34 is a primary source of PAHs in sediment at MS-01:

- PAH forensic analysis (i.e., fingerprinting) for source signatures of the following:

  - Sediment at MS-01.
  - Sediment from storm water catch basins and/or offshore sediment adjacent to storm water outfall locations (on the shipyard).
  - Sediment adjacent to storm water outfall locations below mid-tide (off the shipyard).
  - Sediment from select reference station locations to determine the pattern of typical urban runoff.
  - Ash/soil from Site 34.

- Microscopic analysis of the sediment to evaluate the presence of ash or coal in the sediment.

- Determine whether PAH concentrations are increasing over time using current and existing data, as necessary based on the following:

  - Concentration trend plots of existing PAH sediment concentrations normalized to total organic carbon (TOC) or grain size (using percent silt). This will be used to determine whether PAH concentrations are related to TOC or percent silt levels in the sample.

  - Concentration trend plots for PAHs at individual sample locations within MS-01. This will be used to determine whether the apparent increase in concentrations is being driven by one sample location.

  - Sediment and sample location descriptions to determine whether there are factors that may be influencing chemical concentrations in sediment (i.e., unable to sample same locations, heterogeneous sediment, etc.) and sample duplicate (i.e., precision) data from sediment collected at MS-01 during previous sampling rounds. These will be used to evaluate the heterogeneity of the samples to determine whether the increasing concentration trend is an anomaly of the data.

- Determine whether there is a current migration pathway for PAHs from Site 34 to the offshore area using the following:

  - Observations of complete migration pathways from the ash to offshore sediment (i.e., signs of erosion, locations of drainage ditches, observation of runoff during a rain event, etc.).

- Spatial distribution of PAH concentrations in sediment.

- The following data are needed to determine whether Site 34 was a past primary source of 4,4'-DDT in the sediment at MS-01:

  - Sample duplicate (i.e., precision) data from sediment collected at MS-01 during previous sampling rounds to determine whether elevated detections are anomalies and not representative of station conditions.

  - Spatial distribution of pesticide concentrations in sediment.

- Pesticide concentrations in catch basins at PNS that collect runoff from areas where pesticides, specifically 4,4'-DDT, have been historically applied to the soil that may erode into the catch basins.

The following are the target parameters for soil/sediment samples collected for PAH forensics analysis:

- Total petroleum hydrocarbons (TPH) ranging from C9 to C36.
- Parent PAH compounds, alkyl homologues, and an expanded list of selected individual PAH isomers and biomarkers.
- TOC.

The following are the target parameters for sediment samples collected for the evaluation of 4,4'-DDT:

- Pesticides.
- TOC.

2.2.4 Study Boundaries

The study boundaries for the additional scrutiny at MS-01 are listed below:

- Sediment from catch basins that collects storm water runoff from parking areas not impacted by Site 34 to determine whether the PAH "fingerprint" and/or pesticide levels in offshore sediment samples at MS-01 are similar to that of sediment in the catch basins.

- Sediment below mid-tide adjacent to storm water outfalls from nearby urban areas (not at PNS) to determine whether the PAH "fingerprint" in that sediment is similar to the "fingerprint" in the offshore sediment samples at MS-01.

- Sediment from select reference station locations to determine the pattern of typical urban runoff.

- Sediment samples at MS-01 at locations far enough from the potential source area to evaluate the spatial distribution of PAHs and pesticides.

- Surficial (e.g., top 2 inches) soil/ash samples at Site 34, especially from areas where soil/ash has the potential for eroding to the offshore area, to determine whether the PAH "fingerprint" in the offshore sediment samples at MS-01 is similar to that of the soil/ash.

2.2.5 D cision Rules

Decision Rules for Problem Statement No. 1 (Evaluation of PAHs)

If Site 34 is clearly a primary source of PAHs at MS-01, or if it may be a primary source, evaluate source control for offshore migration as part of the RI/removal actions for Site 34 (soil/ash) or OU4 (sediment) and further refine ecological risks in the offshore area as part of OU4.

If Site 34 is clearly not a primary source, do not evaluate source control for offshore migration or further refine ecological risks in the offshore area and consider modifying the interim offshore monitoring program.

The following questions will be answered in a line of evidence approach to determine whether Site 34 is a primary source of the elevated levels of PAHs in sediment at MS-01:

- Does the forensic analysis indicate that the source signature of PAHs in Site 34 soil/ash and signatures of PAHs in sediment at MS-01 are similar but are different from the signature(s) in other samples?

- Are concentrations of PAHs increasing in sediment? This could indicate a continuing significant source versus an historic source.

- Does the microscopic analysis of sediment indicate the presence of ash and/or coal from Site 34 that could be the source of the PAHs?

- Is there a complete migration pathway from the exposed site soil/ash to the sediment?

Decision Rules for Problem Statement No. 2 (Evaluation of 4,4'-DDT)

If past pesticide rinsing operations associated with Site 34 are clearly a primary source of 4,4'-DDT in the sediment at MS-01, consider a removal action for OU4 and/or consider further refining ecological risks in the offshore area as part of OU4.

If it cannot be determined whether past pesticide rinsing operations associated with Site 34 are clearly a primary source of 4,4'-DDT in the sediment at MS-01, hold discussions with the regulators and consider modifying the interim offshore monitoring program to reflect the importance of Site 34 as a potential offshore contaminant source of 4,4'-DDT to MS-01.

If past pesticide rinsing operations associated with Site 34 are clearly not a primary source, do not consider a removal action for OU4 or further refine ecological risks in the offshore area as part of OU4 and consider modifying the interim offshore monitoring program to reflect the importance of Site 34 as a potential offshore contaminant source of 4,4'-DDT to MS-01.

The following questions will be answered in a line-of-evidence approach to determine whether historical rinsing operations associated with Site 34 are a past source of 4,4'-DDT in sediment at MS-01:

- Do the data from sediment samples collected at MS-01 during previous sampling rounds show that the elevated 4,4'-DDT levels may be anomalies?

- Does the spatial distribution of the data suggest a specific source of pesticides in sediment in the offshore area?

- Are similar levels of pesticides present in sediment from catch basins that did not receive runoff from Site 34 compared to the levels of pesticides in the catch basin by the wash pad at Site 34?

2.2.6 Sampling Design and Rationale

Section 4.0 of this QAPP presents details on the samples that will be collected for MS-01, a summary table listing the analyses that will be performed on each sample (Table 4-2), and sample location figures (Figures 4-1 and 4-6 through 4-8). Sediment will be collected from two catch basins, if an adequate volume of sediment is available. Neither catch basin collects storm water runoff that may contain soil eroded from Site 34; the catch basins collect storm water runoff from areas not related to Site 34. One of the catch basins collects runoff from a grass field where pesticides may have been sprayed in the past as part of application for pest control. Composite samples will be collected within each catch basin to obtain a sediment sample that is more representative of the sediment discharging into the offshore area than a single grab sample from each catch basin. If an inadequate volume of sediment is available from the selected catch basins, a composite sample will be collected across nearby catch basins that drain through the same outfall, or other appropriate catch basins, as necessary. The sediment in one catch basin will be analyzed for pesticides and PAH and sediment from the other catch basin will only be analyzed for pesticides.

The data will be evaluated to determine the following:

- Whether the PAH source signature of sediment in the catch basin matches the source signature of the offshore sediment, indicating that sediment from catch basins are potential sources of PAHs to the offshore area.

- Whether the concentrations of pesticides in the catch basin sediment samples are similar to the concentrations in the catch basin sediment associated with the wash pad and/or the offshore sediment samples.

Two surface soil samples will be collected from Site 34 in areas where the potential for ash/soil erosion is the greatest. One sample will be collected in the vegetated area just north of Building 62 and the other sample will be collected in the vegetated area north of the paved area north of Building 62. The sample with the greater TPH concentration will be selected for PAH forensics analysis unless the patterns in the chromatograms of the two samples are sufficiently different to indicate that the PAHs in the soil samples may be from different sources. In that case, both samples will be selected for PAH forensics analysis. Each soil sample will be a composite of five samples collected within approximately 10 feet of each other to better represent that area that may erode to the offshore. The samples will be collected from 0 to 2 inches in areas where ash is present to represent the layer of soil that is eroding.

Seven sediment samples will be collected from the offshore area. The sediment samples will be collected from 0 to 10 cm to be consistent with the depth of the sediment samples collected as part of the interim offshore monitoring program. The locations where the samples will be collected and the rationale for the collecting the samples are as follows:

- One sediment sample will be collected just east of the main gate bridge between outfalls OF-45 and OF-46 to determine the levels of pesticides and PAHs. It is assumed that the pesticides and PAHs in this area, if present, are not related to pesticides and/or PAHs in the soil at Site 34. Therefore, if the source signature of the PAHs in the sample collected from this area is similar to the source signatures of the PAHs at MS-01, it may indicate that Site 34 is not a primary source of the PAHs at MS-01.

- Two subtidal sediment samples will be collected close to monitoring station MS-01, Loc. 1 and Loc. 3 and three subtidal sediment samples will be collected further out from MS-01, Loc. 1 and Loc. 3. The purpose of these samples is to determine the spatial variability of pesticides and PAHs in the subtidal area in conjunction with the historical data and to determine whether the PAH signature is similar to signature of the PAHs in the catch basin and/or soil samples. All five samples will be analyzed for pesticides and TPH, and based on those results, two samples will be selected for PAH forensic analysis.

- One intertidal sediment sample will be collected east of MS-01, Loc. 2. The purpose of this sample is to determine the extent of pesticides and PAHs in the intertidal area in conjunction with the historic

data and to determine whether the PAH signature is similar to signature of the PAHs in the catch basin and/or soil samples.

Three sediment samples will be collected from two of the interim offshore monitoring program reference stations. Reference stations RS-02 and RS-03 are the closest to PNS and are the most likely to be impacted by urban runoff. Location 4 (intertidal but not saltmarsh) generally had the greatest PAH concentrations at reference station RS-02, while locations 2 and 3 (both subtidal) generally had the greatest PAH concentrations at reference station RS-03. At RS-03, there was some variability in PAH concentrations at locations 2 and 3 between Rounds 1 through 7, so the sample with the greater TPH result from the additional scrutiny sample will be selected for PAH forensics analysis. Therefore, although three reference samples will be analyzed for TPH, only two will be selected for full PAH forensics analysis; one from RS-02 and one from RS-03.

Two reference (non-PNS) sediment samples will be collected offshore of outfalls associated with storm water runoff. The sediment sample with the greater TPH result will be selected for forensics analysis.

Two samples will be selected for microscopic analysis to determine whether the sediment that has elevated levels of PAHs has visible signs of ash. One of the samples will be from a soil sample that contains ash and the other sample will be from the sediment sample with the greatest concentration of PAHs. The soil sample with ash will be used as a "reference" sample for comparing the physical characteristics (i.e., grain size, presence of ash, coal, etc.) between the soil sample and the sediment sample.

2.3 MONITORING STATION MS-05

As discussed in Section 1.5, this monitoring station is located in Jamaica Cove (along with monitoring station MS-06), adjacent to the wetland constructed as part of the remedy for OU3 (see Figure 1-5). Additional scrutiny was recommended for this station because the OU3 construction activities caused increased metals concentrations in the sediment at MS-05, Loc. 1, which disrupted the concentration trend line for this monitoring station (Round 8 of the interim offshore monitoring program will be used to re-establish the trend line). Copper was the only chemical detected at concentrations greater than the IRG; but the concentration of nickel in sediment increased significantly after the OU3 construction activities. Lead was also detected at concentrations greater than the ER-M value (Long et al., 1995) during Round 7.

2.3.1 Probl m Statem nt

Although metals concentrations greater than the IRG (copper) and ER-M (lead) were only found at MS-05, Loc 1, the extent of sediment with elevated levels of these metals has not been adequately defined. Also, it is not known whether there are areas where nickel concentrations in sediment are greater than the IRG.

The extent of sediment with elevated levels of metals is needed to determine the approximate area of sediment impacted by the OU3 construction activities. The extent of sediment with elevated concentrations is expected to be bounded by the location of the turbidity curtain that was placed in Jamaica Cove during the OU3 construction activities.

2.3.2 Decision Statement

Study Question: After collecting additional data, has the extent of elevated metal (copper, nickel, and/or lead) concentrations in Jamaica Cove been defined?

Decision Statement: After collecting additional data, determine whether the extent of metals contamination in Jamaica Cove is bounded.

- If the extent of contamination is bounded, stop data collection for this purpose
- If the extent of contamination is not bounded, evaluate whether additional sampling is needed

2.3.3 Decision Inputs

The following data are needed to determine the extent of contamination in Jamaica Cove:

- Sediment samples in Jamaica Cove, both inside and outside the approximate location of the turbidity curtain, for analysis of copper, lead, and nickel.

The target parameters to determine the extent of contamination in Jamaica Cove:

- Copper, lead, and nickel.

The IRGs for copper and nickel and the ER-M for lead will be used as part of data evaluation as discussed in Section 2.3.5.

2.3.4 Study Boundaries

Only one of the existing monitoring station locations (MS-05, Loc. 1) is within the former location of the turbidity curtain, but the other two station locations at MS-05 and all three stations locations at MS-06 are outside the former location of the turbidity curtain. This is supported by the fact that samples from all locations except MS-05, Loc. 1 had relatively low chemical concentrations during Round 7 and do not appear to have been impacted by the OU3 construction activities. Therefore, the spatial boundary for determining the extent of contamination in Jamaica Cove is the shoreline adjacent to the newly created wetland to monitoring locations MS-05, Loc. 3 and MS-06, Loc. 2. The sampling depth is 0 to 10 cm to be consistent with the depth of sediment collection from the interim offshore monitoring program.

2.3.5 Decision Rule

If none of the locations furthest from the shoreline have metals concentrations greater than the IRG (for copper and nickel) or ER-M (for lead), determine that the contamination is bounded and stop data collection for this purpose. Professional judgment will be used to determine the boundary of the area of contamination based on the spatial distribution of the data.

If any of the locations furthest from the shoreline have metals concentrations greater than the IRG (for copper and nickel) or ER-M (for lead), conclude that the contamination is not bounded, and evaluate whether additional sampling is needed.

2.3.6 Sampling Design and Rationale

Section 4.0 of this QAPP presents details on the samples that will be collected for MS-05, a summary table listing the analyses that will be performed on each sample (Table 4-2), and sample location figure (Figure 4-2). Samples were proposed to be collected every 25 feet in the technical memorandum for MS-05 (see Appendix B) because the location of the turbidity curtain was not known at that time. However, the approximate location of the turbidity curtain was estimated using site and aerial photographs and based on the location, the spacing between the samples was increased from what was originally proposed. The sampling methodology for MS-05 is discussed below.

Sediment samples from fourteen locations will be collected during the sampling event. The sediment samples will be located throughout Jamaica Cove within the study boundary (between the OU3 shoreline and MS-05, Loc. 3 and MS-06, Loc. 2). A greater density of samples will be located close to either side of the approximate former location of the turbidity curtain because the curtain was expected to limit the amount of sediment migration in Jamaica Cove. Also, three samples will be collected within 25 feet of MS-01, Loc. 3 to ensure that the elevated detection is not an anomaly.

All samples will be held by the analytical laboratory until it is determined that analysis should proceed. The sediment samples will be analyzed in three phases based on their location relative to the OU3 shoreline. Samples analyzed in Phase 1 will consist of the samples closest to the shoreline. Samples analyzed in Phase 2 will consist of the samples near the former location of the turbidity curtain, and samples analyzed in Phase 3 will consist of samples furthest from the shoreline. The samples in Phase 1 will be analyzed within two weeks of collection. If the concentrations in any of these samples are greater than IRGs (for copper and nickel) or ER-M (for lead), the appropriate Phase 2 sediment samples will be analyzed within the next two weeks to bound the samples with elevated chemical concentrations. Finally, if the concentrations in any of the Phase 2 samples are greater than IRGs (for copper and nickel) or ER-M (for lead), the appropriate Phase 3 sediment samples will be analyzed for copper, lead, and nickel with the next 28 days to bound the samples with elevated chemical concentrations.

2.4 MONITORING STATION MS-09

As discussed in Section 1.5, this monitoring station is located in Clark Cove, adjacent to OU3 (see Figure 1-6). Additional scrutiny was recommended for this station because the OU3 construction activities caused increased chemical concentrations in the sediment at MS-09, which disrupted the concentration trend lines for this monitoring station (Round 8 of the interim offshore monitoring program will be used to re-establish the trend line). Copper, nickel, fluorene and HMW PAHs were detected at concentrations greater than IRGs during at least one round; 4,4'-DDT was detected at concentrations greater than the PRG. The extent of sediment samples with chemical concentrations greater than IRGs has not been determined for the area.

2.4.1 Problem Statement

Although MS-09 chemical concentrations greater than IRGs and PRGs were found at all three station locations, the extent of sediment with elevated levels of these chemicals has not been adequately defined.

The extent of sediment with elevated levels of metals is needed to determine the approximate area of sediment impacted by the OU3 construction activities. However, the extent of sediment with elevated concentrations is expected to be bounded by the turbidity curtain that was placed in Cark Cove during the OU3 construction activities. Although the former location of the turbidity curtain is not known with the same accuracy as the curtain in Jamaica Cove, it is estimated that the curtain was within 30 to 40 feet of the shoreline.

2.4.2 Decision Statement

Study Question: After collecting additional data, has the extent of elevated chemical concentrations at MS-09 been defined?

Decision Statement: After collecting additional data, determine whether the extent of PAH and metals contamination at MS-09 is bounded.

- If the extent of contamination is bounded, stop data collection for this purpose
- If the extent of contamination is not bounded, evaluate whether additional sampling is needed

The source for the contamination at MS-09 is assumed to be from the disturbance of OU3 landfill materials during the remedial construction activities. The landfill materials include organic and inorganic contaminants; therefore, the assumption is that all the chemicals will be collocated and bounding the sediment based on the concentrations copper, nickel, and PAHs should bound the sediment for the other chemicals. Also, IRGs have only been developed for copper, nickel, and PAHs.

2.4.3 Decision Inputs

The following data are needed to determine the extent of contamination at MS-09:

- Sediment samples at MS-09 both further from shore and further south along the shoreline from the locations of the interim offshore monitoring program samples and both inside and outside the approximate former location of the turbidity curtain for analysis for metals and PAHs.

The target parameters to determine the extent of contamination at MS-09:

- Copper and nickel.
- PAHs.

The IRGs for copper, nickel, and PAHs will be used as part of data evaluation as discussed in Section 2.4.5.

2.4.4 Study Boundaries

The spatial boundary for the extent of contamination beyond MS-09 is based on the approximate former location of the turbidity curtain. Although the location of the turbidity curtain is not known with the same accuracy that it is known for Jamaica Cove, it is suspected that all three sediment locations at MS-09

were within the curtain based on the elevated chemical concentrations in the samples collected during Round 7 of the interim offshore monitoring program. Therefore, the spatial boundary for the extent of contamination in Jamaica Cove is the OU3 shoreline approximately 100 feet from the shoreline because it is thought that the turbidity curtain was located less than 100 feet from the shoreline. The vertical boundary is 0 to 10 cm to be consistent with the depth of sediment collection from the interim offshore monitoring program.

2.4.5 Decision Rule

If any of the locations furthest from or along the shoreline have PAH or metals concentrations greater than IRG, determine that the contamination is not bounded, and evaluate whether additional sampling is needed. Professional judgment will be used in determining the boundary of the area of contamination based on the spatial distribution of the data.

If none of the locations furthest from the shoreline have PAH or metals concentrations that are greater than IRGs conclude that the contamination is bounded, and stop data collection for this purpose.

2.4.6 Sampling Design and Rationale

Section 4.0 of this QAPP presents details on the samples that will be collected for MS-09, a summary table listing the analyses that will be performed on each sample (Table 4-2), and sample location figure (Figure 4-3). Three additional scrutiny samples were proposed to be collected at MS-09 in the technical memorandum (see Appendix B) for analysis for the same parameters that will be analyzed for in the Round 8 interim offshore monitoring program sampling event. However, to better determine the extent of contamination, the analytical suite was decreased to copper, nickel, and PAHs, and the number of samples was increased to six. Increasing the number of samples will allow for better spatial coverage. It is assumed that the chemical concentrations of the other parameters will follow a similar pattern of deposition as metals and PAHs as discussed above.

2.5 MONITORING STATION MS-11

As discussed in Section 1.6, this monitoring station is located in the Main Channel, just offshore of OU2 (see Figure 1-7). Additional scrutiny was recommended at this station because the concentrations of metals exceeded their IRGs, and the contaminant concentration trend lines for offshore sediment indicated that the concentrations are increasing. Also, the concentrations of lead exceeded the ER-M at this station, and the trend lines indicated that the concentrations are increasing. Sediment is only present at one of the three station locations, MS-11, Loc. 3. At the other two locations, mussel data along with BSAFs are used to estimate sediment concentrations for comparisons to IRGs.

2.5.1 Problem Statement

Unacceptable levels of copper, lead, and nickel are present in the sediment at MS-11, Loc. 3 and although erosion of contaminated soil from the OU2 shoreline and possibly the wooded area to the east of Building 310 is suspected, this has not been confirmed. The Navy needs to identify whether an IRP source is the source of the metals in sediment to justify an action for this area under the Navy's IRP.

The potential IRP sources for metals at MS-11 include the following:

- Direct erosion of soil (associated with OU2) that contains high levels of metals into the offshore area.
- Erosion of soil (associated with OU2) that contains high levels of metals into the offshore area via storm sewers.

The potential non-IRP sources for metals at MS-11 include the following:

- Erosion of storm water runoff containing metals from nearby onshore areas that that are not related to OU2.
- Non-PNS sources such as urban runoff, boat traffic, etc.

2.5.2 Decision Statement

Study Question: Are the concentrations of select metals in the offshore sediment at MS-11, Loc. 3 caused by erosion of contaminated soil from the OU2 shoreline and/or just east of the current OU2 boundary?

Decision Statement: Determine whether erosion of contaminated soil is the likely source of elevated levels of select metals in sediment at MS-11, Loc. 3.

- If it is, recommend a removal action in the areas where contaminated soil is eroding into the offshore area

- If it is not, recommend continuing the investigation to determine the source of the metals at MS-11, Loc. 3

2.5.3 Decision Inputs

The following data are needed to link the chemicals in the sediment at MS-11 and the soil at OU2:

- Visual inspection of the shoreline to determine whether soil is eroding into the river (some inspections have already been conducted and was used to establish study boundaries).

- Analysis of eroding soil (and catch basin sediment) for comparisons to chemical concentrations in sediment for copper, lead, and nickel. These parameters were selected to represent metals because they have IRGs (copper and nickel) and/or are associated with OU2.

- Copper, lead, and nickel concentrations in onshore soils at Sites 6 and 29.

The following are the target parameters for samples to be collected from the OU2 shoreline:

- Copper, lead, and nickel.

The IRGs for copper and nickel and the ER-M for lead will be used as part of data evaluation as discussed in Section 2.5.5.

2.5.4 Study Boundaries

The study boundary is the surficial (e.g., top 2 inches) soil along the shoreline of OU2 and in the wooded area east of Building 310 as well as sediment in the catch basin that may collect eroded soil from OU2.

2.5.5 Decision Rule

If OU2 is clearly the primary source of metals at MS-11, or if it may be a primary source, evaluate source control for offshore migration as part of the FS for OU2 (soil) or OU4 (sediment).

If OU2 is clearly not a primary source, do not evaluate source control for offshore migration or further refine ecological risks in the offshore area and consider modifying the interim offshore monitoring program.

The following questions will be answered in a line-of-evidence approach to determine whether OU2 is a primary source of the elevated levels of metals in the sediment at MS-11, Loc. 3:

- Are there visual signs of soil erosion that would indicate potentially contaminated soil is being released to the offshore area?

- Is there debris in the soil (i.e., metal pieces) that would indicate a high potential for the soil to have elevated levels of metals?

- Are elevated levels of metals found in soil eroding to the offshore area? Elevated levels will be defined as concentrations greater than the IRG (for copper and nickel) or ER-M (for lead)?

- Are concentrations of metals increasing in the sediment?

2.5.6 Sampling Design and Rationale

Section 4.0 of this QAPP presents details on the samples that will be collected for MS-11, a summary table listing the analyses that will be performed on each sample (Table 4-2), and sample location figure (Figure 4-4). Surface soil samples will be collected in two areas of visual signs of erosion; one composite sample will be collected along the shoreline of OU2 west of the seawall, and one composite sample will be collected in the wooded area east of Building 310. Composite samples will be collected in each area of potential contamination to obtain an average chemical concentration over the eroding area because composite samples are more representative of what is actually eroding into the offshore area than a single grab sample from each area. The samples will be collected from 0 to 2 inches to represent the layer of soil that is eroding.

Sediment will be collected from one catch basin, if an adequate volume of sediment is available. The catch basin is located south of Building 298 in an area that collects storm water runoff that may contain soil eroded from the berm along the river. A composite sample (of five aliquots) will be collected within the catch basin to obtain a sediment sample that is more representative of the sediment discharging into the offshore area than a single grab sample from the catch basin. If an inadequate volume of sediment is available from the selected catch basin, a composite sample will be collected across the two catch basins that drain through the same outfall.

2.6 MONITORING STATION MS-12

As discussed in Section 1.7, this monitoring station is located in the dry docks area offshore of Site 10. Additional scrutiny is recommended at this station because the concentrations of PAHs exceed their IRGs and because the MS-12 contaminant trend lines for offshore sediments indicate that concentrations are increasing. Also, the concentrations of lead exceeded the ER-M at this station, and the trend lines indicate that concentrations are increasing.

2.6.1 Problem Statements

Unacceptable levels of PAHs and lead are present in the sediment at MS-12, but the source of PAHs and lead in sediment is not known. The Navy needs to identify whether an IRP source is the source of the PAHs and lead in the sediment to justify an action or further evaluations of this area under the Navy's IRP.

The potential IRP sources for lead at MS-12 include the following:

- Migration of groundwater containing lead related to operations at Site 10.
- Migration of soil containing lead related to operations at Site 10.

Although currently, there are no known potential IRP sources for PAHs at MS-12, a potential IRP source may be identified in the future, so references to potential IRP sources for PAHs are discussed in this section.

The potential non-IRP sources for PAHs and/or lead at MS-12 include the following:

- Storm water runoff containing PAHs from onshore areas that that are not related to an IRP site.
- Activities associated with Building 178.
- Non-PNS sources such are urban runoff, boat traffic, outdoor burning, etc.

2.6.2 Decision Statements

A release of PAH and lead contamination is evident because concentrations of these chemicals exceed IRGs. There are two categories of sources: non-IRP and IRP. The actions taken for these two different situations are different.

Study Question No. 1: Can elevated lead or PAH concentrations in MS-12 sediments be linked a current IRP source, or can they be linked to a non-IRP source?

Decision Statement No. 1: Determine whether lead and PAHs in offshore sediment can be linked to a current IRP source.

If lead or PAHs are linked to a current IRP source, evaluate source controls for offshore migration, evaluate the need for a removal action in the offshore area, and further refine ecological risks in the offshore area as part of OU4 for that parameter.

If neither lead nor PAHs are linked to a current IRP source:

- Do not evaluate source controls for offshore migration.
- Do not evaluate the need for a removal action in the offshore area as part of the IRP.
- Do not further refine ecological risks in the offshore area as part of OU4.
- Consider modifying the interim offshore monitoring program.

Study Question No. 2: Can elevated lead or PAH concentrations in MS-12 sediments be linked to a historical IRP source, or can they be linked to a non-IRP source?

Decision Statement No. 2: Determine whether lead and PAHs in sediment can be linked to a historical IRP source.

If lead, PAHs, or both parameters are linked to a historical IRP source, evaluate the need for a removal action in the offshore area and further refine ecological risks in the offshore area as part of OU4 for that parameter.

If neither lead nor PAHs are linked to a historical IRP source:

- Do not evaluate the need for a removal action in the offshore area as part of the IRP.
- Do not further refine ecological risks in the offshore area as part of OU4.
- Consider modifying the interim offshore monitoring program.

2.6.3 Decision Inputs

The following data are needed to determine whether an IRP source is the source of PAHs and/or lead in the sediment at MS-12:

- PAH forensic analysis for source signatures of the following:
  - Sediment at and in the surrounding area of MS-12.
  - Sediment adjacent to storm water outfall locations below mid-tide (off the shipyard).
  - Sediment from select reference station locations to determine the pattern of typical urban runoff.
- Microscopic analysis of the sediment for visible signs of debris (e.g., metals, blast grit)

- Determine whether PAH concentrations are increasing over time using the following new and existing data, as necessary:

  - Concentration trend plots using PAH sediment concentrations normalized to TOC or grain size (using percent silt).

  - Concentration trend plots for PAHs at individual sample locations within MS-12. This will be used to determine whether the apparent increase in concentrations is being driven by one sample location.

  - Sediment and sample location descriptions to determine whether there are factors that may be influencing chemical concentrations in sediment (i.e., unable to sample same locations, heterogeneous sediment, etc.).

  - Field duplicate (i.e., precision) data from sediment samples collected at MS-12 during previous sampling rounds.

- Determine, based on the following, whether there is a current or historical migration pathway for PAHs and/or lead from an onshore source to the offshore area:

  - Description of Building 178 (i.e., flooring materials, storm drains) and descriptions of present and historical operations that occurred in the building.

  - Observations of complete migration pathways from the source to the offshore sediment.

  - Elevated levels of lead and/or PAHs in sediment collected from catch basins that ultimately discharge to the offshore area. Sediment from these catch basins represents potential current sources of contamination to the offshore area.

The following data are needed to determine whether Site 10 is a source of lead in sediment at MS-12:

- MS-12 concentration trend plots using lead sediment concentrations. These may be normalized to grain size and/or aluminum (percent silt)

- Sediment samples around Site 10 to determine whether the concentrations of lead are similar. If Site 10 is the source of lead, concentrations of lead in sediment around Site 10 should be similar because groundwater flow from Site 10 lead sources is radial.

The following are the target parameters for samples collected for PAH forensics analysis:

- TPH ranging from C9 to C36.
- Parent PAH compounds, alkyl homologues, and an expanded list of selected individual PAH isomers and biomarkers.
- TOC.

Lead is the target parameter for sediment samples for evaluating the source of lead

2.6.4 Study Boundaries

The study boundaries at MS-12 are as follows:

- Sediments at MS-12 and the surrounding area to evaluate PAH or lead concentration gradients to help establish where actual sources of MS-12 PAH and lead contamination originate. The sediment samples will be collected from 0 to 10 cm to be consistent with the depth of sediment collection from the interim offshore monitoring program.

- Sediment from select reference station locations to determine the pattern of typical urban runoff.

- Sediment from within Building 178 for comparison of PAH and lead concentrations in these samples to PAH and lead concentrations in the offshore sediment samples.
- Sediment from catch basins at Site 10 that ultimately discharge to the offshore area.

2.6.5 Decision Rules

The decision rules are identified below. Lines of evidence may include one or more of the data inputs identified in Section 2.6.3.

Decision Rule No. 1: If the lines of evidence indicate that the source of MS-12 sediment PAH or lead contamination is a current IRP source, evaluate source controls for offshore migration and the need for a removal action in the offshore area and further refine ecological risk estimates in the offshore area as part of OU4 for that parameter.

If neither lead or PAHs are linked to a current IRP source:

- Do not evaluate source controls for offshore migration.
- Do not evaluate the need for a removal action in the offshore area as part of the IRP.
- Do not further refine ecological risk estimates in the offshore area as part of OU4.
- Consider modifying the interim offshore monitoring program.

D cision Rule No. 2: If the lines of evidence indicate that the source of MS-12 sediment PAH or lead contamination is a historic IRP source, evaluate the need for a removal action in the offshore area and further refine ecological risks in the offshore area as part of OU4 for that parameter.

If neither lead nor PAHs are linked to an historical IRP source:

- Do not evaluate the need for a removal action in the offshore area as part of the IRP.
- Do not further refine ecological risks in the offshore area as part of OU4.
- Consider modifying the interim offshore monitoring program.

2.6.6 Sampling Design and Rationale

Section 4.0 of this QAPP presents details on the samples that will be collected for MS-12, a summary table listing the analyses that will be performed on each sample (Table 4-2), and sample location figure (Figure 4-5). The reference station and reference sediment samples adjacent to the non-PNS outfalls will be the same as those presented for MS-01 (see Figures 4-6 through 4-8).

Eight sediment samples will be collected from the offshore area for analysis of TPH. Two locations are considered reference sample locations for the sediment samples collected by MS-12; sediment from one of these locations will be selected for PAH forensic analysis. Samples from six locations will be collected to obtain better spatial coverage for PAHs; sediment from three of these locations will be selected for PAH forensic analysis.

Fourteen sediment samples will be collected from the offshore area for analysis of lead. Two locations are considered reference sample locations for sediment samples collected by MS-12 for comparison of lead concentrations. Eleven samples will be collected to obtain better spatial coverage for lead and to determine whether there is a concentration gradient from either Site 10 or Building 178. Finally, sediment from two locations will be collected to help determine whether Site 10 is the source of lead at MS-12.

Two sediment samples will be collected from within Building 178 in an area that is covered with water during high tide. PAH forensics analysis and lead analysis will be conducted on these sediment samples.

One sample will be selected for microscopic analysis to determine whether the elevated levels of PAHs in the sediment are associated with visible signs of debris (e.g., metals, blast grit). The sediment sample will be the sample with the greatest concentration of PAHs that is located closest to Building 178.

Sediment will be collected from two catch basins at Site 10, if an adequate volume of sediment is available. The sediment in one catch basin will be analyzed for PAHs to determine whether elevated levels of PAHs are discharging to the offshore area. Sediment from both catch basins will be analyzed for lead to determine whether soil containing lead is entering the storm water system through cracks (if present) and ultimately discharging to the offshore area.

3.0 PROJECT ORGANIZATION

This section discusses the general project organization and personnel responsibilities.

3.1 PROJECT ORGANIZATION CHART

A project organization chart depicting the agencies and contracting personnel involved with the additional scrutiny at monitoring stations MS-01, MS-05, MS-09, MS-11, and MS-12 is shown on Figure 3-1. The Navy is the lead agency for implementing this investigation, and TtNUS (the Navy contractor) will implement the investigation. Names and telephone numbers are provided in the organization chart, as appropriate.

3.2 COMMUNICATION PATHWAYS

Pathways have been established to transfer information and to make alterations to project methods that may be required because of unforeseen circumstances. It will be the responsibility of the TtNUS project manager (PM) to keep both the TtNUS project team and the Navy informed of the following:

- Schedule, deliverables, meetings, and milestones
- Recent data collected from the site
- Technical changes made to the plans and specifications
- Developments that will cause changes in the schedule

The TtNUS PM will be in frequent verbal and electronic mail communication with the Navy Remedial Project Manager (RPM). The project team will communicate any changes in the plans and specifications, field methodology, sampling protocol, or data objectives to the Navy in a timely manner. As appropriate, a field modification record will be used to identify the need for a change and a recommended course of action. The Navy will consult with USEPA and MEDEP on any major scope changes that may occur while the fieldwork is proceeding.

The TtNUS PM will, by telephone or electronic mail, communicate directly with the field team and indirectly with the designated Contract Laboratory Program (CLP) laboratories (through the lead chemist). The lead chemist will provide technical guidance and assess data as they become available. The laboratories, by telephone or electronic mail, will notify the Navy immediately of any issues that develop with the data or quality assurance/quality control (QA/QC) requirements. The Navy will be notified if significant issues arise with the laboratories regarding data, DQOs, or schedule.

The field operations leader (FOL) will verbally notify the TtNUS PM of the daily sample shipping information and will be in daily contact with the TtNUS PM. The PM will provide sample shipping information to the sample shipping coordinator. The FOL and the required subcontractors will communicate directly on site. During site activities, project sample logsheets, logbook notations, and appropriate field forms will be completed in the field and maintained at the TtNUS office. The TtNUS Lead Chemist will be in contact with the laboratories during sample receipt, sample analysis, receipt of data, and data validation and verification.

3.2.1 Modifications to the Approved QAPP

This section documents the procedures that will be followed when any project activity described in the approved QAPP requires real-time modification to achieve the project goals.

TtNUS will present proposed changes to the Navy and follow up with a field modification record for significant changes. The documentation will describe why the change is necessary, the nature of the proposed change, and the impacts of the change on the project. The change will be implemented after Navy concurrence. Minor changes will be documented in the field logbook.

When changes require immediate action, the proposed change will be briefly discussed internally by TtNUS and approved, as appropriate, by the TtNUS PM or designee (i.e., QA officer). The Navy RPM will be notified as soon as possible. Concurrence from USEPA and MEDEP will be sought for any major scope changes, as determined by the Navy. In the event of conditions requiring a major scope change, the investigation will be put on hold until concurrence is obtained. The Navy will consult with USEPA and MEDEP on any major scope changes that may occur while fieldwork is proceeding.

3.3 PERSONNEL RESPONSIBILITIES AND QUALIFICATIONS

John Trepanowski, the program manager, is responsible for the overall management and implementation of the Navy CLEAN contract for TtNUS. Deborah Cohen serves as the TtNUS facility coordinator for PNS and will oversee the coordination of the Additional Scrutiny investigation with other site investigations. She serves as the primary liaison between the Navy RPM and TtNUS for work at PNS. Aaron Bernhardt will serve as the TtNUS PM for the Additional Scrutiny investigation and will also serve as the TtNUS task manager for the work assignment, with primary responsibility for the implementation and execution of the work assignment, including technical quality, oversight and review, control of costs and schedule, and implementation of appropriate QA procedures during all phases.

Mr. Bernhardt (or designee) will also serve as the TtNUS FOL for the Additional Scrutiny investigation. The TtNUS FOL is the primary person who implements the field work activities outlined in this QAPP.

Responsibilities include supervising TtNUS field staff and field operations, coordinating with the various subcontractors on site ensuring the procedures specified in the QAPP are properly implemented, identifying and documenting necessary field changes, maintaining daily schedules, and reporting to the facility coordinator on a regular basis regarding the status and progress of the field activities. Before starting field work, Mr. Bernhardt will ensure that field SOPs are consistent with the QAPP and that any questions affecting the quality of planned field work are resolved. Mr. Bernhardt will also be responsible for ensuring that the field staff adhere to the primary duties of the health and safety plan (HASP), reporting any health and safety issues to the TtNUS health and safety officer and reporting any hazards, injuries, or decisions to stop work to the TtNUS PM.

The TtNUS QA officer will provide input on all aspects of adherence to the QAPP to the PM as needed. The sample management coordinator (SMC) will be responsible for ensuring that the laboratory supplies the appropriate sample containers and preservatives to the field, for verifying receipt of samples and their integrity at the laboratory, for ensuring that the data supplied by the laboratory are complete, and for providing liaison with the laboratory contact to obtain data in a format that is suitable for validation.

The Natural Resources Trustees and RAB (not listed in the organizational chart but included on the PNS distribution list for reports) will review and provide input on this QAPP and successive reports.

Table 3-1 lists the TtNUS additional scrutiny investigation personnel and includes their respective roles, names, and titles. Resumes of the TtNUS personnel are available on request.

3.4 SPECIAL TRAINING REQUIREMENTS AND CERTIFICATIONS

Field activities that require special training are summarized in Table 3-2.

3.5 ASSESSMENTS AND RESPONSE ACTIONS

Assessment activities ensure that the data quality is adequate for the data's intended use and that appropriate corrective actions are implemented to address nonconformances and deviations from the plan.

3.5.1 Planned Assessments

The planned assessments are system audits and field audits. The assessments planned for this project are identified in Table 3-3.

System audits will be performed as appropriate to ensure that work is being implemented in accordance with the approved project SOPs and in an overall satisfactory manner. These audits will be performed in the following manner:

- The FOL will supervise and check on a daily basis that the equipment is visually decontaminated, samples are collected and handled properly, and fieldwork is accurately and neatly documented. Documentation includes verifying that the sample names on sample log sheets, field notes, chain-of-custody records, and sample labels are identical matches to sample names in the plan.

- System audits for the laboratory will be performed regularly and in accordance with Naval Facilities Engineering Service Center (NFESC) guidance, as provided in the Laboratory Quality Assurance Plan (LQAP).

- The data validator will review the chemical analytical data packages submitted by the laboratory. The data validator will check that the data were obtained through use of the approved methodology, that the appropriate level of QC effort and reporting was conducted, and whether or not the results are in conformance with QC criteria. On the basis of these factors, the data validator will generate a report describing data limitations that will be reviewed internally by the data validation manager (DVM) before submittal to the TtNUS PM.

- The PM will maintain contact with the DVM to ensure that management of the acquired data proceeds in an organized and expeditious manner.

Additionally, an independent performance audit of field activities may be conducted at the discretion of and under the direction of the QA officer. If a formal field audit is conducted, the QA officer will check that sample collection, handling, and shipping protocols, as well as equipment decontamination and field documentation procedures, are being performed in accordance with the approved project planning documents and SOPs.

Performance audits of laboratories are coordinated through the NFESC and are conducted periodically by the NFESC's independent QA contractor.

3.5.2 Assessment Findings and Corrective Action Responses

Assessment findings that require corrective action initiate a sequence of events that include documentation of deficiencies, notification of findings, request for corrective action, implementation of corrective action, and follow-up assessment of the corrective action effectiveness.

Potential problems may involve nonconformance with the SOPs and/or analytical procedures established for the project or other unforeseen difficulties. Any person identifying a condition adverse to project quality will notify the TtNUS PM. The TtNUS PM, with the assistance of the QA officer, will be responsible for developing and initiating appropriate corrective action through the FOL and verifying that the corrective action has been effective. Corrective actions may include: resampling and/or reanalyzing a sample or amending or adjusting project procedures. If warranted by the severity of the problem (e.g., if a change in the approved plan is required), the Navy will be notified in writing and the Navy's approval will be obtained before any change is implemented. The USEPA and MEDEP will be consulted about any significant scope changes that may occur while fieldwork is underway. Communication and correspondence to the RAB will occur via mailing to the distribution list or updates at RAB meetings. Minor changes will be documented in the main file by the TtNUS PM. Additional work that depends on a nonconforming activity will not be performed until the problem has been eliminated. The overall corrective action responsibility for system audits will reside with the TtNUS PM. The overall corrective action responsibility for field audits will reside with the TtNUS QA officer.

For QA issues involving the analytical laboratory to be used for the project, the laboratory also maintains an internal closed-loop corrective action system that operates under the direction of the laboratory QA coordinator. The United States Department of Defense (DoD) has developed specific corrective actions for laboratory analyses when the analyses do not meet specified QC criteria. The applicable actions are specified in Appendix D and in Tables B-1 through B-10 of the Appendix DOD-B of the DoD Quality Systems Manual for Environmental Laboratories-Version 2 Final (DoD, June 2002).

The laboratory is expected to make reasonable efforts to prevent the release of qualified data. The laboratory must contact the PM or designee when it is evident that data quality will be compromised. This may occur, for example, when an analytical run yielded data of substandard quality but insufficient sample remains for re-analysis. Another example is when spiking concentrations are not sufficient to at least double the native analyte concentration in the sample. Flagging data with qualifier flags as described in Appendix DOD-B without an attempt to restore an analytical system to an "in-control" condition will generally not be acceptable.

3.5.3 Additional QAPP Nonconformances

Deviations from the QAPP that are noted by project personnel outside the formal assessment process will be documented and resolved using the procedures and personnel detailed in Sections 3.5.1 and 3.5.2.

3.6 QA MANAGEMENT REPORTS

This section presents the activities that will be performed to keep management updated on the project status. Open communication pathways will benefit the project by allowing all appropriate personnel to be aware of activities and have the ability to provide input in a timely manner. Input from these parties will be used to make necessary corrective actions so project quality objectives are met.

The information to be included in each of the QA Management Reports listed in Table 3-4 is summarized below.

Verbal Status Reports

The project chemist and FOL will give verbal status reports to the TtNUS PM and facility coordinator on a daily basis or more frequently if needed. The status reports will include the field activities completed for the day, the personnel who completed each activity, the anticipated activities to be completed during the next day, and any issues or problems identified.

Project Status Reports

The field logbooks will serve as records of field activities.

Field Audit Report

Field audits may be performed at the discretion of the QA officer. The audits will be performed by the QA officer or designee during field investigations. The audits will include checks on adherence to the QAPP and all applicable SOPs. The QA officer will prepare an audit report summarizing the findings. Nonconformance quality notices will be issued to document each observation, deficiency, or concern discovered during the audit. This report is distributed to the Navy RPM, the TtNUS PM, and the project files. Any findings that require immediate corrective action will be communicated immediately to the TtNUS PM.

Data Validation Reports

Tier II and Tier III data validation reports will be developed for this project. Tier II validation will be performed on the PAH forensics data. Tier III validation will be performed for the other laboratory analytical data. The data validation reports will be prepared and formatted as described in Section 6.2. The data validation reports will be included in the data package for additional scrutiny.

Data validation will not be conducted on the results for the physical parameters (i.e., TOC). However the laboratory results will be verified for completeness, and results will be checked as discussed in Section 6.0.

3.7 PROJECT SCHEDULE

Draft reports will be submitted for regulatory, National Resources Trustee, and RAB review as per the following schedule:

Sampling SOPs	90 days prior to initiation of field sampling
Laboratory SOPs and detection limits	90 days prior to initiation of field sampling
Draft Additional Scrutiny Report	270 days after completion of field work

The Additional Scrutiny Report will be reviewed and finalized in accordance with the primary document schedule in the Federal Facility Agreement. The Additional Scrutiny Report will contain an evaluation of data based on the DQOs in Section 2. In addition, a data package will be submitted to the regulators, Natural Resources Trustees, and RAB members 90 days prior to receiving the draft Additional Scrutiny Report. The data package will contain sampling methodologies, analytical results, and data validation reports.

The sampling activities are scheduled to be conducted in August and September 2005.

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TABLE 3-1

**PERSONNEL RESPONSIBILITIES AND QUALIFICATIONS
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE**

Name	Organizational Affiliation	Responsibilities	Location of Personnel	Education and Experienc Qualifications
John Trepanowski/ Garth Glenn	TtNUS	Program Manager/Deputy	TtNUS, King of Prussia, PA	Available on request
Deborah Cohen	TtNUS	Facility Coordinator	TtNUS Pittsburgh, PA	Available on request
Aaron Bernhardt	TtNUS	PM, FOL	TtNUS, Pittsburgh, PA	Available on request
Kelly Carper	TtNUS	QA Officer	TtNUS, Pittsburgh, PA	Available on request
Matt Soltis	TtNUS	Health & Safety Officer	TtNUS, Pittsburgh, PA	Available on request
Douglas Schloer	TtNUS	Lead Chemist	TtNUS, Pittsburgh, PA	Available on request
Tom Johnston	TtNUS	QA Advisor	TtNUS Pittsburgh, PA	Available on request

TABLE 3-2

SPECIAL PERSONNEL TRAINING REQUIREMENTS
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Project Function	Specialized Training Title of Course or Description	Training Provided By	Training Date	Personnel/Groups Receiving Training	Personnel Titles/ Organizational Affiliation	Location of Training Records/Certificates
Soil Sampling	• 40-hour OSHA training, 8-hour annual refresher training • Supervisory training (1)	Health and safety training specialists	Various	• All field (on-site) personnel • FOL	FOL and field sampling team members	Training records are maintained by the Navy or its contractor

OSHA – Occupational Safety and Health Administration

Specialized training is not required for sediment sampling activities.

1 - Only required if soil sampling team has two or more people.

TABLE 3-3

PROJECT ASSESSMENT
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person responsible for performing assessment, title and organizational affiliation	Person responsible for responding to assessment findings, title and organizational affiliation	Person responsible for identifying and implementing corrective actions (CA), title and organizational affiliation	Person responsible for monitoring effectiveness of CA, title and organizational affiliation
System Audit	See Section 3.5.1	Internal	TtNUS	TtNUS PM, A. Bernhardt	TtNUS FOL	TtNUS FOL	TtNUS Program Manager, J. Trepanowski
Field Audit	Conducted at the discretion of the QA officer	Internal	TtNUS	TtNUS QA Officer, K. Carper (or designee)	TtNUS PM, A. Bernhardt	TtNUS FOL	TtNUS QA Officer, K. Carper

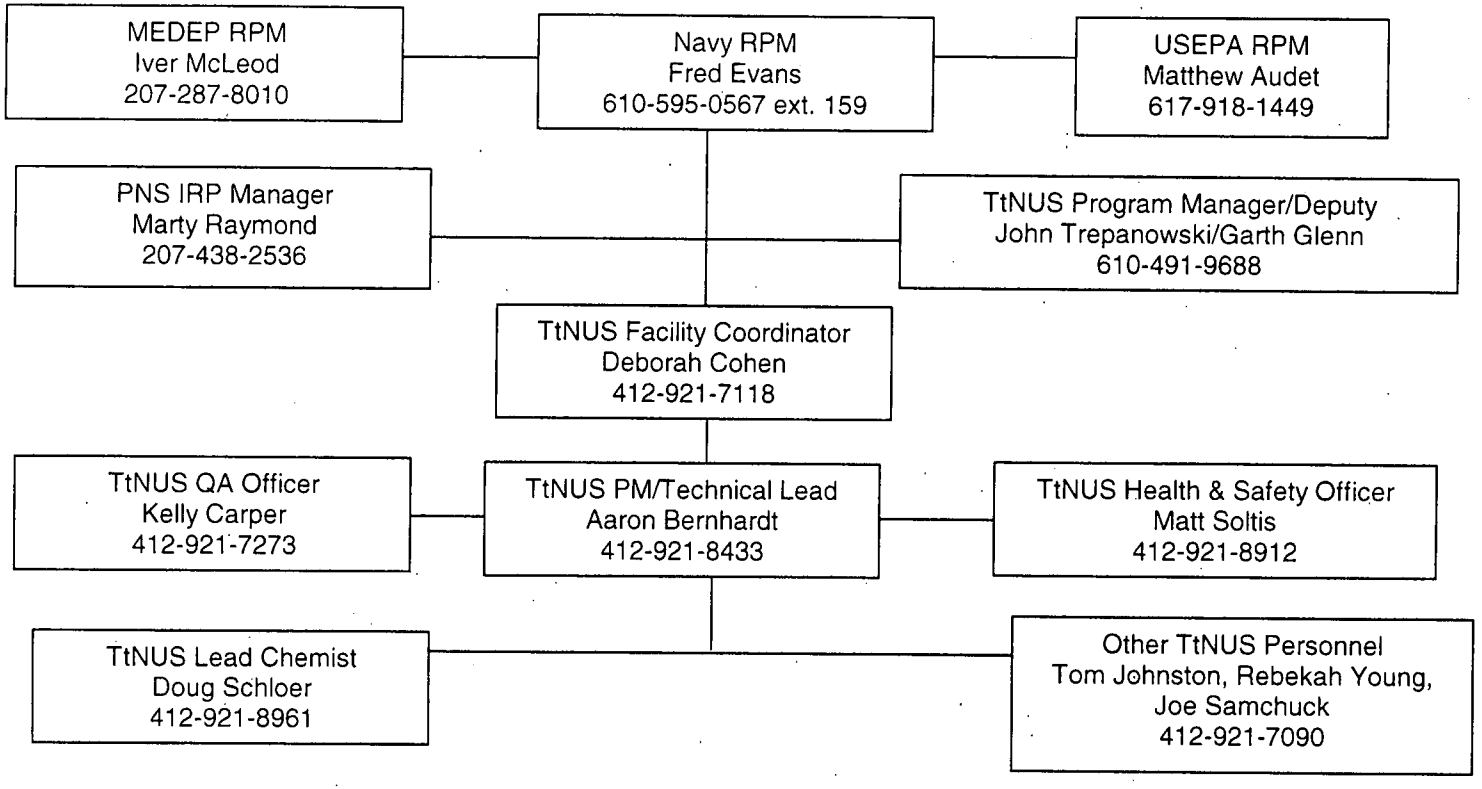
TABLE 3-4

QUALITY ASSURANCE MANAGEMENT REPORTS
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Type of Report	Frequency	Project Delivery Date	Person Responsible for Report Preparation	Report Recipients
Verbal Status Report	Daily during field activities	At the end of every day of field activities or as needed	TtNUS FOL	TtNUS PM, A. Bernhardt
Field Audit Report	Conducted at the discretion of the Navy	10 days after audit	TtNUS QA Officer, K. Carper	TtNUS PM, A. Bernhardt

FIGURE 3-1

**PROJECT ORGANIZATION CHART
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE**



* All contact with TtNUS personnel should be made through Mr. Fred Evans.

4.0 FIELD SAMPLING AND ANALYSIS PLAN

This section describes the procedures for collecting sediment and soil samples for additional scrutiny. The SOPs for the offshore sediment, catch basin sediment, and soil sampling activities are listed in Table 4-1 and provided in Appendix C.

Field documentation forms are also included in Appendix C. A complete listing of sampling locations, sample identification numbers, analytical requirements, and sample volumes/containers/preservation requirements/holding times, are presented in Tables 4-2 and 4-3. Tables 4-4 and 4-5 provide QA/QC sample information. Sample locations are shown on Figures 4-1 through 4-8.

4.1 SITE UTILITY CLEARANCE AND DIGGING PERMIT

Before any surface soil sampling activities deeper than 2 inches commence at the site, utility maps of the facility will be obtained and thoroughly reviewed by the FOL. A utility surveyor will locate and map the utilities in the field. No intrusive activities (i.e., digging) will occur until the proposed areas intended for sampling have been completely cleared in accordance with TtNUS SOP HS-1.0, as necessary. TtNUS will be responsible for pre-marking the proposed locations, and a PNS subcontractor will be responsible for conducting the utility survey.

4.2 SEDIMENT/CATCH BASIN SAMPLING

Subtidal sediment samples will be collected from a boat using a Smith-MacIntyre grab sampler or equivalent sediment sample collection device (that can be opened from the top) and is capable of providing adequate quantities of sediment from 0 to 10 cm. . One grab will be collected from each subtidal sample location. As each grab is retrieved, the water from the sampler will be slowly decanted (or suctioned off) immediately before collecting the sediment sample for analysis. A portion of sediment from the grab (from 0 to 10 cm) will be removed from the sampler and placed in a chemically-cleaned, stainless steel mixing bowl. If additional grabs are necessary to obtain an adequate volume of sediment from a location, other grabs will be collected from slightly different locations (within a few feet of each other). These samples will be collected in accordance with the Eyak Round 8 and Additional Scrutiny Sampling SOP.

For sediment sample locations that can be accessed by foot, the sample will be collected from 0 to 10 cm using a stainless steel spoon or similar device and placed in a chemically-cleaned, stainless steel mixing bowl. These samples will be collected in accordance with the Eyak Round 8 and Additional Scrutiny Sampling SOP.

Catch basin sediment samples will be collected from the top 2 inches using a scoop sampler by scraping the sediment from different areas along the bottom of the catch basin or by using a small dredge sampler. These samples will be collected in accordance with TtNUS SOP SA-1.2.

For each sampling location, when a sufficient volume of sediment has been collected in the bowl, it will be mixed until homogenous and then apportioned to appropriate sample containers for shipment to the laboratory(s). Excess water in the sample jars will be decanted after the sample is placed in the jar.

The following paragraphs discuss the sediment and catch basin samples that will be collected for the additional scrutiny at each monitoring station.

MS-01: Figure 4-1 presents the locations of the proposed samples that will be collected at MS-01. Table 4-2 summarizes the chemical analysis that will be conducted on each sample and the rationale for the collection of each sample.

Seven sediment samples will be collected from the offshore area for TPH and pesticide analysis. PAH forensics analysis (TOC, PAH, and biomarker analyses) also will be conducted on four of the sediment samples, as discussed below. In addition, the sediment samples will be held by the laboratory for microscopic analysis to determine the presence of ash or coal in the sediment. The sediment sample will be selected for microscopic analysis after TtNUS and the Navy review the PAH forensics data. The following samples will be collected:

- One sample will be collected at AS01-SD01, just east of the main gate bridge between outfalls OF-45 and OF-46. This sample will be selected for PAH forensics analysis.

- Five samples will be collected at subtidal locations (AS01-SD02 through AS01-SD06), which are near monitoring station MS-01, Loc. 3 and Loc. 1. Two of these samples will be selected for PAH forensics analysis based on the TPH results.

- One sample will be collected at an intertidal location east of MS-01, Loc. 2. This sample (AS01-SD07) will be selected for PAH forensics analysis.

Sediment, if available, will be collected from two catch basins (as described above) for PAH forensic analysis (including TPH) and/or analysis of pesticides.

Sediment samples will be collected at AS01-CB01 and AS01-CB02, which collect storm water runoff from areas not associated with Site 34. The sediment sample from AS01-CB01 will be analyzed for PAH forensics and pesticides, while the sediment sample from AS01-CB02 will be analyzed for pesticides. If sediment is not available at AS01-CB01 or AS01-CB02, sediment will be collected from other appropriate catch basins depending upon the availability of sediment.

MS-05: Figure 4-2 presents the locations of the proposed samples that will be collected in Jamaica Cove. Table 4-2 summarizes the chemical analysis that will be conducted for each sample and the rationale for the collection of each sample. [Sediment samples from MS-05, Loc. 1, Loc. 2, and Loc. 3 are being collected as a part of Round 8 of the Interim Offshore Monitoring Program and are not included in this QAPP.]

Fourteen sediment samples, as listed below, will be collected from the offshore area for analysis of copper, lead, and nickel. The samples will be grouped and analyzed in three phases (as necessary) as described below, based on comparisons of concentrations to IRGs (for copper and nickel) or to the ER-M value (for lead):

- Phase 1: Sediment samples AS05-SD01 through AS05-SD05 will be analyzed first, with a 14-day turnaround time.

- Phase 2: Sediment samples from AS05-SD06 through AS05-SD11, as necessary, will be analyzed with a 14-day turnaround time if any of the concentrations in the sediment samples from AS05-SD01 through AS05-SD05 are greater than the IRGs or ER-M.

- Phase 3: Sediment samples from AS05-SD12 through AS05-SD14, as necessary, will be analyzed with a 28-day turnaround time if any of the concentrations in the sediment samples from AS05-SD06 through AS05-SD11 are greater than the IRGs or ER-M.

MS-09: Figure 4-3 presents the locations of the proposed samples that will be collected in Clark Cove. Table 4-2 summarizes the chemical analysis that will be conducted for each sample and the rationale for the collection of each sample. [Sediment samples from MS-09, Loc. 1, Loc. 2, and Loc. 3 are being collected as a part of Round 8 of the Interim Offshore Monitoring Program and are not included in this QAPP.]

Six sediment samples (AS09-SD01 through AS09-SD06) will be collected from the offshore area and will be analyzed for copper, nickel, and PAHs.

MS-11: Figure 4-4 presents the locations of the proposed samples that will be collected at MS-11. Table 4-2 summarizes the chemical analysis that will be conducted for each sample and the rationale for the collection of each sample.

Sediment will be collected, if available, from one catch basin, AS11-CB01, for analysis for copper, lead, and nickel. AS11-CB01 collects storm water runoff that may contain soil that erodes from along the bank south of Building 298 and discharges through OF-79.

MS-12: Figure 4-5 presents the locations of the samples proposed to be collected at MS-12. Table 4-2 summarizes the chemical analysis that will be conducted on each sample and the rationale for the collection of each sample.

Eight sediment samples will be collected from the offshore area for TPH analysis as listed below. PAH forensics analysis (TOC, PAH, and biomarker analyses) also will be conducted on four of the sediment samples, as discussed below. In addition, the sediment samples will be held by the laboratory for microscopic analysis to determine the presence of visible signs of debris (e.g., metals, blast grit) in the sediment. The sediment sample for microscopic analysis will be selected after TtNUS and the Navy review the PAH forensics data.

- One sample will be collected by OF-11 and OF-11A (AS12-SD01) and one sample will be collected in Dry Dok. No. 2 (AS12-SD14), for use as reference samples. One of these samples will be selected for PAH forensics analysis based on the TPH results.

- Sediment samples will be collected from AS12-SD02, -SD04, -SD05, -SD07, -SD09, and -SD10 to obtain better spatial coverage for PAHs; three of the locations (AS12-SD05, -SD07, and -SD09) are the same as the three interim offshore monitoring station locations associated with MS-12. Three of these six samples will be selected for PAH forensics analysis based on TPH results.

Two sediment samples at AS12-SD15 and AS11-SD16 will be collected from inside Building 178 in areas that are covered with water during high tide. TPH analysis, PAH forensics analysis (TOC, PAH, and biomarker analyses), and lead analysis will be conducted on both of these samples.

Fourteen sediment samples will be collected from the offshore area for analysis of lead as follows:

- One sample will be collected by OF-11 and OF-11A (AS12-SD01) and one sample will be collected in Dry Dok. No. 2 (AS12-SD14) for use as reference samples.

- Sediment samples will be collected from AS12-SD02 through AS12-SD11 to obtain better spatial coverage for lead; three of the locations (AS12-SD05, -SD07, and -SD09) are the same as the three interim offshore monitoring station locations associated with MS-12.

- Sediment samples will be collected from AS12-SD12 and AS12-SD13 to help determine whether Site 10 is the source of lead in the sediment.

Sediment, if available, will be collected from two catch basins (as described above) for PAH and/or lead analysis.

- Sediment samples will be collected at AS12-CB01 and AS12-CB02 and analyzed for lead to determine whether lead-contaminated soil is entering the storm water system through cracks (if present) and ultimately discharging to the offshore area. The sediment sample collected at AS12-CB01 will also be analyzed for PAHs to determine whether elevated levels of PAHs are entering the storm water system via surface runoff and ultimately discharging to the offshore area at MS-12. The sediment sample from AS12-CB01 will not be analyzed for PAH forensics.

Reference Samples: Figure 1-3 presents the locations of the reference stations that are samples as part of the Interim Offshore Monitoring Program. Table 4-2 summarizes the chemical analysis that will be conducted for each sample and the rationale for the collection of each sample.

Three sediment samples will be collected from two of the interim offshore monitoring program reference stations for TPH analysis as follows (see Figures 4-6 and 4-7).

- One sample will be collected at RS-02, Loc. 4 (AS00-SD03), which is an intertidal location. This sample will also be selected for PAH forensics analysis (TOC, PAH, and biomarker analyses).

- Two samples will be collected at RS-03; one at Loc. 2 (AS00-SD04) and one at Loc. 3 (AS00-SD05). The sample with the greater TPH concentration will be selected for PAH forensics analysis.

Two sediment samples will be collected offshore of two storm water outfalls not associated with PNS as follows (see Figure 4-8). Both samples will be analyzed for TPH, and the sample with the greater TPH concentration will be selected for the full PAH forensics analysis (TOC, PAH, and biomarker analyses).

- One sample will be collected in Kittery, Maine, near a storm water outfall that collects parking lot runoff from a school (AS00-SD01).

- One sample will be collected in Portsmouth, New Hampshire, near a storm water outfall that drains part of the downtown (AS00-SD02).

4.3 SOIL SAMPLING

At each soil sample location, five sub-samples will be collected within 10 feet of each other using a stainless steel spoon or similar device and placed in a chemically-cleaned, stainless steel mixing bowl to form a single composite sample for each sampling location. The soil samples will be collected from 0 to 2 inches bgs in accordance with TtNUS SOP SA-1.3.

For each sampling location, when a sufficient volume of soil has been collected in the bowl, it will be mixed until homogenous and then apportioned to appropriate sample containers for shipment to the laboratory(s).

The following paragraphs discuss the surface soil samples that will be collected for additional scrutiny at each monitoring station.

MS-01: Figure 4-1 presents the locations of the proposed samples that will be collected at MS-01. Table 4-2 summarizes the chemical analysis that will be conducted for each sample and the rationale for the collection of each sample.

Two surface soil samples will be collected from Site 34 for PAH forensic analysis as described below. The sample with the greater TPH concentration will be selected for PAH forensics analysis (TOC, PAH, and biomarker analyses). However, if the patterns in the TPH chromatograms of the two samples are sufficiently different to indicate that the PAHs in the soil samples may be from different sources, both samples will be selected for PAH forensics analysis.

- Soil from AS01-SS01 will be collected in the vegetated area just north of Building 62.
- Soil from AS01-SS02 will be collected in the vegetated area north of the paved area north of Building 62.

MS-11: Figure 4-4 presents the locations of the proposed samples that will be collected at MS-11. Table 4-2 summarizes the chemical analysis that will be conducted on each sample and the rationale for the collection of each sample.

Two surface soil samples will be collected for analysis of copper, lead, and nickel as follows:

- AS11-SS01 will be located in the erosional area just west of the end of the seawall.
- AS11-SS02 will be located in the wooded area where metal debris is present along the shoreline, just east of Building 310.

4.4 SURVEYING

Each sediment sample location will be identified and mapped using a Global Positioning System (GPS) accurate to within 1 meter. All locations/coordinates will be recorded in the field notebook. In addition, a known survey benchmark will be surveyed using the GPS equipment as a control point. Base datum will be identified and recorded. Location information will be converted to the state plane system [North American Datum (NAD) 83] for consistency in past and future mapping efforts. The soil sample locations will be measured from known landmarks or estimated from aerial photographs.

4.5 SAMPLE IDENTIFICATION SYSTEM

4.5.1 Environmental Samples

All environmental samples collected as part of this investigation will be properly labeled with a sample label affixed to the sample container. Each sample will be assigned a unique sample tracking number. The sample tracking number will consist of a four segment alphanumeric code that identifies the sample's associated site, sample type, and location. All environmental samples will be identified following TtNUS SOP CT-04.

The alphanumeric coding to be used for surface soil samples, catch basin sediment samples, and offshore sediment samples in this investigation is explained in the following diagram and the subsequent definitions:

AANN	AA	A or N 2 to 4 characters
Site	Sample Type	Location

Character Type:

A = Alpha

N = Numeric

Site:

AS00 = Additional Scrutiny at non-PNS Stations

AS01 = Additional Scrutiny at Monitoring Station MS-01

AS05 = Additional Scrutiny at Monitoring Station MS-05

AS09 = Additional Scrutiny at Monitoring Station MS-09

AS11 = Additional Scrutiny at Monitoring Station MS-11

AS12 = Additional Scrutiny at Monitoring Station MS-12

Sample Type:

SD = Sediment sample

CP = Composite

Location:

The sample location code is the surface soil (SS), catch basin (CB), or sediment (SD) sample location.

Examples of Sample Nomenclature

Surface soil composite sample -01 associated with the additional scrutiny at MS-01 at an interval of 0 to 2 inches would be designated as AS01-CP-SS01.

4.5.2 Field Quality Assurance/Quality Control Sample Nomenclature

Field QA/QC samples will be designated using a different coding system. The QC code will consist of a three- to four-segment alphanumeric code that identifies the sample QC type, the date the sample was collected, and the number of this type of QC sample collected on that date.

AA	NNNNNN	NN
QC Type	Date	Sequence Number (per day)

The QC types are identified as:

FD = Field Duplicate

RB = Rinsate Blank

The sampling time recorded on the chain-of-custody form, labels, for duplicate samples will be 0000 so that the samples are "blind" to the laboratory. Notes detailing the sample number, time, date, and type will be recorded on the sample log sheets and will document the location of the duplicate sample (sample log sheets are not provided to the laboratory). A source water blank will not be collected as part of this investigation because one will be collected as part of the Round 8 sampling which will occur at the same time as the additional scrutiny sampling event.

Examples of Field QA/QC Nom nclatur

For example, the first duplicate of the day for a sample collected on August 3, 2005 would be designated as FD08030501F. The third duplicate sample collected on September 17, 2005 would be designated as FD09170503.

4.6 FIELD QUALITY CONTROL SAMPLES

QC samples will be collected or generated during environmental sampling activities. QC samples will include field duplicates for intertidal/subtidal sediment, catch basin sediment, and soil (including ash) samples. Field duplicates are obtained during a single act of sampling and are used to assess the overall precision of the sampling and analysis program. Field duplicates will be collected at a frequency of 10 percent per sampling matrix. Duplicates shall be analyzed by the laboratory for the same parameters as their environmental sample counterparts. One duplicate sample will be collected per every 10 sediment and soil sample set. Summary of QA/QC samples requirements are provided in Tables 4-4 and 4-5. The types of field QC samples are defined as follows:

Field Duplicates. Field duplicates are obtained during a single act of sampling and are used to assess the overall precision of the sampling and analysis program. Field duplicates will be collected at a frequency of 10 percent by taking the homogenized soil or sediment out of the mixing bowl and placing it into two separate jars with different sample numbers. Duplicates shall be analyzed by the laboratory for the same parameters as their environmental sample counterparts.

Equipment Rinsate Blanks - Equipment rinsate blanks are obtained under representative field conditions by running analyte-free water through or over decontaminated sample collection equipment. Equipment rinsate blanks will not be collected as part of this investigation for the offshore sediment samples because rinsate blanks for sediment samples will be collected as part of the Round 8 sampling event which will occur at the same time as the additional scrutiny sampling. Rinsate samples will be collected from equipment used to collect soil and catch basin sediment samples.

Source Blank - Source blanks are collected to assess the presence of contamination in the water used to decontaminate the sampling equipment in the field. No source blanks will be collected as part of this investigation as discussed above.

Temperature Blank - Temperature blanks are vials of water inserted into each sample cooler prior to shipment from the field. The temperature of the temperature blank is measured prior to shipment and upon receipt at the laboratory to assess whether samples were properly cooled during transit.

4.7 SAMPLE HANDLING AND MANAGEMENT

The following sections outline the procedures that will be used by field personnel to document project activities and sample collection procedures for the additional scrutiny. Detailed and accurate documentation is necessary in order to ensure data integrity. Documentation and documentation requirements are discussed in Section 4.10.

4.7.1 Sample Custody

Documentation of field observations will be recorded in a field logbook and/or field log sheets including sample collection logs. Field logbooks utilized on this project will consist of bound, water-resistant logbooks. All pages of the logbook will be numbered sequentially and observations will be recorded with indelible ink. Field logbooks will be maintained in accordance with TtNUS SOP SA-6.3. Field sample log sheets will be used to document sample collection details, and other observations and activities will be recorded in the field logbook. Instrument calibration logs will be used to record the daily instrument calibration.

For sampling and field activities, the following types of information will be recorded as appropriate:

- Site name and location
- Date and time of logbook entries
- Personnel and their affiliations
- Weather conditions
- Activities involved with sampling
- Site observations including site entry and exit times
- Site sketches made onsite
- Visitor names, affiliations, arrival and departure times
- Health and safety issues including personal protective equipment (PPE)

Soil and sediment sample collection information will be recorded on TtNUS sampling logs provided in Appendix C. The field logbooks and sample log sheets will remain on site for the duration of the investigation. After the investigation is completed, the field sampling log sheets will be organized by date and media and placed in the project file. The field logbooks will be used for the additional scrutiny investigations only and will be categorized and maintained in the project file. The labels of the field log books will specify the date and activity.

Sample custody procedures are designed to provide documentation of preparation, handling, storage, and shipping of all samples collected. Field chain-of-custody procedures are discussed in TtNUS SOP SA-6.3. Laboratory chain-of-custody procedures are described in the laboratory SOPs.

Integrity of the samples collected during the site investigation will be the responsibility of identified persons from the time the samples are collected until the data are incorporated into the final report. Stringent chain-of-custody procedures will be followed to document sample possession.

4.7.2 Field Custody

The FOL is responsible for the care and custody of the samples collected until they are delivered to the laboratory or are entrusted to a carrier.

Sample logs or other records will be signed and dated by the persons making the entries.

Chain-of-custody forms will be completed to the fullest extent possible before sample shipment. They will include the following information: project name, sample identification, date and time collected, analyses to be conducted, matrix, type of sample, grab or composite designation, preservative, and name of sampler.

These forms will be filled out in a legible manner, using waterproof ink, and will be signed by the sampler. Similar information will be provided on the sample label, which will be securely attached to the sample bottle. The label will also include the general analyses to be conducted. In addition, sampling forms will be used to document collection and preparation procedures. Examples of the forms to be used during field activities are provided in Appendix C.

4.7.3 Transfer of Custody

The following procedures will be used when transferring custody of samples:

- Sample coolers will be custody-sealed for security and accompanied by a chain-of-custody form in accordance with TtNUS SOP SA-6.1.

- When transferring samples, the individuals relinquishing and receiving them will sign, date, and note the time on the chain-of-custody form. This record documents the sample custody transfer from the sampler to the laboratory, often through another person or agency (common carrier).

- Upon arrival at the laboratory, internal sample custody procedures will be followed as defined in the laboratory SOPs.

Prior to shipment to the laboratory for analysis, samples will be properly packaged. Individual custody records will accompany each shipment. Shipping containers will then be sealed for shipment to the laboratory. The methods of shipment, courier name, and other pertinent information will be entered in the "remarks" section of the custody record.

All shipments will be accompanied by the chain-of-custody form identifying the contents. The original record will accompany the shipment and a copy will be retained by the field sampler.

Proper documentation will be maintained (i.e., airbills) for shipments by common carrier.

4.7.4 Sample Shipment Procedures

The following procedures will be followed when shipping samples for laboratory analysis:

- Samples requiring cooling to 4 degrees Celsius (°C) will be promptly chilled with ice or blue ice (or equivalent) and will be packaged in an insulated cooler for transport to the laboratory.
- A temperature blank will be included in each cooler to be used as a temperature indicator. Each temperature blank will be clearly identified by the field sampling team.
- Ice will be sealed in containers to prevent leakage of water. Samples will not be frozen.

Only shipping containers that meet all applicable state and federal standards for safe shipment will be used.

The field chain-of-custody form will be placed inside the shipping container in a sealed, plastic envelope. Shipping containers will be sealed with nylon strapping tape, and custody seals will be signed, dated, and affixed in a manner that will allow the receiver to quickly identify any tampering that may have occurred during transport to the laboratory.

Samples will be delivered to the laboratory by a public courier. After samples have been collected, they will be sent to the laboratory within a suitable timeframe that will ensure that sample holding times are not exceeded under any circumstances.

4.7.5 Laboratory Sample Custody

To ensure the integrity of a sample from collection through analysis, it is necessary to have an accurate, written record that traces the possession and handling of the sample. This documentation is referred to as the chain-of-custody form.

A sample is under custody if:

The sample is in the physical possession of an authorized person.
The sample is in view of an authorized person after being in his/her possession.
The sample is placed in a secure area by an authorized person after being in his/her possession.
The sample is in a secure area, restricted to authorized personnel only.

When samples are received, the chain-of-custody form is signed and dated to acknowledge sample receipt. The sample custodian must examine the shipping containers and verify that the correct number of containers was received. The shipping containers are then opened and the enclosed sample paperwork is removed. Samples are removed from the shipping containers and the bottle condition and temperature of the temperature blank must be noted. The information on the chain-of-custody, the airbill, the containers, and the laboratory request is reviewed for any discrepancies.

The laboratory will be required to fax the chain-of-custody forms and sample log-in information to the Navy after every shipment.

All samples received by the laboratory must be stored at 4°C until analysis. Laboratory holding times are specified by the contract and presented in Table 4-2.

4.8 EQUIPMENT DECONTAMINATION

TtNUS will obtain pre-cleaned sample containers suitable for laboratory analyses. These containers will meet the requirements of the USEPA Specification and Guidance for Contaminant-Free Sample Containers [Office of Solid Waste and Emergency Response (OSWER) Directive No. 9240.0-05A].

Equipment decontamination will follow the procedures described in the TtNUS decontamination SOP SA-7.1. Non-disposable equipment items that come in contact with sediment or soil and will require decontamination include:

- Stainless steel mixing bowls and spoons
- Smith-MacIntyre grab sampler (or equivalent)
- Stainless steel trowel and knife

If the equipment is new, the initial cleaning will consist only of a soapy water wash (i.e., Alconox) followed by a tap water and distilled water rinse.

All non-dedicated reusable sampling equipment used for collecting samples will be decontaminated both before beginning field sampling and between samples.

4.9 INVESTIGATIVE-DERIVED WASTE MANAGEMENT

Two types of investigative-derived waste (IDW) will be generated during this investigation that could be potentially contaminated: sampling equipment decontamination wastewaters and PPE. Based on the historical site activities and types of contaminants present, none of these IDW materials is expected to present a significant risk to human health or the environment if properly managed.

Sampling equipment decontamination wastewaters will be transferred into containers, which will be properly labeled and transported to a central location to be designated by the PNS.

4.10 FIELD DOCUMENTATION AND DOCUMENTATION RESPONSIBILITIES

It will be the responsibility of the FOL to secure all documents produced in the field (e.g., sampling logs, calibration forms) at the end of each work day. Copies of all field logbooks will be sent to the EFANE to the attention of Mr. Fred Evans (Navy RPM). Sample logs and chain-of-custody records will be included as an appendix to the data package.

All logbook and log sheet entries must be made in indelible ink (black pen is preferred). No erasures or liquid paper or white out are permitted. If an incorrect entry is made, the data will be crossed out with a single strike mark, initialed, and dated. The field personnel will sign and date the logbook pages and field forms.

At the completion of field activities, the FOL will send Mr. Aaron Bernherdt (TtNUS PM) all field records, data, field notebooks, logbooks, chain-of-custody forms, sample log sheets, daily logs, etc. The PM will ensure that these materials are entered into the TtNUS document control system in accordance with appropriate administrative guidelines.

Changes in project operating procedures may be necessary as a result of changed field conditions or unanticipated events. A summary of the sequence of events associated with field changes is as follows:

- The FOL will notify the TtNUS PM of the need for the change.
- If necessary, the PM will discuss the change with the pertinent individuals (e.g., Navy RPM, TtNUS QA Manager) and will provide a verbal approval or denial to the FOL for the proposed change. The USEPA and MEDEP will be consulted by the Navy about any major scope changes that may occur while fieldwork is ongoing. Communications and correspondences to the RAB will be handled through inclusion on the distribution list or through written correspondence and updates at RAB meetings.
- The FOL will document the change on a Task Modification Request Form and forward the form to the TtNUS PM at the earliest convenient time.
- The TtNUS PM will sign the form and distribute copies to the Navy RPM, QA officer, FOL, and project file.
- A copy of the completed Task Modification Request Form will be attached to the field copy of the affected document.

The possession of all records will be documented; however, only the project FOL or designee may remove field data from the site for reduction and evaluation.

4.11 SAMPLING SOP MODIFICATIONS

The SOPs associated with investigation are presented in Table 4-1. Each TtNUS SOP has a unique TtNUS reference number. For each SOP, environmental sampling equipment affected is also identified. Additionally, each SOP has been reviewed and revised as necessary to address tasks specific to this investigation.

4.12 FIELD EQUIPMENT MAINTENANCE, TESTING, AND INSPECTION REQUIREMENTS

Equipment, instruments, gauges, and other items requiring preventive maintenance will be serviced, when appropriate, by the equipment supplier or the FOL (or designee) in accordance with the manufacturer's recommendations. Manufacturer's procedures identify the schedule for servicing critical items in order to minimize the downtime of the measurement system. It will be the responsibility of the FOL or subcontractor to adhere to this maintenance schedule and to arrange for any necessary and

prompt service required. Service of the equipment, instruments, tools, gauges, etc. shall be performed to the extent possible by the FOL (or designee). If the service requires a more qualified person, the supplier or manufacturer will be contacted for assistance. Logs shall be established by the FOL (or designee) to record maintenance, service procedures, and schedules. Maintenance records will be documented and traceable to the specific equipment, instruments, and gauges.

It will be the responsibility of the FOL (or designee) to inspect all supplies to be used as part of the field program during mobilization and use. Supplies to be inspected include sampling equipment, and sample containers. If the FOL encounters any problem with the supplies, he will inform the TtNUS PM and the laboratory supplying the containers. The TtNUS PM, in consultation with the Navy RPM and QA officer, will instruct the FOL on any corrective actions that should be implemented.

TABLE 4-1

SUMMARY OF STANDARD OPERATING PROCEDURES
ADDITIONAL SCRUTINY INVESTIGATION QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

SOP Number, Title, and Revision Date	Originating Organization	Equipment Identification	Modified for Project Work (Y or N)
SOP HS-1.0, Utility Locating and Excavation Clearance, December. 2003	TtNUS	Geophysical instruments	N
SOP SA-1.2, Surface Water and Sediment Sampling, September 2003	TtNUS	Stainless steel mixing bowls and scoops, dredge	Y
SOP SA-1.3, Soil Sampling, September. 2003	TtNUS	Stainless steel mixing bowls and spoons	Y
SOP CT-04, Sample Nomenclature, September. 2003	TtNUS	Not applicable	Y
SOP SA-6.3, Field Documentation, September. 2003	TtNUS	Field notebooks, log forms, camera	Y
SOP SA-6.1, Non-Radiological Sample Handling, February. 2004	TtNUS	Sample containers, shipping coolers	Y
SOP SA-7.1, Decontamination of Field Equipment, September. 2003	TtNUS	Decon solutions, 55-gal. drums	Y
Round 8 and Additional Scouting Sampling	Eyak	Stainless steel mixing bowls and scoops, dredge	N

TABLE 4-2

SUMMARY OF SAMPLES PROPOSED FOR COLLECTION
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE
PAGE 1 OF 4

Station/ Sample Type	Sample Number	Forensic Analysis [1]			Copper Nickel	Lead	Pesticides	PAHs	TOC	Comment/Rationale
		TPH	PAH	Biomarkers						
Monitoring Station MS-01										
Catch Basin Sediment	AS01-CP-CB01	X	X	X			X		X	This catch basin collects runoff from the south of Site 34 which discharges west of Site 34. It will be used as a "background" outfall as it relates to Site 34. The sediment data from this location will be compared to the data in the soil samples and offshore sediment samples to determine whether the PAH fingerprints are similar between the samples. This sample will be a composite of sediment from several grabs at the bottom of the catch basin.
	AS01-CP-CB02						X			This catch basin collects runoff from an area south east of Site 34 and will be used as a "background" outfall as it relates to Site 34. The sediment data from this location will be compared to the data in the catch basin at the wash pad at Site 34 and offshore sediment samples. This sample will be a composite of sediment from several grabs at the bottom of the catch basin.
Offshore Sediment [2]	AS01-SD-SD01	X	X	X			X		X	The subtidal sample from this location is considered a reference sample for MS-01 because it is not likely that ash associated with Site 34 would contribute significantly to the PAH levels in the sediment. Also, this would be considered a reference area for pesticides associated with potential Site 34 rinsing activities because it is not likely that runoff from the wash pad would contribute significantly to the pesticide levels in the sediment in this area.
	AS01-SD-SD02	X	X[3]	X[3]			X		X[3]	Subtidal area for extent contamination to the west in the subtidal area.
	AS01-SD-SD03	X	X[3]	X[3]			X		X[3]	Subtidal area near MS-01, Loc. 3.
	AS01-SD-SD04	X	X[3]	X[3]			X		X[3]	Subtidal area for extent contamination to the north in the subtidal area.
	AS01-SD-SD05	X	X[3]	X[3]			X		X[3]	Subtidal area near MS-01, Loc. 1.
	AS01-SD-SD06	X	X[3]	X[3]			X		X[3]	Subtidal area for extent contamination to the east in the subtidal area.
	AS01-SD-SD07	X	X	X			X		X	Intertidal area by OF-51 for extent to the east.
Onshore Soil [2]	AS01-CP-SS01	X	X[4]	X[4]					X[4]	This sample will be a composite of five samples collected from an area where PAHs were elevated in previous samples.
	AS01-CP-SS02	X	X[4]	X[4]					X[4]	This sample will be a composite of five samples collected from an area where PAHs were elevated in previous samples.

TABLE 4-2

SUMMARY OF SAMPLES PROPOSED FOR COLLECTION
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE
PAGE 2 OF 4

Station/ Sample Type	Sample Number	Forensic Analysis [1]			Copper Nickel	Lead	Pesticides	PAHs	TOC	Comment/Rationale
		TPH	PAH	Biomarkers						
Monitoring Station MS-05										
Offshore Sediment	AS05-SD-SD01				X	X				**Phase 1:** These samples will be analyzed first (within 14 days). If the concentrations in any of the samples are greater than the IRG (for copper and lead) or the ER-M level (for lead), the appropriate Phase 2 samples will be analyzed to bound the contamination.
	AS05-SD-SD02				X	X				
	AS05-SD-SD03				X	X				
	AS05-SD-SD04				X	X				
	AS05-SD-SD05				X	X				
	AS05-SD-SD06				X	X				**Phase 2:** These samples will be analyzed second (within 14 days after the Phase 1 sample results are evaluated), if needed, based on the chemical concentrations in the Phase 1 samples. If the concentrations in any of the samples are greater than the IRG (for copper and lead) or the ER-M (for lead), the appropriate Phase 3 samples will be analyzed to bound the contamination.
	AS05-SD-SD07				X	X				
	AS05-SD-SD08				X	X				
	AS05-SD-SD09				X	X				
	AS05-SD-SD10				X	X				
	AS05-SD-SD11				X	X				
	AS05-SD-SD12				X	X				**Phase 3:** These samples will be analyzed last (within 28 days after the Phase 2 sample results are evaluated), if needed, based on the chemical concentrations in the Phase 2 samples.
	AS05-SD-SD13				X	X				
	AS05-SD-SD14				X	X				
Monitoring Station MS-09										
Offshore Sediment	AS09-SD-SD01				X			X		These samples are spatially located with the assumption that are likely outside of the former turbidity curtain boundary with the exception of AS09-SD03, which may be located within the former turbidity curtain boundary.
	AS09-SD-SD02				X			X		
	AS09-SD-SD03				X			X		
	AS09-SD-SD04				X			X		
	AS09-SD-SD05				X			X		
	AS09-SD-SD06				X			X		
Monitoring Station MS-11										
Onshore Soil	AS11-CP-SS01				X	X				The sample will be a composite of five samples from the erosional area west of the seawall by Site 29 where metals debris is present in the soil.
	AS11-CP-SS02				X	X				The sample will be a composite of five samples from the erosional area east Building 310 in the wooded area where metals debris is present in the soil.
Catch Basin Sediment	AS11-CP-CB01				X	X				The storm water system associated with this catch basin collects runoff that may contain eroded soil from the erosional area west of the seawall by Site 29. This sample will be a composite of sediment from several grabs at the bottom of the catch basin.

TABLE 4-2

SUMMARY OF SAMPLES PROPOSED FOR COLLECTION
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE
PAGE 3 OF 4

Station/ Sample Type	Sample Number	Forensic Analysis [1]			Copper Nickel	Lead	Pesticides	PAHs	TOC	Comment/Rationale
		TPH	PAH	Biomarkers						
Monitoring Station MS-12										
Offshore Sediment [2]	AS12-SD-SD01	X	X[6]	X[6]		X			X[6]	This is a "background" sample for comparison of the PAH levels and source signature to the samples collected near MS-12.
	AS12-SD-SD02	X	X[5]	X[5]		X			X[5]	These samples are being collected to obtain better spatial coverage in this area. AS12-SD09, -SD05, and -SD07 are the same locations as MS-12 interim offshore monitoring locations 1, 2, and 3, respectively.
	AS12-SD-SD03					X				
	AS12-SD-SD04	X	X[5]	X[5]		X			X[5]	
	AS12-SD-SD05	X	X[5]	X[5]		X			X[5]	
	AS12-SD-SD06					X				
	AS12-SD-SD07	X	X[5]	X[5]		X			X[5]	
	AS12-SD-SD08					X				
	AS12-SD-SD09	X	X[5]	X[5]		X			X[5]	
	AS12-SD-SD10	X	X[5]	X[5]		X			X[5]	
	AS12-SD-SD11					X				
	AS12-SD-SD12					X				These samples are being collected to determine whether lead concentrations around Site10 are similar and/or elevated compared to the other sediment samples at MS-12 to aid in determining whether Site 10 was the source of lead
	AS12-SD-SD13					X				
	AS12-SD-SD14	X	X[6]	X[6]		X			X[6]	This is a "background" sample for comparison of the PAH levels and source signature to the samples collected near MS-12.
	AS12-SD-SD15	X	X	X		X			X	These samples are being collected from inside Building 178 for comparison of the lead and PAH levels and signatures in these samples to the offshore sediment samples.
	AS12-SD-SD16	X	X	X		X			X	
Catch Basin Sediment	AS12-CP-CB01					X		X		This sample is being collected to determine whether elevated levels of PAHs and lead are present in the catch basin sediment. This sample will be a composite of sediment from several grabs at the bottom of the catch basin.
	AS12-CP-CB02					X				This sample is being collected to determine whether an elevated level of lead is present in the catch basin sediment. This sample will be a composite of sediment from several grabs at the bottom of the catch basin.

TABLE 4-2

SUMMARY OF SAMPLES PROPOSED FOR COLLECTION
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE
PAGE 4 OF 4

Station/ Sample Type	Sample Number	Forensic Analysis [1]			Copper Nickel	Lead	Pesticides	PAHs	TOC	Comment/Rationale
		TPH	PAH	Biomarkers						
Background/Reference Samples										
Background Outfall Sediment	AS00-SD-SD01	X	X[7]	X[7]					X[7]	These samples are being collected to determine the PAH levels and signature for sediment near storm water outfalls not related to PNS.
	AS00-SD-SD02	X	X[7]	X[7]					X[7]	
Reference Sediment	AS00-SD-SD03	X	X	X					X	This sample will be collected at reference station RS-02, Loc. 4 to determine the PAH levels and signature from sediment not related to PNS.
	AS00-SD-SD04	X	X[8]	X[8]					X[8]	This sample will be collected at reference station RS-03, Loc. 2 to determine the PAH levels and signature from sediment not related to PNS.
	AS00-SD-SD05	X	X[8]	X[8]					X[8]	This sample will be collected at reference station RS-03, Loc. 3 to determine the PAH levels and signature from sediment not related to PNS.

Footnotes:

1 - All samples for forensic analysis will have TPH analysis conducted and based on the results of the TPH analysis, samples will be selected for PAH, biomarkers, and TOC analyses as noted for each monitoring station.
2 - The microscopic analysis will be conducted on one soil sample (for MS-01) and one offshore sediment sample (one for MS-01 and one for MS-12).
3 - Two of these five sediment samples will be selected for forensics analysis (including TOC) based on the results of the TPH analysis.
4 - One of these two soil samples will be selected for forensics analysis (including TOC) based on the results of the TPH analysis (Note: both of these samples may be selected for forensics snalysis after a review of the TPH results).
5 - Three of these six sediment samples will be selected for forensics analysis (including TOC) based on the results of the TPH analysis.
6 - One of these two sediment samples (SD01 or SD14) will be selected for forensics analysis (including TOC) based on the results of the TPH analysis.
7 - One of these two sediment samples will be selected for forensics analysis (including TOC) based on the results of the TPH analysis.
8 - One of these two sediment samples will be selected for forensics analysis (including TOC) based on the results of the TPH analysis.

TPH - total petroleum hydrocarbons
PAH - polycyclic aromatic hydrocarbons
TOC - total organic carbon

IRG - Interim Remediation Goal
ER-M - Effects range-median

TABLE 4-3

SAMPLE CONTAINERS, PRESERVATION METHODS, AND HOLDING TIMES
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Analytical Method	Parameter	Container Material	Container Volume(1)	Preservation	Holding Time(2)
SOIL/SEDIMENT SAMPLES					
SW-846 8270C	PAHs	Clear wide-mouth jar	8 oz.	Cool to 4°C	14 days to extraction, 40 days from extraction to analysis
SW-846 8081A	Pesticides	Clear wide-mouth jar	4 oz.	Cool to 4°C	7 days to extraction, 40 days from extraction to analysis
SW-846 6020	Copper, Lead, Nickel	Clear wide-mouth jar	4 oz.	Cool to 4°C	180 days to analysis

1 Container volume may vary based on laboratory.
2 Measured from time of sample collection.

PAHs Polycyclic aromatic hydrocarbons

TABLE 4-4

AQUEOUS SEMIVOLATILES, PESTICIDES, AND METALS FIELD SAMPLING QC
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Field QC	Number	Method/SOP QC Acceptance Limits	Corrective Action (CA)	Person(s) Responsible for CA	Data Quality Indicator (DQI)	Measurement Performance Criteria
Rinse Blank	1 per day	No target analyte ≥QL	Evaluate data. Compare to acceptance limits.	Data validator	Accuracy/bias/ contamination	No target analyte ≥QL
Source Blank(1)	1 per sampling event	No target analyte ≥QL	Evaluate data. Compare to acceptance limits.	Data validator	Accuracy/bias/ contamination	No target analyte ≥QL
Cooler Temperature Blanks	1 per cooler	4°C ± 2°C	Resample or qualify the data	Data validator, field sampler	Accuracy/bias/ preservation	4°C ± 2°C
Field Duplicate Pairs (Duplicate Samples)	1 per 10 samples	< 35% RPD – (organics) < 30% RPD – (inorganics)	Qualify data	Data validator	Precision	< 35% RPD – (organics) < 30% RPD – (inorganics)

Note:
QC - Quality control.
RPD - Relative percent difference.
TAL - Target Analyte List.
QL – Quantitation limit.

1 - The source blank will be collected as part of the Round 8 sampling event which will occur at the same time as the additional scrutiny sampling event.

TABLE 4-5

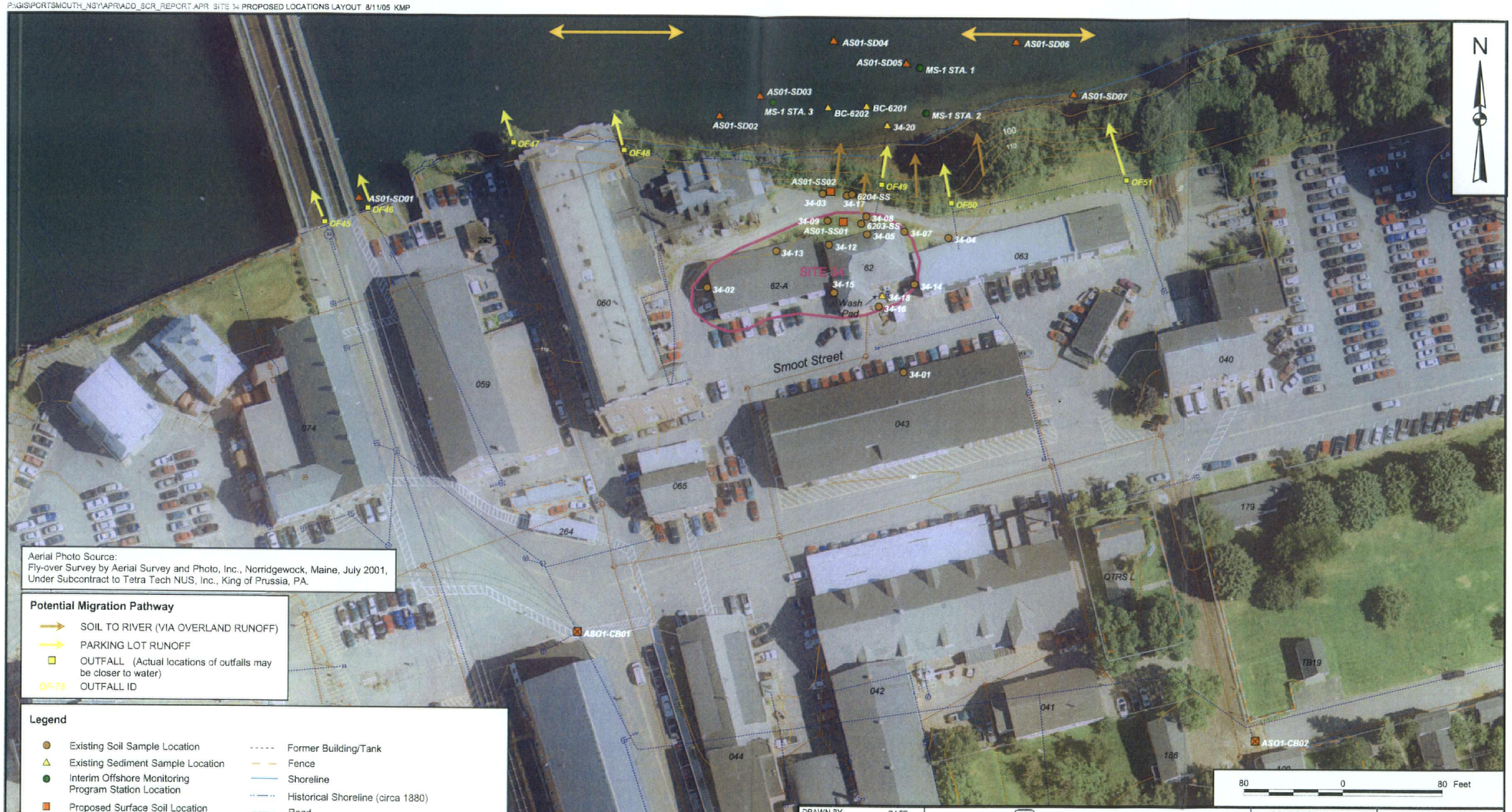
SUMMARY OF QA/QC SAMPLES AND ANALYSIS
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Analysis	Method	Environmental Samples	Rinse Blank	Field Duplicates	MS/MSD Samples
PAHs	SW-846 8270B	7	(1)	1	1
Pesticides	SW-846 8081A	7	(1)	1	1
Copper, Nickel	SW-846 6020	23	(1)	3	2
Total Organic Carbon	EPA - 9060	15	NA	2	NA
PAH Forensic	SW-846 8270B	15	NA	2	1
TPH	SW-846 8015	25	NA	3	2
Biomarkers	Sw-846 8270	15	NA	2	1
Lead	SW-846 6020	35	(1)	4	2

NA-Not Applicable.

1 - Rinse Blanks will be collected at a minimum frequency of one per day during sample collection.

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR SITE 34 PROPOSED LOCATIONS LAYOUT 8/11/05 KMP



Aerial Photo Source:
Fly-over Survey by Aerial Survey and Photo, Inc., Norridgewock, Maine, July 2001, Under Subcontract to Tetra Tech NUS, Inc., King of Prussia, PA.

Potential Migration Pathway

- SOIL TO RIVER (VIA OVERLAND RUNOFF)
- PARKING LOT RUNOFF
- OUTFALL (Actual locations of outfalls may be closer to water)
- OF-78 OUTFALL ID

Legend

- Existing Soil Sample Location
- Existing Sediment Sample Location
- Interim Offshore Monitoring Program Station Location
- Proposed Surface Soil Location
- Proposed Sediment Sample Location
- Proposed Catch Basin Sample Location
- Approximate Site Boundary
- Former Building/Tank
- Fence
- Shoreline
- Historical Shoreline (circa 1880)
- Road
- Railroad
- Topographic Contour (PNS 2002 datum - feet)
- Storm Sewer Inlet
- Utility Drain
- Sewer Utility

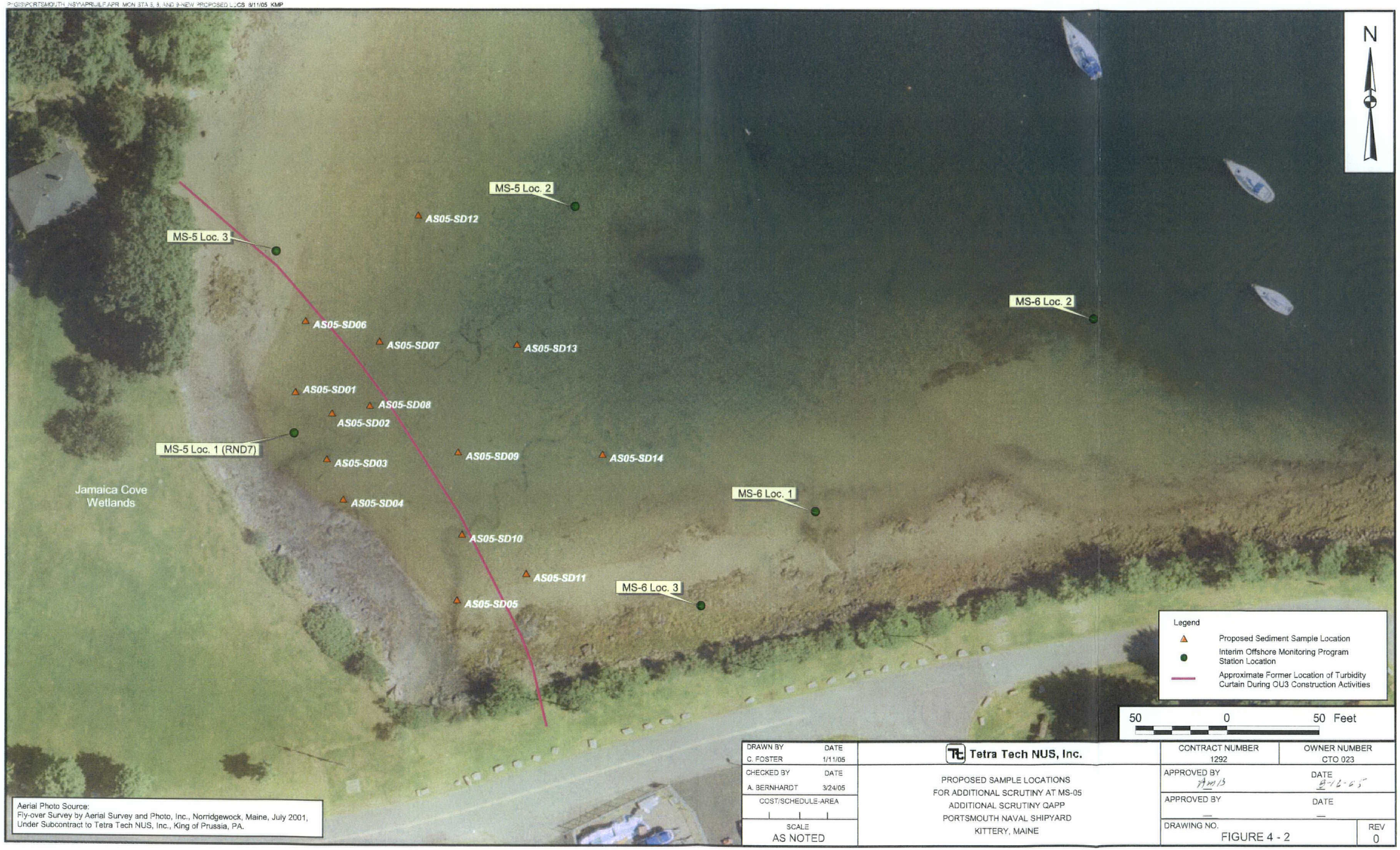
DRAWN BY	DATE
C. FOSTER	1/18/05
CHECKED BY	DATE
A. BERNHARDT	3/29/05
COST/SCHEDULE-AREA	
SCALE	AS NOTED

Tetra Tech NUS, Inc.

PROPOSED SAMPLE LOCATIONS FOR
ADDITIONAL SCRUTINY AT MS-01
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD
KITTERY, MAINE

CONTRACT NUMBER	OWNER NUMBER
1292	CTO 023
APPROVED BY: AMB	DATE: 8-12-05
APPROVED BY: —	DATE: —
DRAWING NO.: FIGURE 4 - 1	REV: 0

P:\GIS\PORTSMOUTH_NSY\APR\UILF\APR_MON STA 5, 6, AND 9-NEW PROPOSED LOCS 8/11/05 KMP



DRAWN BY C. FOSTER	DATE 1/11/05	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
CHECKED BY A. BERNHARDT	DATE 3/24/05	PROPOSED SAMPLE LOCATIONS FOR ADDITIONAL SCRUTINY AT MS-05 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY	DATE
COST/SCHEDULE-AREA			APPROVED BY —	DATE —
SCALE AS NOTED			DRAWING NO. FIGURE 4 - 2	REV 0

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR MS-09 PROPOSED LOCATION LAYOUT 8/11/05 KMP

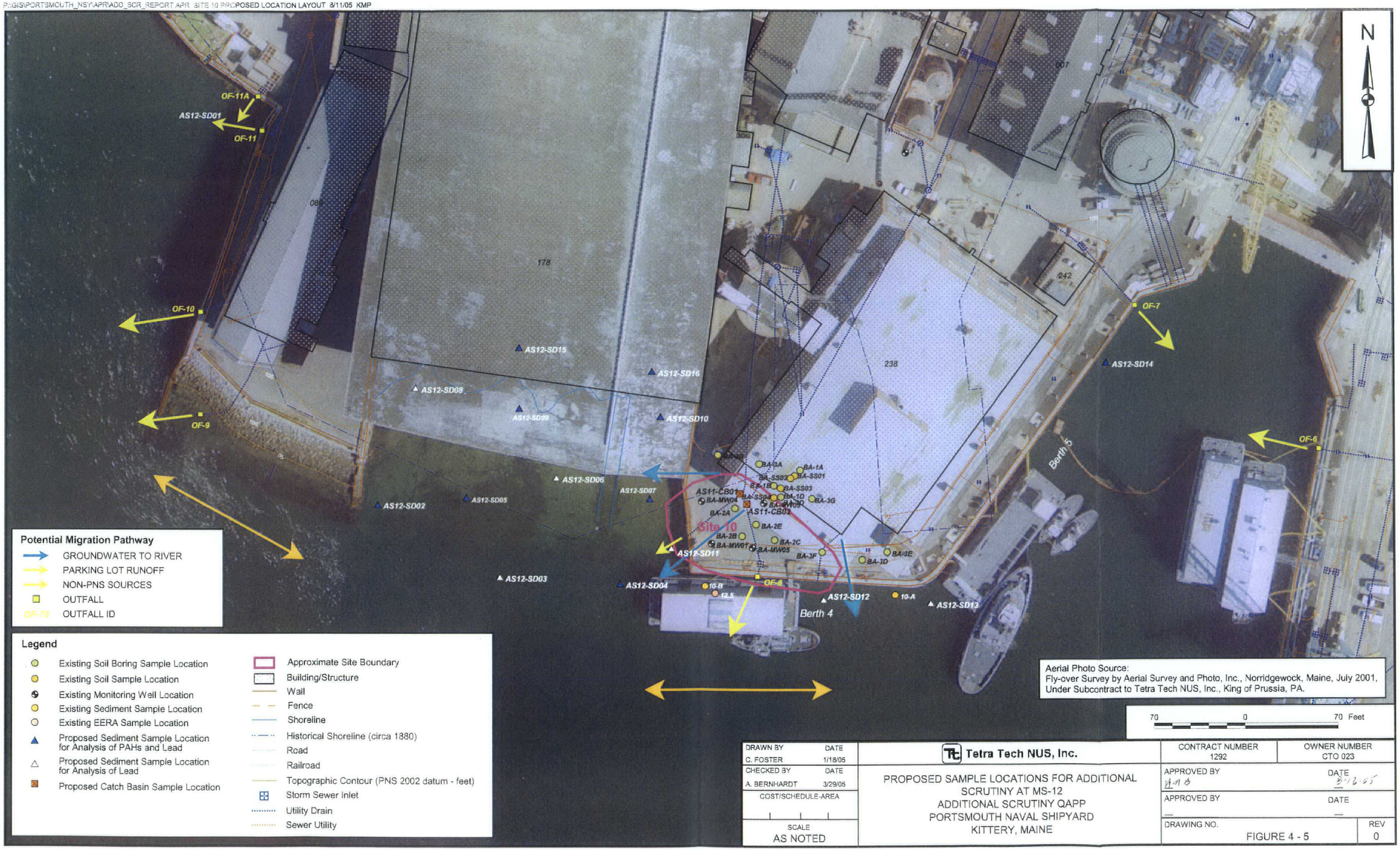
Aerial Photo Source:
Fly-over Survey by Aerial Survey and Photo, Inc., Norridgewock, Maine, July 2001, Under Subcontract to Tetra Tech NUS, Inc., King of Prussia, PA.

DRAWN BY C. FOSTER — DATE 01/27/05	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
CHECKED BY A. BERNHARDT — DATE 3/29/05	PROPOSED SAMPLE LOCATIONS FOR ADDITIONAL SCRUTINY AT MS-09 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY AMB	DATE 8-12-05
COST/SCHEDULE-AREA		APPROVED BY —	DATE —
SCALE AS NOTED		DRAWING NO. FIGURE 4 - 3	REV 0

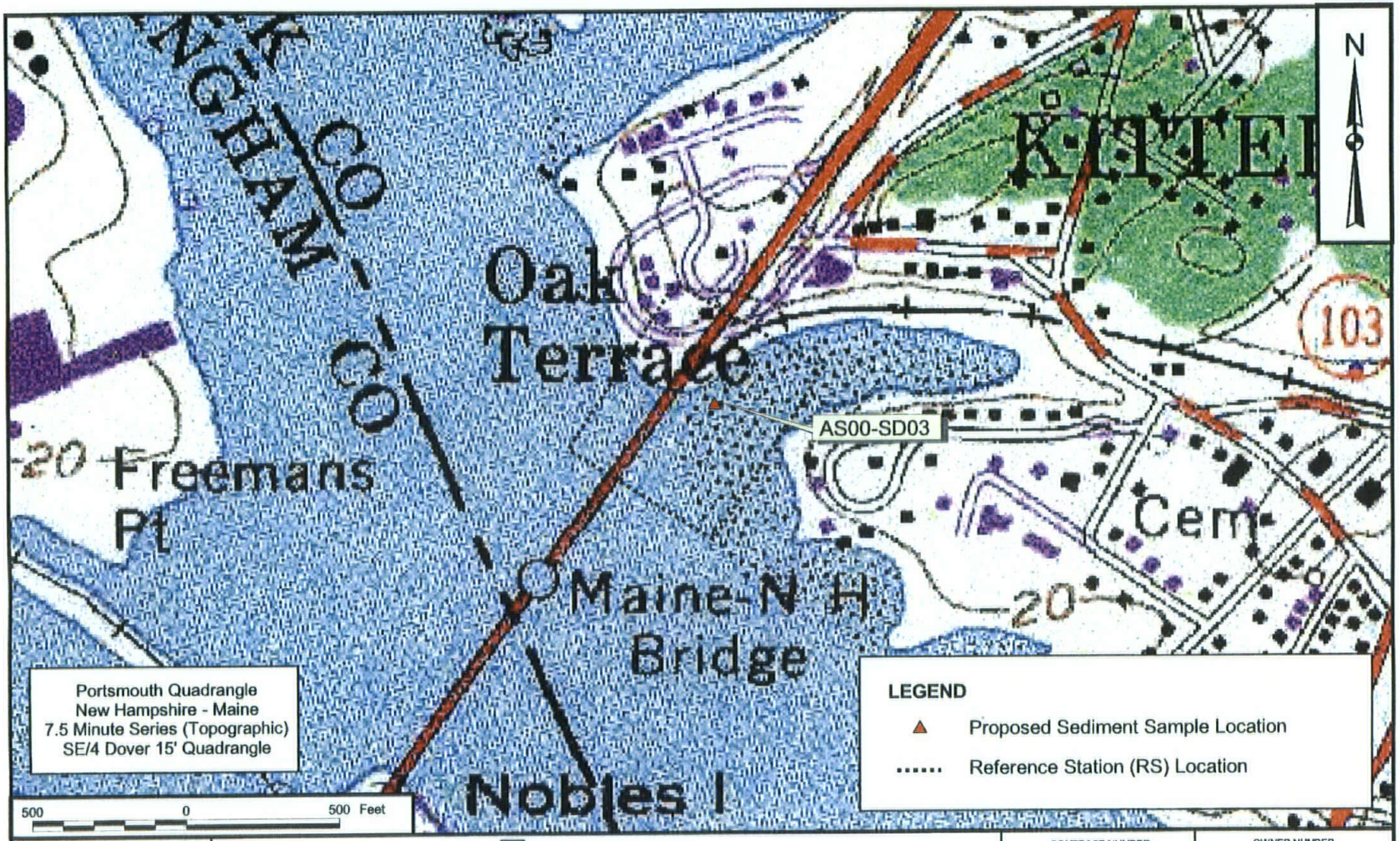
P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR SITE 3 & 29 PROPOSED LOCATION LAYOUT 8/11/05 KMP

DRAWN BY	DATE	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
C.FOSTER	2/14/05			
CHECKED BY	DATE	PROPOSED SAMPLE LOCATIONS FOR ADDITIONAL SCRUTINY AT MS-11 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY	DATE
A. BERNHARDT	3/29/05			
COST/SCHEDULE-AREA			APPROVED BY	DATE
SCALE AS NOTED			DRAWING NO. FIGURE 4 - 4	REV 0

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT APR SITE 10 PROPOSED LOCATION LAYOUT 8/11/05 KMP

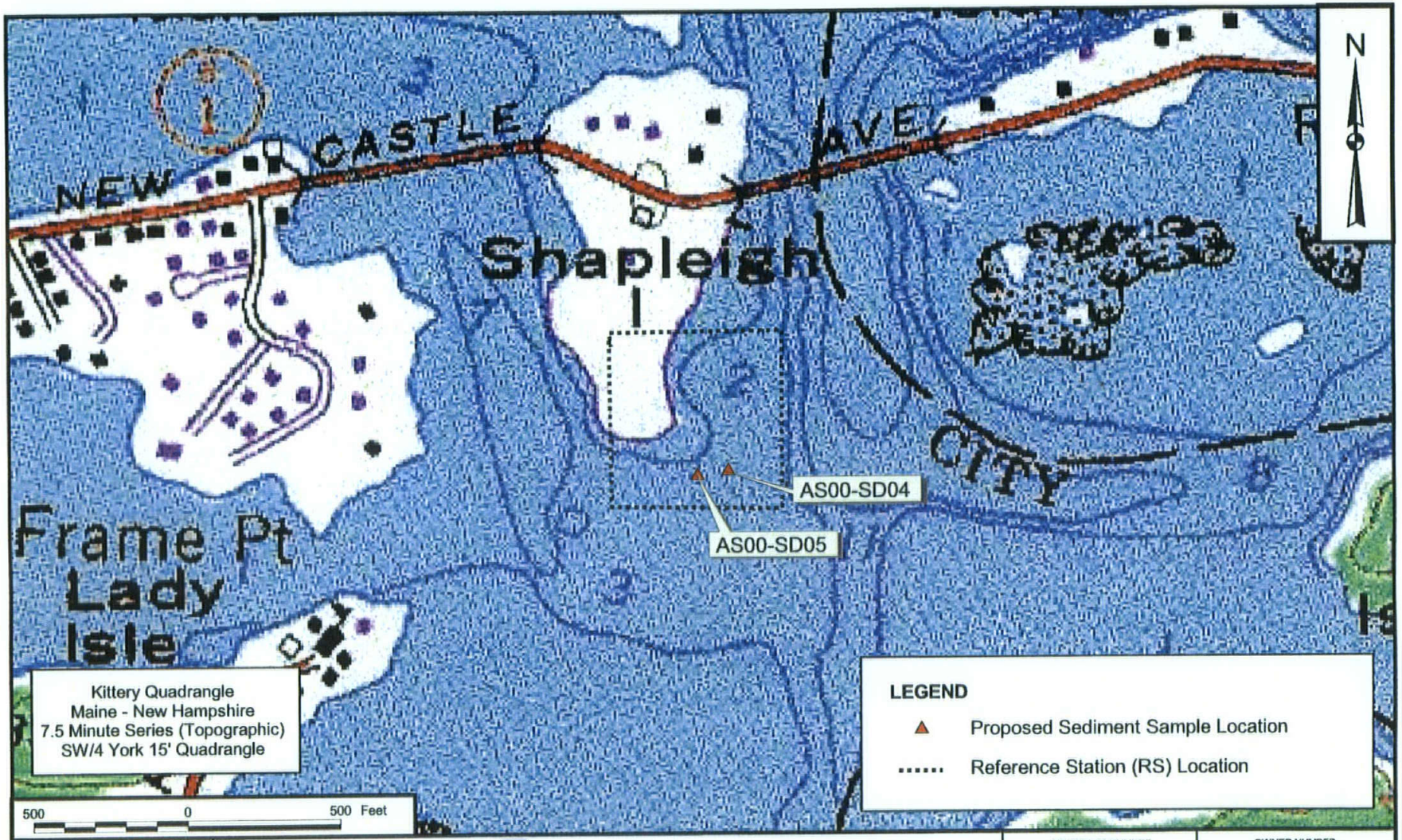


DRAWN BY	DATE	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
C. FOSTER	1/18/05	PROPOSED SAMPLE LOCATIONS FOR ADDITIONAL SCRUTINY AT MS-12 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY	DATE
CHECKED BY	DATE			
A. BERNHARDT	3/29/05		APPROVED BY	DATE
COST/SCHEDULE-AREA			DRAWING NO. FIGURE 4 - 5	REV 0
SCALE AS NOTED				



DRAWN BY J. LAMEY DATE 4/21/04	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
CHECKED BY A. SCHEETZ DATE 4/21/04	PROPOSED LOCATION OF SEDIMENT SAMPLES AT RS-02 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY AMB	DATE 8-12-05
COST/SCHEDULE-AREA		APPROVED BY —	DATE —
SCALE AS NOTED		DRAWING NO. FIGURE 4 - 6	REV 0

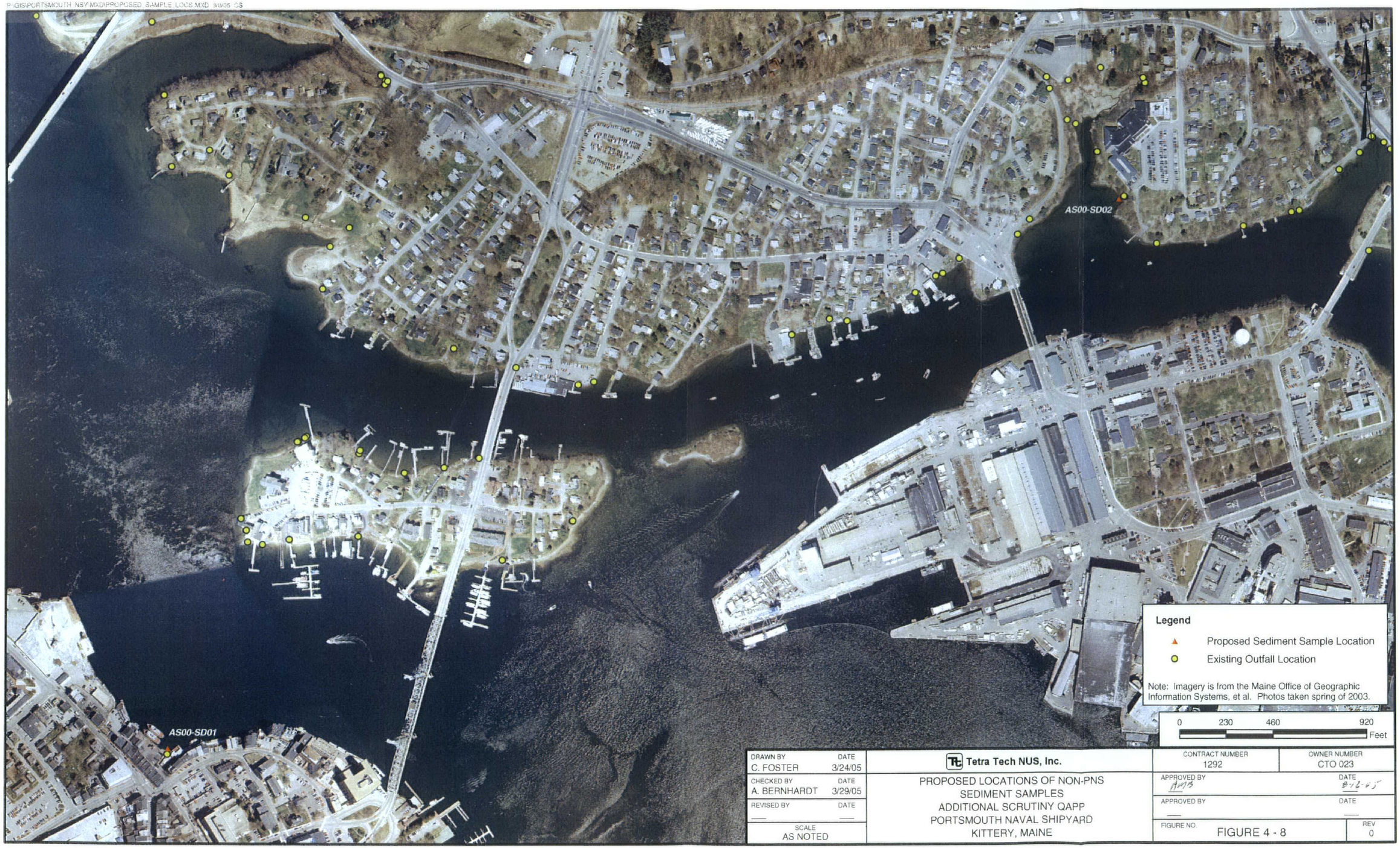
P:\GIS\PORTSMOUTH_NSY\APR\INTERIM_OFFSHORE_MONITORING.APR PROPOSED SEDIMENT LOCATION 8/8/05 KMP



DRAWN BY J. LAMEY DATE 4/21/04	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
CHECKED BY A. SCHEETZ DATE 4/21/04	PROPOSED LOCATION OF SEDIMENT SAMPLE AT RS-03 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY AMB	DATE 8-12-05
COST/SCHEDULE-AREA		APPROVED BY —	DATE —
SCALE AS NOTED		DRAWING NO. FIGURE 4 - 7	REV 0

P:\GIS\PORTSMOUTH_NSY\APR\INTERIM_OFFSHORE_MONITORING.APR PROPOSED RS-3 SEDIMENT LOCATION 8/8/05 KMP

P:\GIS\PORTSMOUTH_NSY\MXD\PROPOSED_SAMPLE_LOCS.MXD 3/8/05 CS



DRAWN BY C. FOSTER	DATE 3/24/05	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292 / OWNER NUMBER CTO 023
CHECKED BY A. BERNHARDT	DATE 3/29/05	PROPOSED LOCATIONS OF NON-PNS SEDIMENT SAMPLES ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY AMB / DATE 8-12-05
REVISED BY —	DATE —		APPROVED BY — / DATE —
SCALE AS NOTED			FIGURE NO. FIGURE 4 - 8 / REV 0

5.0 FIXED-BASE LABORATORY ANALYTICAL PLAN

This section of the QAPP describes the analytical techniques that will be used by the fixed-base laboratory to generate definitive data for the project. The section documents the fixed-base laboratory analytical methods and SOPs that will be used to meet measurement performance criteria and to achieve project-required quantitation limits for the site-related contaminants and other target compounds.

All analytical testing will be accomplished by a laboratory that has successfully completed the Navy's laboratory evaluation program as described in the Navy Installation Restoration Chemical Data Quality Manual (IRCDQM), September 1999, as amended in October 2002. In the event that a laboratory does not have current Navy audit status, the Navy may perform an audit on the laboratory they intend to use. The laboratory cannot be used until successful completion of the QA audit.

Two different laboratories will be utilized for the analysis of samples collected as part of this additional scrutiny. Woods Hole Group will conduct the PAH forensics analysis, as described in Section 2.0. The analytical plan for the forensics analysis is included in Appendix D. Therefore, the PAH forensics analysis, including TOC analysis, are not included in Section 5.0 of this QAPP.

5.1 METHOD DETECTION/QUANTITATION LIMITS

The analytical methods to be used for analysis of samples were selected based on the existing analytical data and data needs as discussed in Section 2.0. The suite of analyses for additional scrutiny include PAHs by SW-846 8270C selective ion monitoring (SIM), pesticides by SW-846 8081A, and copper, lead, and nickel by SW-846 6020. These parameters will be used as a part of the additional scrutiny at the selected monitoring stations.

Tables 5-1 through 5-6 provide summaries of all target analytes and associated practical quantitation limits (PQLs) for aqueous and solid matrices. The laboratory-specific instrument detection limits (IDLs) and method detection limits (MDLs) are also provided in Tables 5-1 through 5-6.

5.2 ANALYTICAL METHODS/SOPs AND MODIFICATION

Analytical methods to be used by the laboratory for solid and aqueous sample analyses are presented in Table 4-3. Specific analytical laboratory SOPs are presented in Appendix C.

It is anticipated that the analysis of PAHs, pesticides, copper, lead, and nickel, will be performed without modification to the standard analytical methods. The laboratory SOP titles, references and project-

specific modifications (if applicable) are presented in Appendix C. The information presented in the example Table 5-7 may be found in the laboratory SOPs.

5.3 CALIBRATION AND PREVENTATIVE MAINTENANCE OF LABORATORY INSTRUMENTS

To ensure that the methods performed by the laboratories meet the project requirements for selective, sensitive, accurate, and precise detection and quantitation of the chemicals for additional scrutiny, the calibration QA/QC procedures provided in the example Table 5-7 will be followed by the laboratory. The calibration procedures for each analytical method are presented in the laboratory-specific SOPs in Appendix C.

The procedures will be followed by the chosen laboratory to ensure that the laboratory instruments are available and in working order to meet the required turnaround times of these analyses. The procedures are included in laboratory SOPs, and the instrument and equipment maintenance, testing, and inspection intervals are provided in Appendix C.

The laboratories will check the performance of instruments used for the analyses required for the project. The instruments are monitored daily for potential failure. The analysis of internal blanks and control standards at the start and at the end of the day provides real-time information to the analyst on the conditions of the instruments. Equipment maintenance logs are maintained for the inductively coupled plasma (ICP) and all instruments used.

5.4 INTERNAL QUALITY CONTROL CHECKS

The chosen laboratories will operate QC programs that assure data users of the reliability and validity of the analyses performed at the laboratory. Each laboratory's QA plan describes the policies, organization, objectives, QC activities, and specific QA functions used by that laboratory. All analytical procedures are documented as SOPs. Each analytical SOP specifies minimum QC requirements for the procedure. As previously noted, SOPs for all analyses to be performed during this investigation are provided in Attachment C. In addition, the laboratories maintain SOPs regarding general laboratory QA operations.

Internal laboratory analytical QC requirements beyond those used for instrument calibration QC are highlighted in the remainder of this section. Additional QC requirements specific to the Navy's Installation Restoration Laboratory Quality Assurance/Quality Control Program (Lab QA/QC Program) are also specified, as applicable, for each of the QC checks. Target precision and accuracy values (control limits) are presented in Tables 5-8 and 5-9. The applicable analytical SOPs should be consulted for calibration QC measures.

5.4.1 Laboratory Control Sampl s

Laboratory control samples (LCSs) provide a means to monitor the overall performance of each step of the analysis, including the sample preparation. These are blank spikes (water analyses) that contain concentrations of analytes that are known with a specified degree of certainty.

Based on the requirements of the Navy's Lab QA/QC Program (IRCDQM, October 2002), LCSs for metals analyses must contain all analytes of interest. Also based on Navy's Lab QA/QC Program requirements, if recovery of an LCS falls outside the control limits, the laboratory will reject the data for the analytical batch and take corrective action. The associated samples, extracts, or digestates may be reanalyzed a single time, and if the LCS recoveries meet acceptance criteria, the data will be reported. If LCS analyte recovery is still outside the acceptance limits, the associated samples in the preparation batch will be reprocessed if sufficient sample is available and holding times have not lapsed. If repreparation or reanalysis is not possible, the data will be flagged and the sample delivery group (SDG) narrative will include details of the failed LCS.

5.4.2 Laboratory Duplicates

Laboratory duplicates will be analyzed for metals to measure the cumulative uncertainty (i.e., precision) of the sample handling, subsampling, preparation, laboratory storage, and analysis operations within the laboratory, as well as sample heterogeneity that is not eliminated through simple mixing in the laboratory. Laboratory duplicates are two subsamples obtained by the laboratory analyst after the sample is mixed. If chemical analysis relative percent difference (RPD) values exceed QC limits for laboratory duplicates, the analytical process will be investigated to assess whether the observed RPD is an indication of a deficient analytical system or of excess sample heterogeneity.

5.4.3 Laboratory Method Blanks

A laboratory method blank or preparation blank is an analyte-free matrix prepared and analyzed in accordance with the analytical method employed to determine whether contaminants originating from laboratory sources have been introduced and have affected environmental sample analyses. Analyte-free matrix is used as a blank for analyses.

Acceptance criteria for laboratory method blanks and corrective actions for non-compliant results are described in the applicable analytical SOPs, which will be provided under separate cover. Under no circumstances should laboratory method blank contaminant values be subtracted from environmental sample analytical results.

5.4.4 Matrix Spikes

Matrix spikes (MSs) are environmental samples to which known quantities of analytes are added prior to sample preparation (digestion or extraction). These samples provide information about the heterogeneity of the samples as well as the effect of the sample matrix on the sample digestion and measurement methodology.

To conform to Navy requirements, MSs will contain as many representative analytes as practicable. For many analyses, the spiking list will consist of most or all the target analytes.

If MS recovery is not within applicable control limits, the laboratories will assess the batch to determine whether the spike results are attributable to a matrix effect or are the result of other problems in the analytical process. Based on Navy requirements, if all the batch QC elements that are not affected by the sample matrix are in control (e.g., method blank, LCS, calibration checks) and if no evidence shows that spiking was not properly performed, the poor spike recovery may be attributed to matrix effects. In this case, the associated data will be flagged, but repreparation and reanalysis will not be required. If any of the batch QC elements that are not affected by the sample matrix are out of control, or if any evidence shows that spiking may have been improperly performed, the MS sample will be reprocessed through the entire analytical sequence. If insufficient sample is available or if holding times have passed, the laboratories will flag the associated data. Details of non-compliant and laboratory duplicate results will be included in the SDG narrative.

5.4.5 Post-Digestion Spikes

Post-digestion spikes (PDSs) are similar to MSs except that the sample digestate, rather than the original sample, is spiked. These spikes are analyzed only for metal target analytes if the MS recovery falls outside control limits. Comparing percent recoveries for PDSs and MSs helps to identify where in the analytical process accuracy problems are occurring. PDSs will contain all target analytes of interest and will be used to assist in determining whether unacceptable MS recoveries are a result of matrix effects.

5.4.6 Performance Evaluation Samples

The fixed-base laboratories analyzing the additional scrutiny samples will be evaluated in accordance with the Navy's Lab QA/QC Program. Performance Evaluation Samples (PESs) are not required for this project because the selected laboratory performs PESs in accordance with the Navy's Lab QA/QC Program.

In addition to the evaluation of PESs, laboratories conducting chemical analyses for the Navy are subject to periodic assessment. Those assessments include a review of the laboratory QA plan and SOPs, an on-site audit of the facility and its technical systems, and analysis of PESs designed to mimic the analytes, matrices, and concentrations likely to be encountered by the laboratories when analyzing Navy samples.. The audit/review cycle is approximately 18 months.

5.5 REQUIREMENTS FOR SUPPLIES/SAMPLE CONTAINERS

All supplies used by the laboratories will be free of COCs, other target compounds, and interferences. Method blanks will be performed at the rate specified in each method to ensure that reagents and equipment are free of contamination. The corrective actions specified in the laboratories statements of work will be followed if laboratory contamination is detected.

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TABLE 5-1

SOIL/SEDIMENT MDLs AND LABORATORY REPORTING LIMITS – PAHs
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Target MDL[1] (µg/kg dry weight)	Laboratory MDL (µg/kg dry weight)
1-Methylnaphthalene	20	0.0962
1-Methylphenanthrene	20	0.120
2-Methylnaphthalene	20	0.125
2,6-Dimethylnaphthalene	20	0.0822
2,3,5-Trimethylnaphthalene	20	0.0941
Acenaphthene	20	0.141
Acenaphthylene	20	0.0799
Anthracene	20	0.132
Biphenyl	20	0.0886
Dibenzothiophene	20	0.113
Fluorene	20	0.157
Naphthalene	20	0.111
Phenanthrene	20	0.416
Benz(a)anthracene	20	0.314
Benzo(a)pyrene	20	0.207
Benzo(b)fluoranthene	20	0.668
Benzo(e)pyrene	20	0.188
Benzo(g,h,i)perylene	20	0.680
Benzo(k)fluoranthene	20	0.54
Chrysene	20	0.634
Dibenz(a,h)anthracene	20	1.18
Fluoranthene	20	0.558
Indeno(1,2,3-c,d)pyrene	20	0.921
Perylene	20	0.470
Pyrene	20	0.547

1 - The target method detection limits (MDLs) are from the QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations: Chemical Evaluations USEPA, Office of Water, Office of Science and Technology. EPA 823-B-95-001, 1995. The laboratory will report nondetected values down to the MDL. MDLs provided by Severn Trent Laboratories, Inc.

TABLE 5-2

AQUEOUS PQLs AND LABORATORY DETECTION LIMITS – PAHs
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Aqueous PQL (µg/L)	Laboratory MDL (µg/L)
1-Methylnaphthalene	10	0.041
1-Methylphenanthrene	10	0.0038
2-Methylnaphthalene	10	0.0052
2,6-Dimethylnaphthalene	10	0.0042
2,3,5-Trimethylnaphthalene	10	0.0036
Acenaphthene	10	0.0059
Acenaphthylene	10	0.0054
Anthracene	10	0.0060
Biphenyl	10	0.0043
Dibenzothiophene	10	0.0037
Fluorene	10	0.0047
Naphthalene	10	0.005
Phenanthrene	10	0.0041
Benz(a)anthracene	10	0.0078
Benzo(a)pyrene	10	0.0050
Benzo(b)fluoranthene	10	0.0094
Benzo(e)pyrene	10	0.0043
Benzo(g,h,i)perylene	10	0.0091
Benzo(k)fluoranthene	10	0.0114
Chrysene	10	0.0129
Dibenz(a,h)anthracene	10	0.0072
Fluoranthene	10	0.0076
Indeno(1,2,3-c,d)pyrene	10	0.0056
Perylene	10	0.0030
Pyrene	10	0.0091

1 - Practical Quantitation Limits (PQLs) are provided as a general guideline. The laboratory will report nondetected values down to the MDL. MDLs provided by Severn Trent Laboratories, Inc.

TABLE 5-3

SOIL/SEDIMENT MDLs AND LABORATORY REPORTING LIMITS – PESTICIDES
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Target MDL[1] (µg/kg dry weight)	Laboratory MDL (µg/kg dry weight)
2,4' DDD	10	0.046
2,4' DDE	10	0.039
2,4' DDT	10	0.039
4,4'-DDD	10	0.038
4,4'-DDE	10	0.040
4,4'-DDT	10	0.039
Aldrin	10	0.042
alpha Chlordane	10	0.042
alpha HCH	10	0.043
beta HCH	10	0.036
cis-Nonachlor	10	0.039
delta HCH	10	0.037
Dieldrin	10	0.040
Endosulfan II	10	0.027
Endrin	5	0.054
gamma Chlordane	10	0.044
gamma HCH	10	0.040
Heptachlor Epoxide	10	0.040
Heptahclor	10	0.042
Hexachlorobenzene	10	0.076
Mirex	10	0.10
Oxychlordane	10	0.044
Trans-Nonachlor	10	0.045

1 - The Target method detection limits (MDLs) are from the QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations: Chemical Evaluations USEPA, Office of Water, Office of Science and Technology. EPA 823-B-95-001, 1995. The laboratory will report nondetected values down to the MDL. MDLs provided by Severn Trent Laboratories, Inc.

TABLE 5-4

AQUEOUS PQLs AND LABORATORY DETECTION LIMITS – PESTICIDES
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Aqueous PQL[1] (µg/L)	Laboratory MDL (µg/L)
2,4' DDD	0.01	0.00118
2,4' DDE	0.01	0.00042
2,4' DDT	0.01	0.00020
4,4'-DDD	0.01	0.00014
4,4'-DDE	0.01	0.00021
4,4'-DDT	0.01	0.00057
Aldrin	0.05	0.00042
alpha Chlordane	0.05	0.00027
alpha HCH	0.05	0.00041
beta HCH	0.05	0.00059
cis-Nonachlor	0.1	0.00022
delta HCH	0.05	0.00055
Dieldrin	0.10	0.00031
Endosulfan II	0.10	0.00056
Endrin	0.10	0.00019
gamma Chlordane	0.05	0.00048
gamma HCH	0.05	0.00021
Heptachlor Epoxide	0.05	0.00073
Heptahclor	0.05	0.00042
Hexachlorobenzene	0.1	0.00056
Mirex	0.1	0.00063
Oxychlordane	0.1	0.00036
Trans-Nonachlor	0.1	0.00053

1 - Practical Quantitation Limits (PQLs) are provided as a general guideline. The laboratory will report nondetected values down to the MDL. MDLs provided by Severn Trent Laboratories, Inc.

TABLE 5-5

SOIL/SEDIMENT IDLs AND LABORATORY REPORTING LIMITS – METALS
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Target IDL[1] (mg/kg dry weight)	Laboratory IDL (mg/kg dry weight)
Copper	5	0.5
Lead	5	0.3
Nickel	5	0.25

1 - The target instrument detection limits (IDLs) are from the QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations: Chemical Evaluations USEPA, Office of Water, Office of Science and Technology. EPA 823-B-95-001, 1995. The laboratory will report nondetected values down to the IDL. IDLs provided by Severn Trent Laboratories, Inc.

TABLE 5-6

AQUEOUS IDLs AND LABORATORY REPORTING LIMITS – METALS
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Aqueous IDL (µg/L)	Laboratory IDL (µg/L)
Copper	1	0.05
Lead	1	0.05
Nickel	1	0.1

1 - The instrument detection limits (IDLs) are from the QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations: Chemical Evaluations USEPA, Office of Water, Office of Science and Technology. EPA 823-B-95-001, 1995. The laboratory will report nondetected values down to the IDL. IDLs provided by Severn Trent Laboratories, Inc.

TABLE 5-7

EXAMPLE
LABORATORY ANALYTICAL METHOD/SOP REFERENCE TABLE
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

EXAMPLE
LABORATORY ANALYTICAL METHOD / SOP REFERENCE TABLE

Reference Number	Fixed Base Laboratory Performing Analysis	Title, Revision Date and/or Number	Definitive or Screening Data	Region I NESTS Method Code	Analytical Parameter	Instrument	Modified for Project Work (Y or N)
L1	TBD	Equipment Maintenance, CA-101	NA	NA	Metals	ICP, CVAA, ICP-MS, IC	N
L2	TBD	Trace Metals Analysis by ICP-AES using using USEPA Method 6010, CA-608	Definitive	NA	Metals (Except mercury and thallium)	ICP	N

Definitive - An analytical method generating data of known quality.

EXAMPLE
FIXED LABORATORY INSTRUMENT MAINTENANCE AND CALIBRATION

Instrument	Analysis	Maintenance, Testing, and Inspection Activities	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	Method/SOP Reference[1]
ICP	ICP Metals	Clean torch assembly and spray chamber when discolored or when degradation in data quality is observed, clean nebulizer, check argon, replace peristaltic pump tubing.	ICAL – At the beginning of each day or if QC does not meet criteria	NA	Recalibrate	Analyst/ Supervisor	L1, L12
			ICV – Immediately after every ICAL	90 – 110%	Recalibrate or reanalyze affected data	Analyst/ Supervisor	
			CCV – Every 10 samples or every two hours and at end of run	90 – 110%	Recalibrate or reanalyze affected data	Analyst/ Supervisor	

TABLE 5-8

EXAMPLE LABORATORY ANALYTICAL QC SAMPLE TABLE – PAHs AND PESTICIDES
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE
PAGE 1 OF 2

Laboratory QC	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action (CA)	Person(s) Responsible for CA	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per batch	No target analyte ≥ QL	Qualify data	Data validator	Accuracy/bias contamination	No target analyte ≥QL
Reagent Blank	NA	NA	NA	NA	Accuracy/bias contamination	NA
Storage Blank	NA	NA	NA	NA	Accuracy/bias contamination	NA
Instrument Blank	NA	NA	NA	NA	Accuracy/bias contamination	NA
Laboratory Duplicate	NA	NA	NA	NA	Precision	NA
Laboratory Matrix Spike	1 per 20 samples	Within laboratory established limits	Qualify data	Data validator	Accuracy/bias	Within laboratory established limits
Matrix Spike Duplicate	1 per 20 samples	Within laboratory established limits	Qualify data	Data validator	Precision	Within laboratory established limits
LCS	1 per 20 samples	Within laboratory established limits	Reanalyze after appropriate corrective action has been taken	Laboratory Analyst	Accuracy/Bias	Within laboratory established limits
Surrogates	3 per each sample (PAHs), 2 per each sample (Pests) 1 per each sample (TPH)	Within method established limits	Re-extract and reanalyze, then qualify data	Laboratory Analyst / Data Validator	Accuracy/bias	Within method established limits

TABLE 5-8

EXAMPLE LABORATORY ANALYTICAL QC SAMPLE TABLE – PAHs AND PESTICIDES
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE
PAGE 2 OF 2

Laboratory QC	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action (CA)	Person(s) Responsible for CA	Data Quality Indicator (DQI)	Measurement Performance Criteria
Internal Standards[1]	3 per each sample (PAHs)	+100%/-50% internal standard area	Re-extract and reanalyze, then qualify data	Laboratory Analyst / Data Validator	Accuracy	+/- 50% internal standard area

LCS Laboratory control sample.
NA Not applicable.
PAH Polycyclic aromatic hydrocarbons.
PEST Pesticides.
QC Quality control.
QL Quantitation limit.
RPD Relative percent difference.
SOP Standard operating procedure.
TPH Total petroleum hydrocarbons.

1 – Pesticide and TPH methods do not use internal standards.

TABLE 5-9

EXAMPLE LABORATORY ANALYTICAL QC SAMPLE TABLE – METALS
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE
PAGE 1 OF 2

Laboratory QC:	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action (CA)	Person(s) Responsible for CA	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per batch	No target analyte ≥ QL	Qualify data	Data validator	Accuracy/bias contamination	No target analyte ≥QL
Reagent Blank	NA	NA	NA	NA	Accuracy/bias contamination	NA
Storage Blank	NA	NA	NA	NA	Accuracy/bias contamination	NA
Instrument Blank	1 every 10 samples and as needed	No target analyte ≥ QL	Qualify data	Data validator	Accuracy/bias contamination	No target analyte ≥ QL
Laboratory Duplicate	1 per 20 samples	<20% RPD Aqueous <35% RPD Solid	Qualify data	Data validator	Precision	<20% RPD, Aqueous <35% RPD, Solid
Laboratory Matrix Spike	1 per 20 samples	+/-25% Recovery (Solid and Aqueous)	Qualify data	Data validator	Accuracy/bias	+/-25% Recovery
Matrix Spike Duplicate	NA	NA	NA	NA	Precision	NA
LCS	1 per 20 samples	+/-20% Recovery (Solid and Aqueous)	Reanalyze after appropriate corrective action has been taken	Laboratory Analyst	Bias	+/-20% Recovery
Internal Standards	Each sample	NA	NA	Laboratory Analyst / Data Validator	Instrument Response	NA

TABLE 5-9

EXAMPLE LABORATORY ANALYTICAL QC SAMPLE TABLE – METALS
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE
PAGE 2 OF 2

LCS	Laboratory control sample.
NA	Not applicable.
QC	Quality control.
QL	Quantitation limit.
RPD	Relative percent difference.
SOP	Standard operating procedure.

6.0 DATA MANAGEMENT AND QUALITY ASSESSMENT PLAN

6.1 DOCUMENTATION, RECORDS, AND DATA MANAGEMENT

This section describes how all analytical information will be managed, organized, and maintained for efficient use by project personnel. The information management process is outlined from the point of data generation to ultimate storage.

6.1.1 Documentation and Records of the Analytical Program

A summary of records and documentation to be generated as a result of the additional scrutiny and stored in the TtNUS project files is provided in Table 6-1. Information to be maintained in the laboratory files is outlined in Section 6.1.3 of this QAPP.

6.1.2 Field Analysis Data Package Deliverables

No field screening will be performed, and no field measurements will be collected.

6.1.3 Fixed-Base Laboratory Data Package Deliverables

A turnaround time of 28 days will be requested for most data. However, a turnaround time of 14 days will be requested for select metals data at MS-05. CLP-like electronic deliverables, formatted according to the requirements stated in the laboratory subcontracts, will be provided by the laboratories.

6.1.4 Data Reporting Formats

Field data will be recorded in field logbooks and on field forms. All logbook and log sheet entries must be made in indelible ink (black pen is preferred). No erasures or liquid paper or white out are permitted. If an incorrect entry is made, the data will be crossed out with a single strike mark, initialed, and dated. The field personnel will sign and date the logbook pages and field forms. Examples of the forms to be used in the field are presented in Appendix C of this QAPP.

The equivalent of CLP data reporting Forms 1 through 14 required in the Statement of Work (SOW) for inorganic analyses will be submitted by the laboratory for the sample results.

6.1.5 Data Handling and Management

The data-handling procedures to be followed by the laboratory will meet the requirements in the laboratory subcontracts. All analytical and field data will be maintained in the project files. The project

files will contain hard copies of the chain-of-custody forms, sample log forms, and sample location maps and documentation of QA of data manipulation.

6.1.6 Data Tracking and Control

A "cradle-to-grave" sample tracking system will be used from the beginning to the end of the investigation. The sample identification system will consist of the format described in detail in Section 4.0. Before field mobilization, the FOL will coordinate with the SMC to initiate the sample tracking process. All sample numbers, requested laboratory analyses, and preservative information will be entered into a sample tracking database before each sampling event. The SMC will use the database to print sample jar labels, if necessary, before field sampling. The FOL and Lead Chemist will review the labels for completeness of information and adherence to QAPP requirements, as well as for accuracy. The SMC will also send an advance paper copy of labels and the sample tracking database to the laboratories.

When field sampling is underway, the FOL will forward the chain-of-custody forms to the SMC via facsimile at the end of each day. The Lead Chemist will compare the entries on the chain-of-custody forms with the sample tracking database and enter the sample date and other sample information as appropriate. The Lead Chemist will also confirm that the chain-of-custody forms provide the information required by the QAPP. This will allow for early detection of errors made in the field so that adjustments can be made while the crew is mobilized. After successful completion of all requested analyses, the laboratories will submit an electronic deliverable for every sample delivery group (SDG). When all electronic deliverables have been received from the laboratories, queries will be run versus the pre-field effort database of sample labels and sample collection information to ensure that the laboratories performed all the requested analyses. The TtNUS PM will be notified of any discrepancies. Ideally, discrepancies will be noted early enough so that all samples can be analyzed within the prescribed holding times.

6.1.6.1 Sample Information

Data from field observations will be recorded directly in field notebooks or on sample logs. The reduction of laboratory data entails the manipulation of raw data instrument output into reportable results. Laboratory data will be verified by the group supervisor and then by the laboratories' QC/Documentation Department.

Before electronic files are received from the laboratories, all sample-specific information will be entered into the data management system. The sample information file will allow the analytical results to be grouped together properly for statistical purposes. The data will be managed in one data structure. For

field data, the FOL will coordinate with the geographical information system (GIS) leader to ensure that all survey technical specifications are consistent with the underlying coordinate system in the GIS.

Electronic data arriving from the laboratories will pass through the SMC to the DVM for database compilation and validation. The DVM will compile all the formatted laboratory electronic deliverables into a working project database. Data that are to be validated will be printed as data packages which include the samples as part of each SDG and the appropriate analytical fraction. The data packages will be distributed to the appropriate data validators. The data validators will enter all data qualifiers and qualifier codes into the database and print out a hard copy and return it to the DVM. The DVM will check the data qualifiers and qualifier codes in the project database and print the final validated data for incorporation into the data validation letter. When all samples and analyses have been accounted for and validated, the DVM will forward the project database to the Information Management Resource Group (IMRG), which will incorporate the analytical data into the relational database located on the Local Area Network (LAN) in the TtNUS Pittsburgh office.

6.1.6.2 Project Data Compilation

The analytical laboratory subcontractors will generate portable document format (pdf) files of the analytical data packages and the electronic data deliverables. The electronic database will be checked against hard-copy results from the pdf file provided by the laboratories and updated as required based on data qualifier flags applied during the data validation process. The data generated under this additional scrutiny program will be incorporated into the PNS database and GIS. All data, such as units of measure and chemical nomenclature, will be manipulated to maintain consistency with the project database. The project database is a relational database that ensures data structure integrity and data quality for all PNS data.

6.1.6.3 Geographical Information System

Data management systems consist of a relational database and GIS used to manage environmental information pertaining to PNS. The relational database stores chemical, geological, hydrogeological, and other environmental data collected during environmental investigations. The GIS is built from the relational database and contains subsets of the larger data pool. Using the GIS, environmental data can be posted on base mapping to provide a graphical representation of the information.

Upon compilation of sample, chemical, and positional data, the data will be incorporated into the PNS GIS. The GIS system can be used to generate various maps for PNS data including site location maps, sample location maps, and contaminant tag maps, as needed. ARC View is the GIS software that will be

used. The sampling locations will be assigned coordinates based on NAD 83 for Maine State Planar Coordinates. The 2002 PNS vertical datum will be used for elevation.

6.2 DATA VERIFICATION AND VALIDATION

Data verification is a process of evaluating the completeness, correctness, and contractual compliance of a data set against the method standard, SOP, or contract requirements documented in this QAPP. Data validation is an analyte- and sample-specific process that extends the qualification of data beyond data verification to determine the quality of a specific data set.

The internal data verification requirements for this project include the maintenance and periodic review of field documentation (i.e., site logbooks, instrument calibration logs, chain-of-custody forms, field summary reports, and field modification records) and laboratory analytical data packages.

Data validation is a systematic review of analytical data packages with respect to sample receipt and handling, compliance with required analytical methods, data reporting and deliverables, and document control. A qualified chemist will review the analytical data packages using USEPA procedures. One hundred percent of the environmental samples will be validated.

After receipt of analytical results, TtNUS will perform data validation according to the most recent Region I guidelines to ensure that the analytical results meet the DQOs defined in Section 2 of this document. Inorganic results will be validated according to the USEPA Region I Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses (June 1988), with consideration given to Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (USEPA, October 2004). Organic results will be validated according to the USEPA Region I Laboratory Data Validation Functional Guidelines for Evaluating Organic Analyses (December 1996), with consideration given to Contract Laboratory Program National Functional Guidelines for Organic Data Review (USEPA, October 1999b). All parameters will be reviewed using applicable sections of the aforementioned guidelines and the laboratory SOPs.

After the data are validated, a list of nonconformities will be generated. Nonconformities require data qualifiers, which are used to alert the data user to inaccurate or imprecise data. For situations in which several QC criteria are out of specification with regard to the limits specified in the Navy Installation Restoration Chemical Data Quality Manual (NFESC, September 1999), the data validator may make professional judgments and/or comments on the validity of the overall data package. In situations where the validity of an entire data package is in question, it may be necessary for the sample(s) to be reanalyzed. The reviewer will then prepare a technical memorandum presenting changes in the data, if necessary, and the rationale for making such changes.

The net result is a data package that has been carefully reviewed for its adherence to prescribed requirements and that is suitable for its intended use. Data validation therefore plays a major role in determining the confidence with which key technical evaluations may be made.

The Tier III data validation reports for all parameters will be generated according to the requirements described in Attachment B of the USEPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (December 1996) with the exception of the PAH forensics. Only a limited validation (Tier II) will be conducted on that data. The final data validation report will include a technical memorandum, qualified analytical results, results reported by the laboratory, Region I worksheets (where appropriate), and documentation to support data qualification. All data will be flagged by an appropriate qualifying symbol.

The data and field records will also be reviewed by project personnel to ensure that the samples represent the intended sampling conditions and populations. Data qualified during validation will be reviewed to assess the impact of the qualifiers on the attainment of project objectives.

6.2.1 Verification

Verification includes field data verification and laboratory data verification.

6.2.1.1 Field Measurement Data Verification

The data verification process for this project includes the maintenance and periodic review of field documentation including the following:

- Field logbook
- Chain-of-custody form
- Field summary report
- Field modification record
- Field log sheets

Field data will not be generated using a field laboratory.

If an error is made in the logbook, the error will be legibly crossed out (single-line strikeout), initialed, and dated by the field member and corrected in a space adjacent to the original (erroneous) entry.

6.2.1.2 Laboratory Data Verification

Data reduction for laboratory analytical data generated via the USEPA SW-846 analytical protocol, QA requirements, and reporting procedures (copper, lead, nickel, TPH, PAHs, pesticides and TOC) will be conducted in accordance with the most current SOW for multi-concentration inorganic and organic analyses, as identified in previous sections of this plan.

Laboratory analytical data will be reported using standard concentration units to ensure comparability with regulatory standards and guidelines and previous analytical results. Reporting units for sediment and soil matrices for the classes of chemicals under consideration are as follows:

- Copper, lead, nickel - mg/kg
- TPH and PAHs - µg/kg
- Pesticides - µg/kg
- TOC - mg/kg

Field QC sample results will be included in the database for PNS. Specifically, the analytical results for field duplicates and rinsate blanks will be provided. The results for field QC samples will be considered during the course of data validation (in concert with laboratory method blanks) to eliminate false positive results according to the "5 times" rules specified in the National Functional Guidelines for Inorganic and Organic Data Review. The results for laboratory QC samples such as method blanks will not be presented in the database.

6.2.2 Data Validation

Validation of field measurements and laboratory analytical data is discussed in this section. Laboratory analytical data will be validated in accordance with current USEPA guidance.

6.2.2.1 Field Measurement Data Validation

No field measurements will be collected as part of this investigation.

6.2.2.2 Analytical Laboratory Data Validation

One hundred percent of the laboratory data from chemical analyses will be validated. Final review and approval of validation deliverables will be completed by the data validation coordinator. All laboratory analytical data will be subjected to validation in accordance with the most recent Region I validation guidelines with consideration given to the National Functional Guidelines for Inorganic and Organic Data

Review to the greatest extent practicable. The components of laboratory data validation are provided in Table 6-2.

As part of the validation process, the validator will check that the laboratories have provided all the documentation required to support the reported analytical results. If any documentation is missing from the data package, the data validator will contact the laboratories to request a resubmittal. If the laboratories fail to resubmit the requested information, the data validator will note this on the data validation cover letter. The usability of such data will then be determined by the TtNUS PM and the Navy, as discussed in Section 6.3.

Data validation will be completed to ensure that the data are of evidentiary quality. Particular emphasis will be placed on holding time compliance, equipment calibration, spike recoveries, and blank results, although all required elements of the validation process will be considered.

6.3 DATA USABILITY AND RECONCILIATION WITH PROJECT QUALITY OBJECTIVES

6.3.1 The PARCC Parameters

The PARCC parameters are precision, accuracy, representativeness, comparability, completeness. Each of these parameters along with sensitivity/quantitation limits is described below.

6.3.1.1 Precision

The precision goals described below will be evaluated. Field duplicate sample results, laboratory duplicate results, sampling procedures, sample transport problems (if any), sample matrix problems (if any), and sample heterogeneity will be considered, as appropriate, to evaluate the overall data precision. For example, field duplicate precision will be compared to laboratory precision. The RPD between a sample or MS (Sample 1) and its duplicate or matrix spike duplicate (MSD) (Sample 2) is calculated for chemical analyses using the following formula:

$$\text{RPD} = \frac{|\text{Amount in Sample 1} - \text{Amount in Sample 2}|}{0.5\,(\text{Amount in Sample 1} + \text{Amount in Sample 2})} \text{ X } 100\,\%$$

6.3.1.2 Accuracy

The data validator evaluates the potential for adverse impacts to the accuracy of data by reviewing laboratory blanks, field blanks, LCSs, MSs, and QC check standards. The data validation process during

which these evaluations are made is described in Sections 6.1 and 6.2. Calculation of accuracy is described below.

Control charts are plotted by the laboratory for each target analyte and are kept on matrix- and analyte-specific bases. The percent recovery (%R) for a spiked sample is calculated by using the following formula:

$$\%R = \frac{\text{Amount in Spiked Sample} - \text{Amount in Sample}}{\text{Known Amount Added}} \times 100\%$$

LCSs and surrogate spikes are also analyzed to assess accuracy. The %R calculation for LCSs and surrogate spikes is as follows:

$$\%R = \frac{\text{Experimental Concentration}}{\text{Certified or Known Concentration}} \times 100\%$$

During data validation, any data not meeting accuracy specifications are identified to the data user through the use of data qualifiers. The field and laboratory blanks provide indications of the potential for having contaminated samples before or during analysis, respectively. Each type of blank will be evaluated for its impact on the sampling or the analytical processes, as appropriate. Laboratory control standards and check standards indicate whether analyte quantitation is accurate and whether the analytical system was capable of generating results within the project accuracy specifications. MS recoveries indicate and will be evaluated to assess the impact of specific sample matrices on the accuracy of project data.

6.3.1.3 Sample Representativeness

Sampling and analysis methods and procedures were selected during project planning to provide data representing environmental media at locations selected for additional scrutiny sampling without bias, except when a bias was intended. Whether biases were intended and how bias was used to an advantage are described in Sections 2.0 and 4.0. To evaluate the representativeness of additional scrutiny data, the actual samples collected will be compared to the samples that were intended to be collected. Furthermore, the data verifications and validations will be reviewed to ensure that data have met project specifications for precision and accuracy. The degree to which project specifications have been met will provide a qualitative assessment of the representativeness of the additional scrutiny data.

6.3.1.4 Comparability

Compliance with the selected methods of sample collection and analyses will produce data of suitable comparability with past and future investigations, as well as within this investigation. Therefore, compliance with the selected methods will be evaluated by reviewing field notes and data validation reports generated during data verification and validation. Data from each matrix collected at the site will be compared with historical and expected data results.

6.3.1.5 Completeness

Completeness will be computed in accordance with the following equation:

$$\%\,\text{Completeness} = \frac{(\text{number of valid measurements})}{(\text{numer of measurements planned})} \times 100\%$$

Completeness is a measure of the amount of valid data obtained from the measurement program, compared to the total amount collected. Valid data are defined as data that have not been rejected or considered unusable during validation or data review. Percent completeness is expressed as the ratio of the number of validated data points to the number of planned data points. For relatively clean, homogeneous matrices, 100 percent completeness is expected. However, as matrix complexity and heterogeneity increase, completeness may decrease. Where analysis is precluded or where DQOs are compromised, the ability to achieve project objectives will be evaluated. Whether any particular sample is critical (i.e., absolutely necessary for the attainment of project objectives) to the investigation will be evaluated in terms of the sample location, the parameter in question, the intended data use, and the effects of an incomplete data set on the attainment of project objectives.

Critical data points may not be identified until all the analytical results are evaluated. If in the evaluation of results it becomes apparent that the data for a specific medium are of insufficient quality (i.e., less than 95 percent completeness), either with respect to the number of samples or an individual analysis, resampling to replace the deficient data points may be necessary. The Navy and TtNUS will determine whether resampling is necessary.

6.3.1.6 Sensitivity and Quantitation Limits

The quantitation and detection limits that are required to ensure attainment of project action levels specified in Section 5.0 will be evaluated. The sample quantitation limits, the low point instrument calibration standard, matrix interferences, and sample dilutions will be evaluated to assess whether the

sensitivity goals were met. Any significant deviations will be indicated during the data validation and overall data review processes.

6.3.2 Data Quality Assessment

After data validation and an overall review of data quality indicators, the data will be reconciled with DQOs to determine whether sufficient data of acceptable quality are available for decision making. A series of inspections and statistical analyses will be performed to estimate several of the data set characteristics. These inspections and statistical analyses will be designed to:

- Identify deviations, if any, from the field sampling SOPs
- Identify deviations, if any, from the laboratory analytical SOPs
- Identify deviations, if any, from the QAPP
- Identify deviations, if any, from the data validation process
- Identify elevated detection limits and explain their impacts on the attainment of project objectives
- Identify unusable data (i.e., data qualified as "R" or "UR")
- Evaluate project assumptions

For mathematical manipulations, non-detect values will be represented by a concentration equal to one-half the sample-specific reporting limit. Duplicate results (original and duplicate) will not be averaged for the purpose of representing ranges of concentrations. However, the average of the original and duplicate will be used to represent the concentration at that sample location.

After all data evaluations are completed, any limitations on the use of data will be known, and the limitations will be considered during decision making. If necessary, investigation objectives may be revised in anticipation of additional data collection in order to meet project objectives for the site.

TABLE 6-1

SAMPLING AND ANALYTICAL PROGRAM DOCUMENTATION AND RECORDS
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Sample Collection Records	Fixed-Base Laboratory Records	Data Assessment Records	Other
Field Logbooks	Sample receipt, custody and tracking records	Audit report and quality notices	All versions of Additional Scrutiny QAPP
Sample Log Sheet-Soil/Sediment	Standards traceability logs	Data validation report	Health and safety plan
Chain-of-Custody Records	Equipment calibration logs		All versions of project reports
Telephone Logs	Sample prep logs		
Field Instrument Calibration Logs	Sample analysis logs		
	Sample disposal records		
	Telephone logs		

TABLE 6-2

DATA VALIDATION SUMMARY TABLE / MODIFICATION
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Medium/ Matrix	Analytical Parameter	Concentration Level	Validation Criteria	Validation Criteria Modified	Data Validation Tier Level Used	Modified Tier Level Used	Data Validator (Name, Title, and Organizational Affiliation)	Responsibility for Data Validations
Soil/ Sediment/ Aqueous Field QC	Copper, Lead and Nickel	Low/Medium	USEPA Region I Functional Guidelines for Evaluating Inorganic Analyses, June 1988; as relevant, National Functional Guidelines for Inorganic Review, October 2004, as relevant; the NFESC document entitled Navy Installation Restoration Chemical Data Quality Manual. (September, 1999) as relevant.	N	Tier III	N	TBD[1]	Data Validation Coordinator
Soil/ Sediment/ Aqueous Field QC	PAHs, Pesticides	Low/Medium	USEPA Region I Functional Guidelines for Evaluating Organic Analyses, December 1996, as relevant; National Functional Guidelines for Organic Review, October 1999b, as relevant; the NFESC document entitled Navy Installation Restoration Chemical Data Quality Manual, (September, 1999) as relevant.	N	Tier III (Tier II validation will be used for PAH forensics)	N	TBD[1]	Data Validation Coordinator

1 Data validator will be determined when the pdf data deliverables arrive from the laboratory.

NFESC Naval Facilities Engineering Service Center.
PAHs Polycyclic aromatic hydrocarbons.
TBD To be determined.

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TtNUS, March 2000. Field Investigation Report, Site 10 (Building 238) and Site 29 (Teepee Incinerator), for Portsmouth Naval Shipyard, Kittery, Maine, TtNUS, King of Prussia, PA.

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TtNUS, February 2004. Investigation of the Approximate Extent of Ash at Site 34, Portsmouth Naval Shipyard, Kittery, Maine. Letter work plan prepared by TtNUS, Inc., 600 Clark Avenue, Suite 3, King of Prussia, Pennsylvania: 19406-1433.

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APPENDIX A

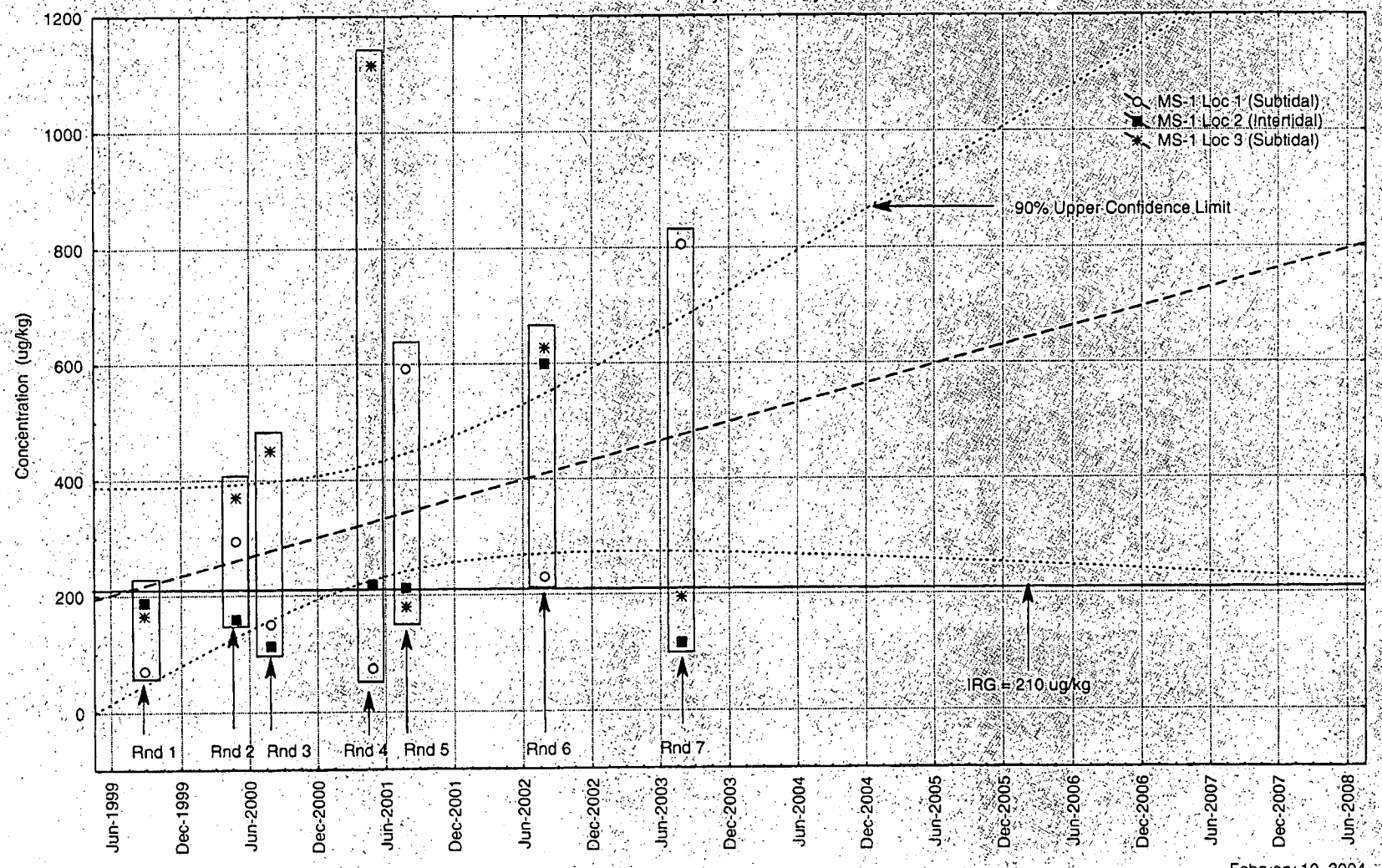
SUPPORTING INFORMATION

- A-1: Concentration Trend Plots and Figures for MS-01
- A-2: Concentration Trend Plots for MS-05 and MS-09, Photographs of the Turbidity Curtains, and Recent Aerial Photograph
- A-3: Concentration Trend Plots for MS-11 and Shoreline Evaluation Memorandum
- A-4: Concentration Trend Plots for MS-12

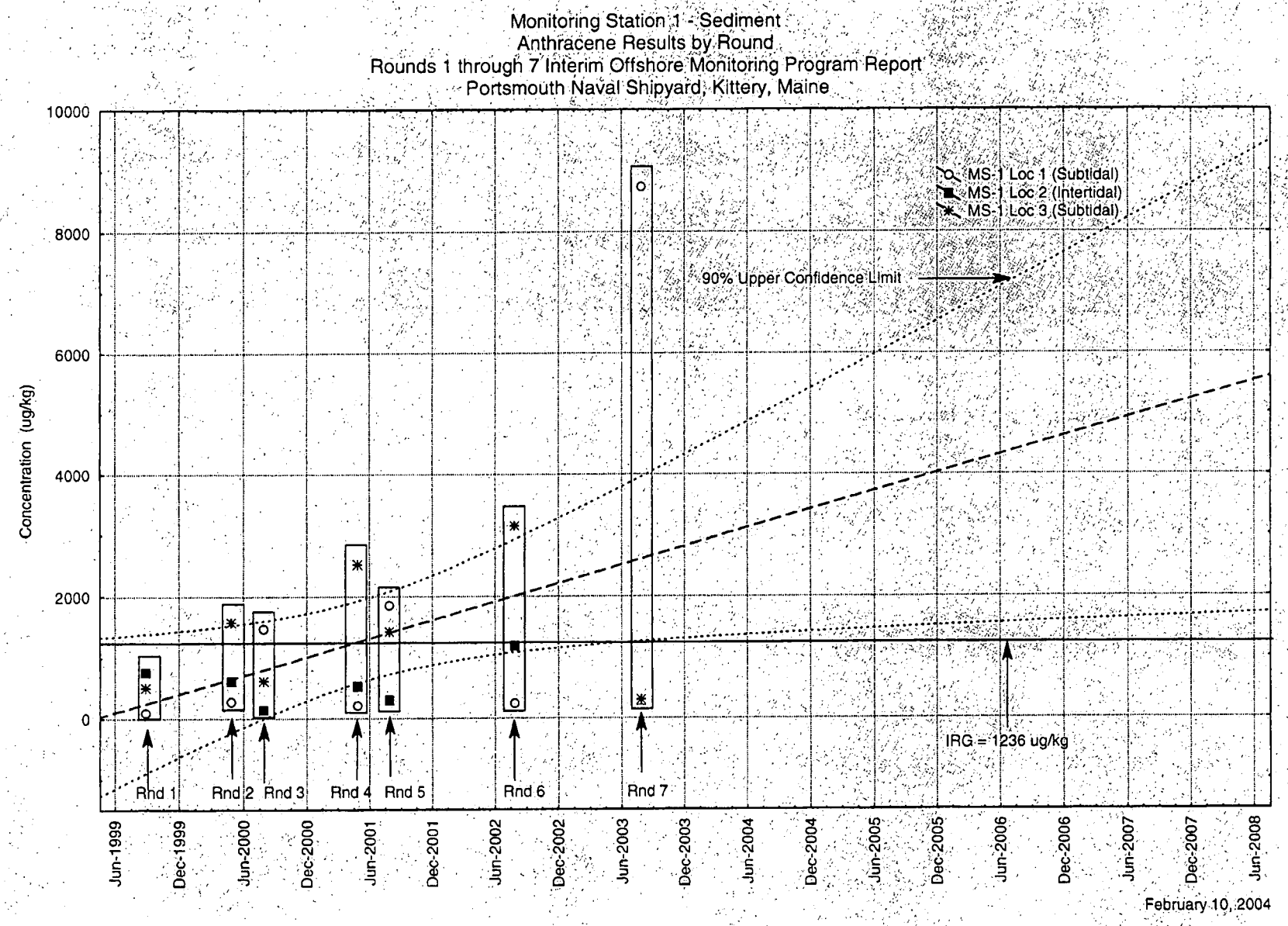
APPENDIX A-1

CONCENTRATION TREND PLOTS AND FIGURES FOR MS-01

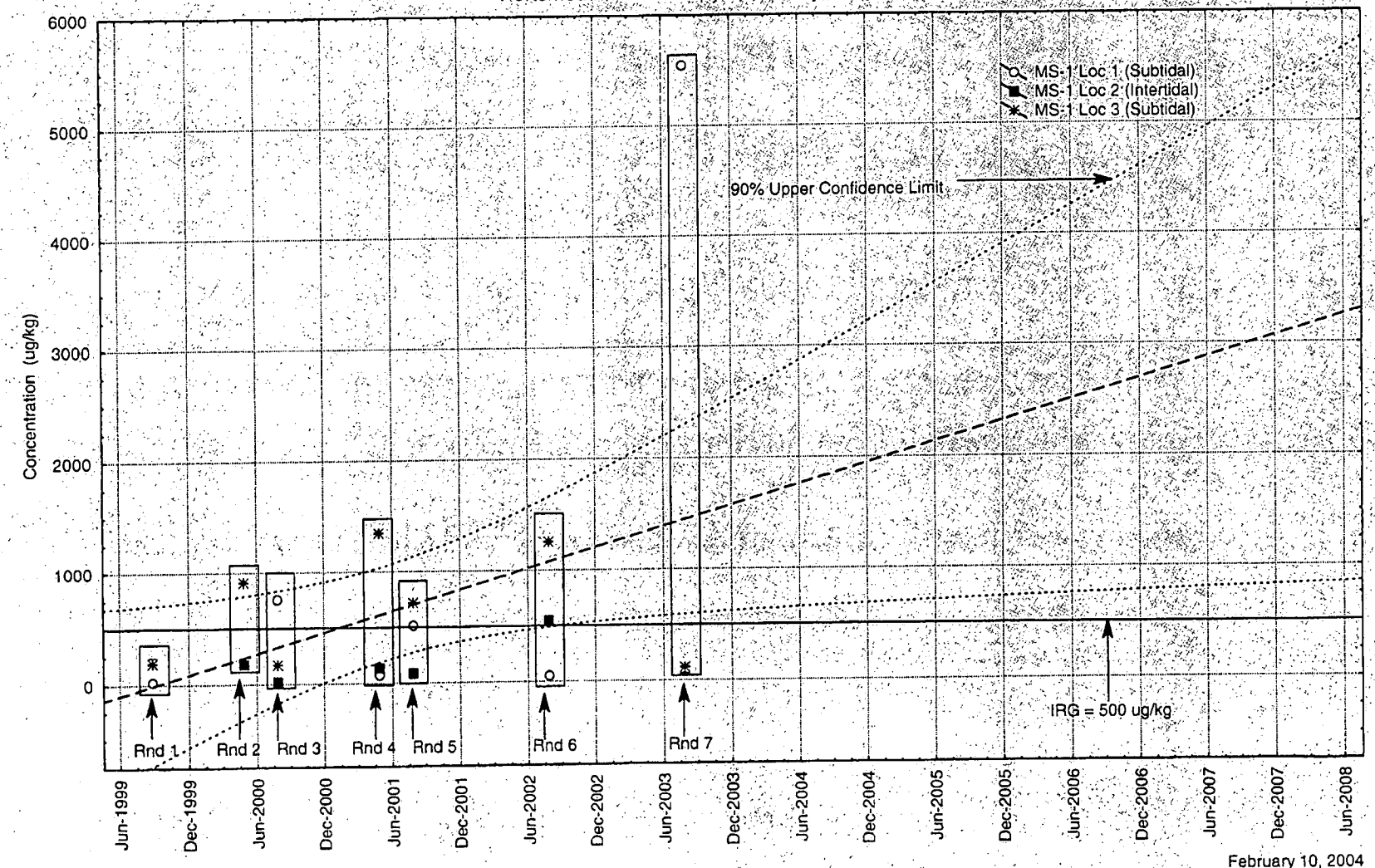
Monitoring Station 1 - Sediment
Acenaphthylene Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



February 10, 2004

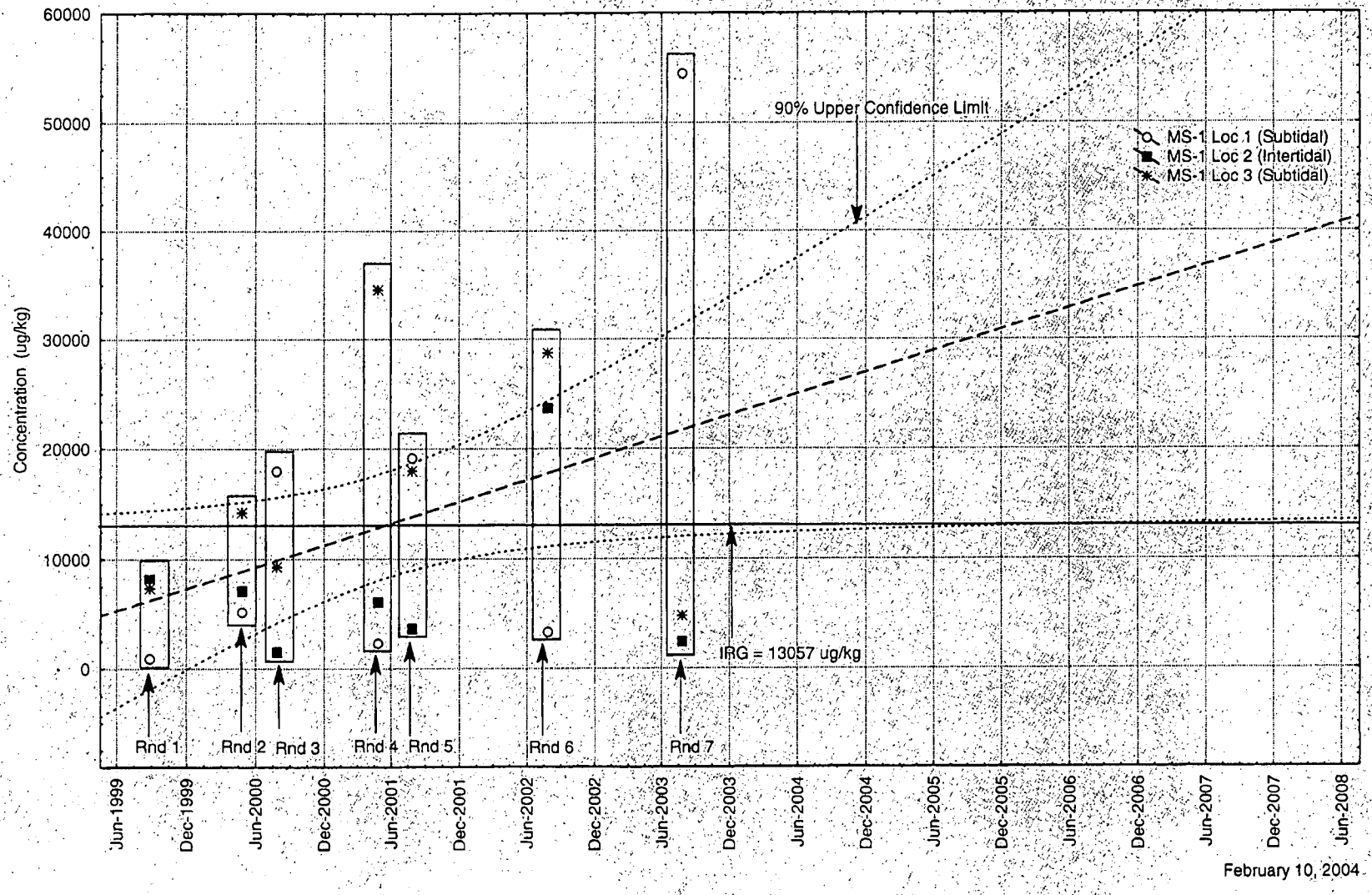

Monitoring Station 1 - Sediment
Anthracene Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine
Concentration (ug/kg)
10000
8000
6000
4000
2000
0
MS-1 Loc 1 (Subtidal)
MS-1 Loc 2 (Intertidal)
MS-1 Loc 3 (Subtidal)
90% Upper Confidence Limit
IRG = 1236 ug/kg
Rnd 1
Rnd 2
Rnd 3
Rnd 4
Rnd 5
Rnd 6
Rnd 7
Jun-1999
Dec-1999
Jun-2000
Dec-2000
Jun-2001
Dec-2001
Jun-2002
Dec-2002
Jun-2003
Dec-2003
Jun-2004
Dec-2004
Jun-2005
Dec-2005
Jun-2006
Dec-2006
Jun-2007
Dec-2007
Jun-2008
February 10, 2004

Monitoring Station 1 - Sediment
Fluorene Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine

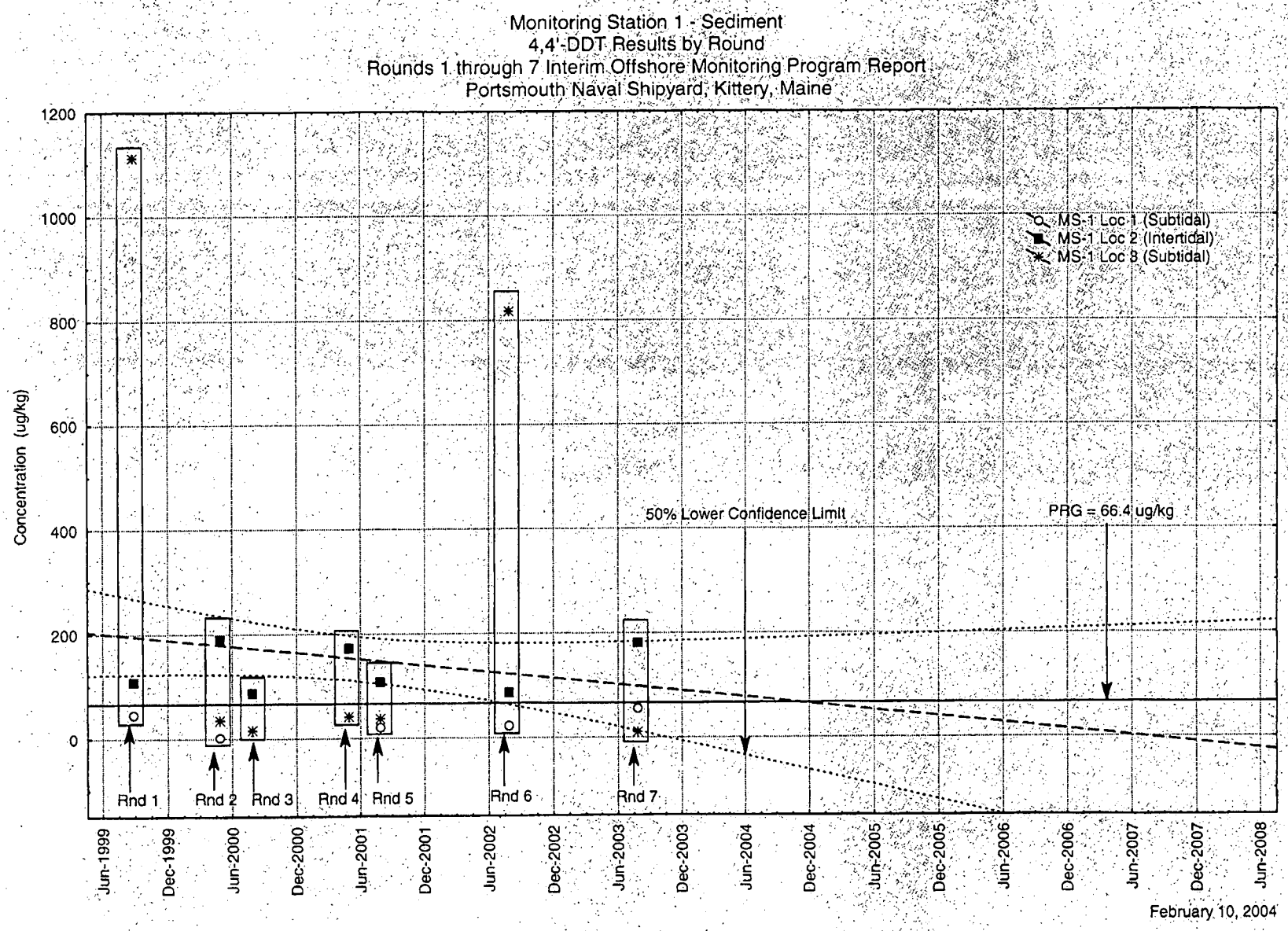


February 10, 2004

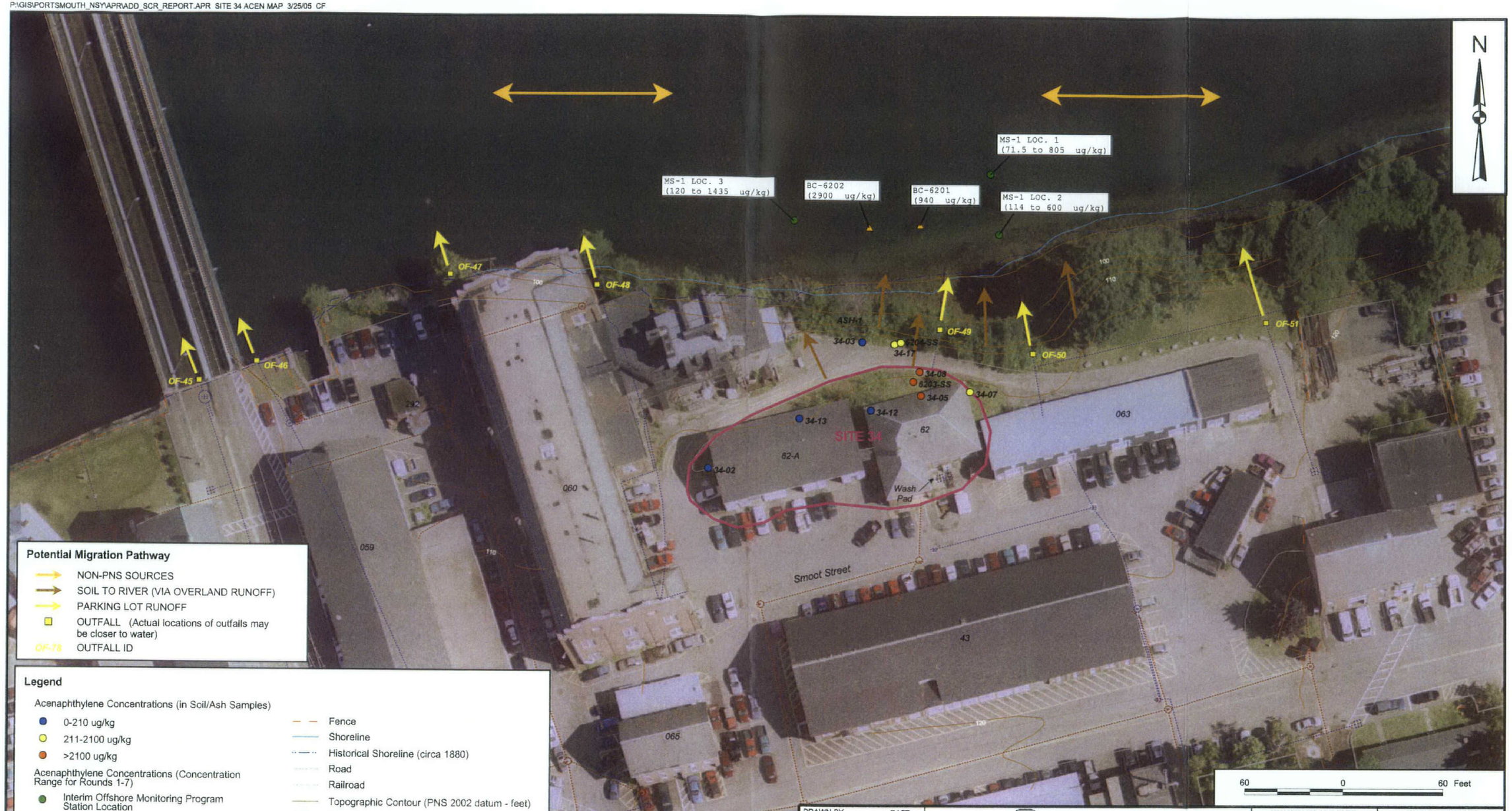
Monitoring Station 1 - Sediment
High Molecular Weight PAH Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



February 10, 2004


Monitoring Station 1 - Sediment
4,4'-DDT Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine
Concentration (ug/kg)
1200
1000
800
600
400
200
0
MS-1 Loc 1 (Subtidal)
MS-1 Loc 2 (Intertidal)
MS-1 Loc 3 (Subtidal)
50% Lower Confidence Limit
PRG = 66.4 ug/kg
Rnd 1
Rnd 2
Rnd 3
Rnd 4
Rnd 5
Rnd 6
Rnd 7
Jun-1999
Dec-1999
Jun-2000
Dec-2000
Jun-2001
Dec-2001
Jun-2002
Dec-2002
Jun-2003
Dec-2003
Jun-2004
Dec-2004
Jun-2005
Dec-2005
Jun-2006
Dec-2006
Jun-2007
Dec-2007
Jun-2008
February 10, 2004

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR SITE 34 ACEN MAP 3/25/05 CF



Potential Migration Pathway

- NON-PNS SOURCES
- SOIL TO RIVER (VIA OVERLAND RUNOFF)
- PARKING LOT RUNOFF
- OUTFALL (Actual locations of outfalls may be closer to water)
- OF-78 OUTFALL ID

Legend

Acenaphthylene Concentrations (in Soil/Ash Samples)

- 0-210 ug/kg
- 211-2100 ug/kg
- >2100 ug/kg

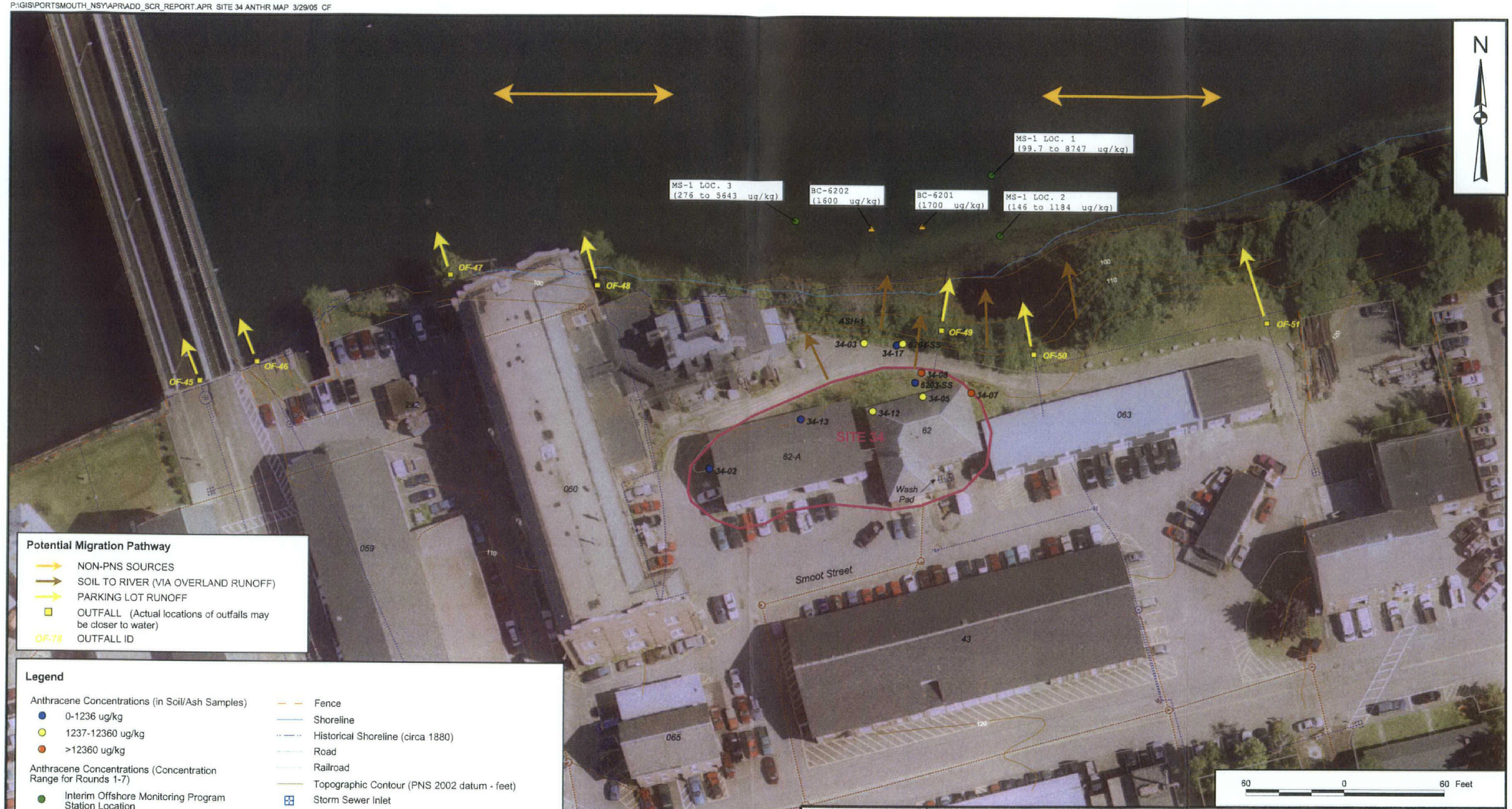
Acenaphthylene Concentrations (Concentration Range for Rounds 1-7)

- Interim Offshore Monitoring Program Station Location
- Sediment Sample Location
- Approximate Site Boundary
- Former Building/Tank
- Fence
- Shoreline
- Historical Shoreline (circa 1880)
- Road
- Railroad
- Topographic Contour (PNS 2002 datum - feet)
- Storm Sewer Inlet
- Utility Drain
- Sewer Utility

Note: This figure only presents the results of the soil samples collected in vegetated areas; soil samples collected under asphalt are not shown on this figure.

DRAWN BY C. FOSTER	DATE 1/18/05	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
CHECKED BY A. BERNHARDT	DATE 3/29/05	ACENAPHTHYLENE CONCENTRATIONS IN SOIL AND SEDIMENT AT MS-01 AND SITE 34 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY —	DATE —
COST/SCHEDULE-AREA			APPROVED BY —	DATE —
SCALE AS NOTED			DRAWING NO. FIGURE A - 1	REV 0

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR SITE 34 ANTHR MAP 3/29/05 CF



Potential Migration Pathway

- NON-PNS SOURCES
- SOIL TO RIVER (VIA OVERLAND RUNOFF)
- PARKING LOT RUNOFF
- OUTFALL (Actual locations of outfalls may be closer to water)
- OF-78 OUTFALL ID

Legend

Anthracene Concentrations (in Soil/Ash Samples)
- 0-1236 ug/kg
- 1237-12360 ug/kg
- >12360 ug/kg

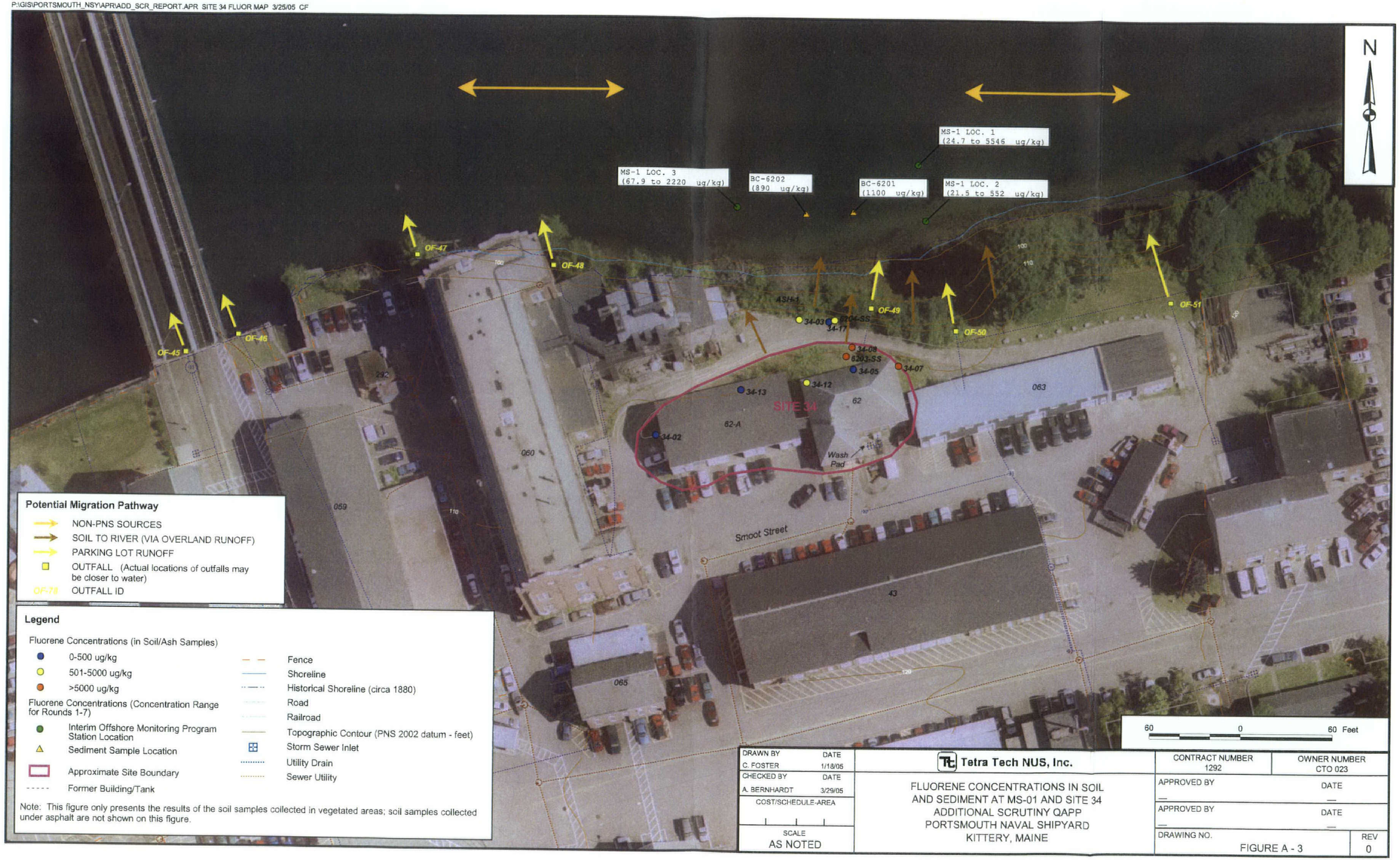
Anthracene Concentrations (Concentration Range for Rounds 1-7)
- Interim Offshore Monitoring Program Station Location
- Sediment Sample Location
- Approximate Site Boundary
- Former Building/Tank

- Fence
- Shoreline
- Historical Shoreline (circa 1880)
- Road
- Railroad
- Topographic Contour (PNS 2002 datum - feet)
- Storm Sewer Inlet
- Utility Drain
- Sewer Utility

Note: This figure only presents the results of the soil samples collected in vegetated areas; soil samples collected under asphalt are not shown on this figure.

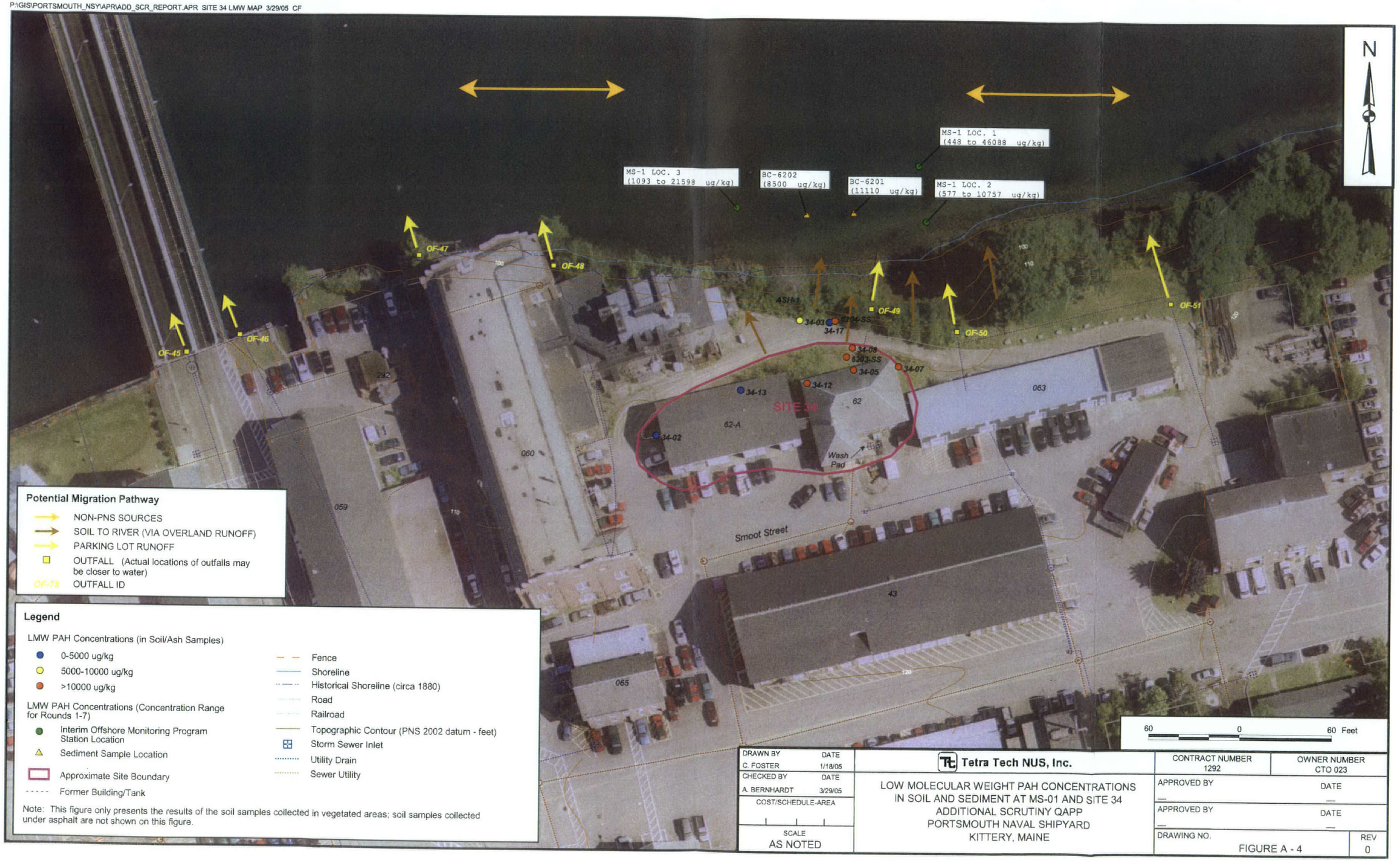
DRAWN BY C. FOSTER	DATE 1/18/05	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
CHECKED BY A. BERNHARDT	DATE 3/29/05	ANTHRACENE CONCENTRATIONS IN SOIL AND SEDIMENT AT MS-01 AND SITE 34 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY —	DATE —
COST/SCHEDULE-AREA			APPROVED BY —	DATE —
SCALE AS NOTED			DRAWING NO. FIGURE A - 2	REV 0

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR SITE 34 FLUOR MAP 3/25/05 CF



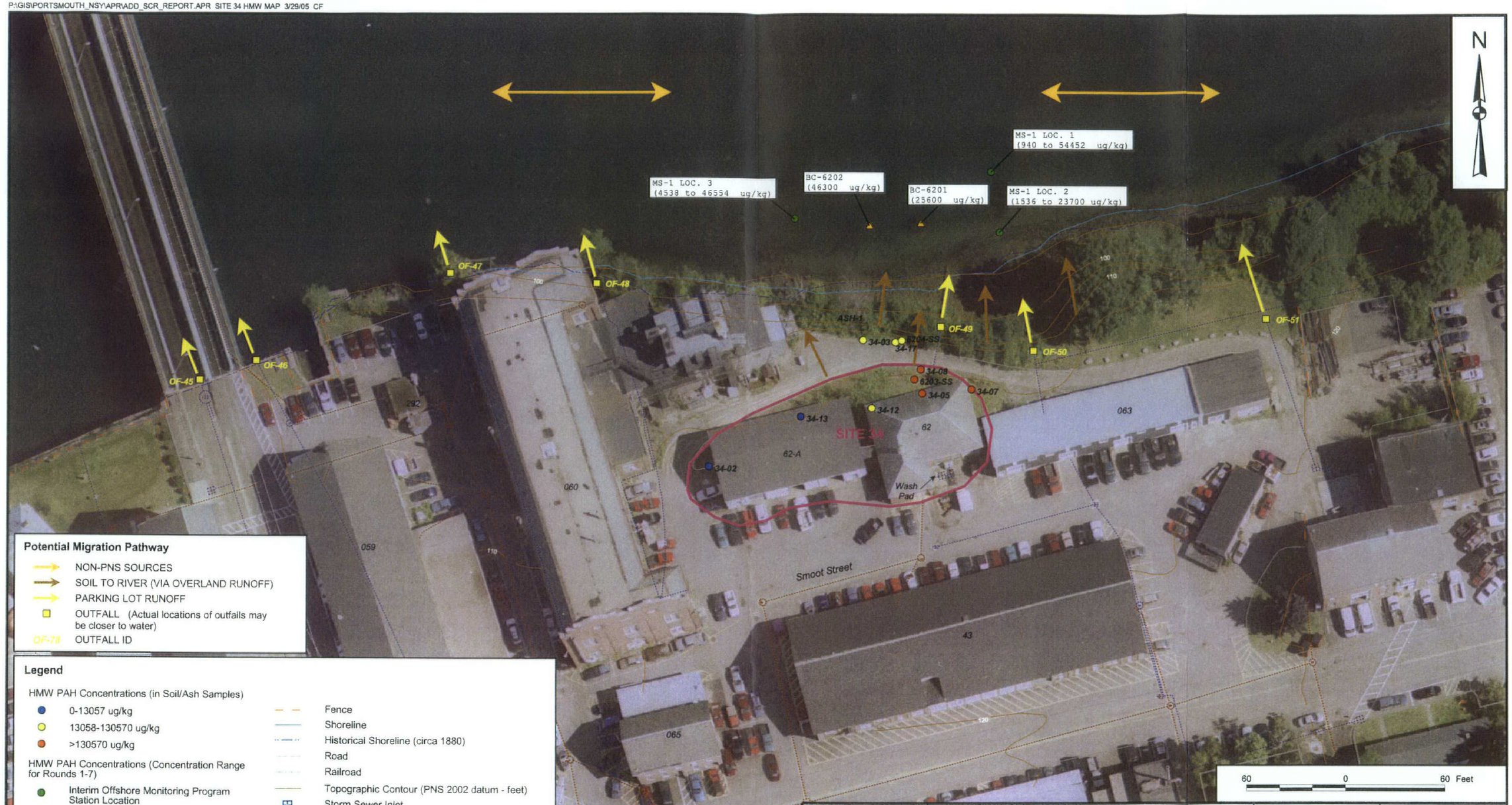
DRAWN BY C. FOSTER	DATE 1/18/05	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292 / OWNER NUMBER CTO 023
CHECKED BY A. BERNHARDT	DATE 3/29/05	FLUORENE CONCENTRATIONS IN SOIL AND SEDIMENT AT MS-01 AND SITE 34 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY — / DATE —
COST/SCHEDULE-AREA			APPROVED BY — / DATE —
SCALE AS NOTED			DRAWING NO. FIGURE A - 3 / REV 0

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR SITE 34 LMW MAP 3/29/05 CF



DRAWN BY C. FOSTER	DATE 1/18/05	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292 / OWNER NUMBER CTO 023
CHECKED BY A. BERNHARDT	DATE 3/29/05	LOW MOLECULAR WEIGHT PAH CONCENTRATIONS IN SOIL AND SEDIMENT AT MS-01 AND SITE 34 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY — DATE —
COST/SCHEDULE-AREA			APPROVED BY — DATE —
SCALE AS NOTED			DRAWING NO. FIGURE A - 4 / REV 0

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR SITE 34 HMW MAP 3/29/05 CF



Potential Migration Pathway

- NON-PNS SOURCES
- SOIL TO RIVER (VIA OVERLAND RUNOFF)
- PARKING LOT RUNOFF
- OUTFALL (Actual locations of outfalls may be closer to water)
- OF-78 OUTFALL ID

Legend

HMW PAH Concentrations (in Soil/Ash Samples)

- 0-13057 ug/kg
- 13058-130570 ug/kg
- >130570 ug/kg

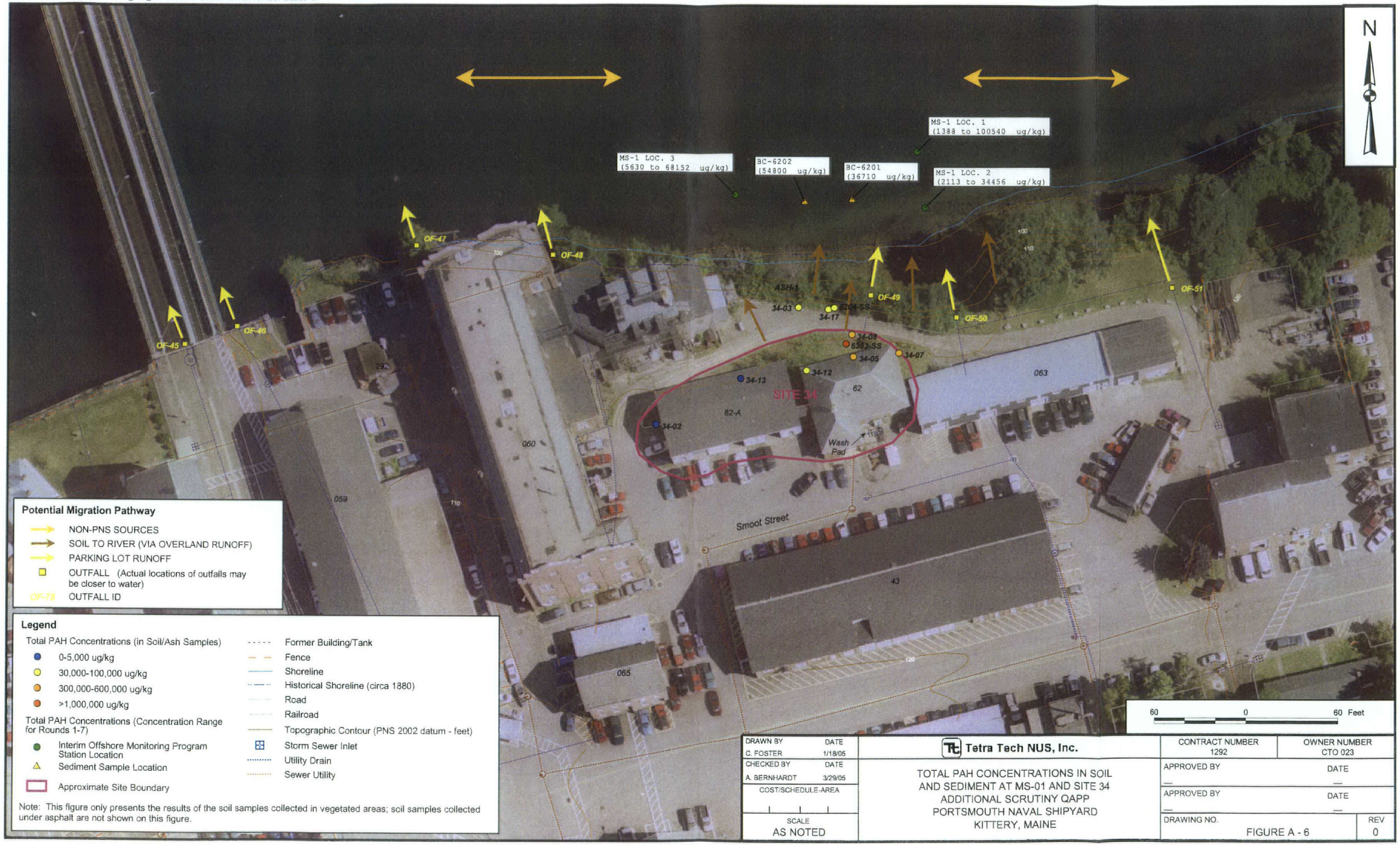
HMW PAH Concentrations (Concentration Range for Rounds 1-7)

- Interim Offshore Monitoring Program Station Location
- Sediment Sample Location
- Approximate Site Boundary
- Former Building/Tank
- Fence
- Shoreline
- Historical Shoreline (circa 1880)
- Road
- Railroad
- Topographic Contour (PNS 2002 datum - feet)
- Storm Sewer Inlet
- Utility Drain
- Sewer Utility

Note: This figure only presents the results of the soil samples collected in vegetated areas; soil samples collected under asphalt are not shown on this figure.

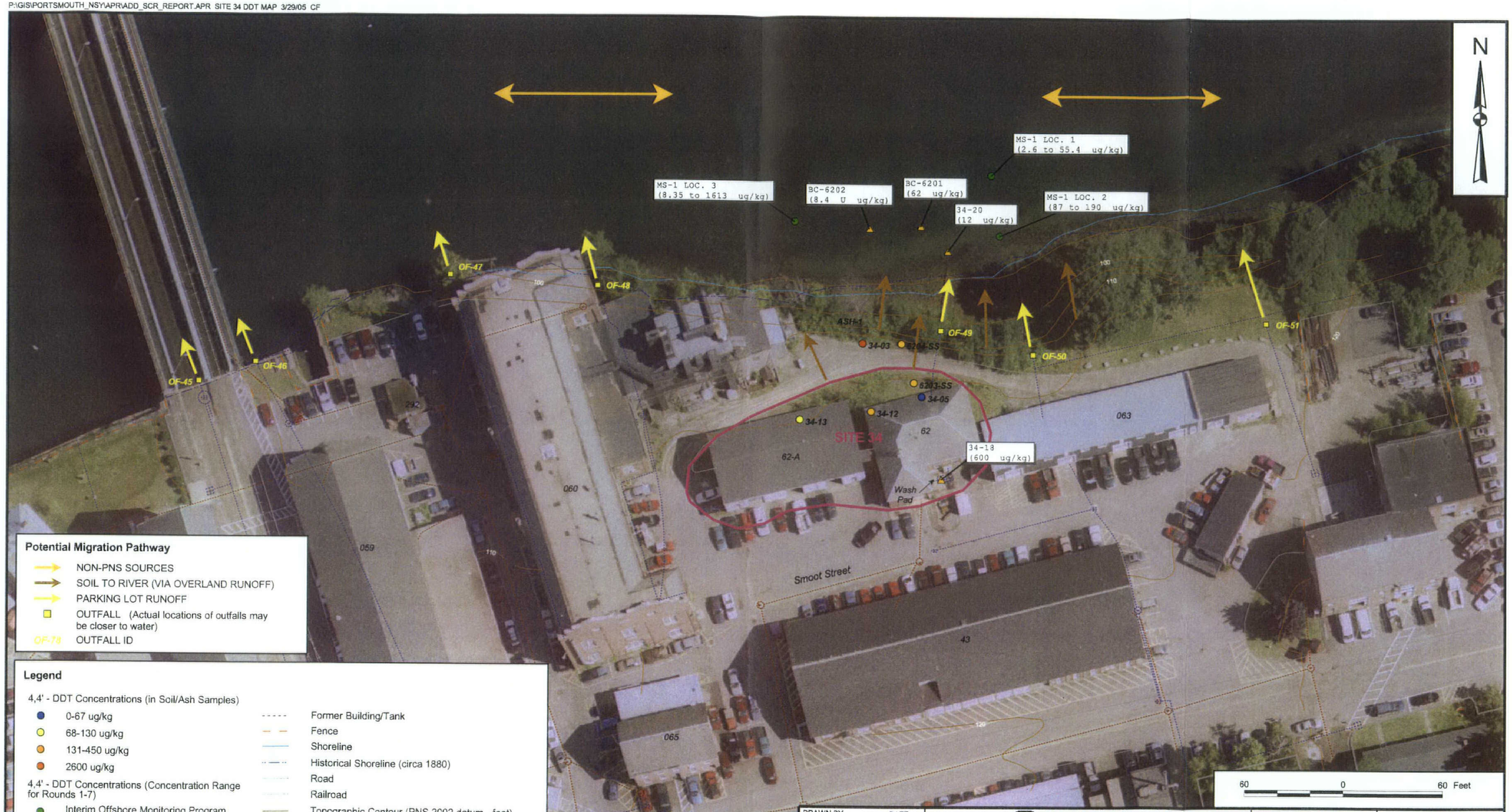
DRAWN BY C. FOSTER DATE 1/18/05	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
CHECKED BY A. BERNHARDT DATE 3/29/05	HIGH MOLECULAR WEIGHT PAH CONCENTRATIONS IN SOIL AND SEDIMENT AT MS-01 AND SITE 34 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY — DATE —	
COST/SCHEDULE-AREA		APPROVED BY — DATE —	
SCALE AS NOTED		DRAWING NO. FIGURE A - 5	REV 0

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR SITE 34 TOTAL PAH MAP 3/29/05 CF



DRAWN BY	DATE	Tetra Tech NUS, Inc.	CONTRACT NUMBER	OWNER NUMBER
C. FOSTER	1/18/05		1292	CTO 023
CHECKED BY	DATE	TOTAL PAH CONCENTRATIONS IN SOIL AND SEDIMENT AT MS-01 AND SITE 34 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY	DATE
A. BERNHARDT	3/29/05		—	—
COST/SCHEDULE-AREA			APPROVED BY	DATE
			—	—
SCALE			DRAWING NO.	REV
AS NOTED			FIGURE A - 6	0

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR SITE 34 DDT MAP 3/29/05 CF



Potential Migration Pathway

- NON-PNS SOURCES
- SOIL TO RIVER (VIA OVERLAND RUNOFF)
- PARKING LOT RUNOFF
- OUTFALL (Actual locations of outfalls may be closer to water)
- OF-78 OUTFALL ID

Legend

4,4' - DDT Concentrations (in Soil/Ash Samples)

- 0-67 ug/kg
- 68-130 ug/kg
- 131-450 ug/kg
- 2600 ug/kg

4,4' - DDT Concentrations (Concentration Range for Rounds 1-7)

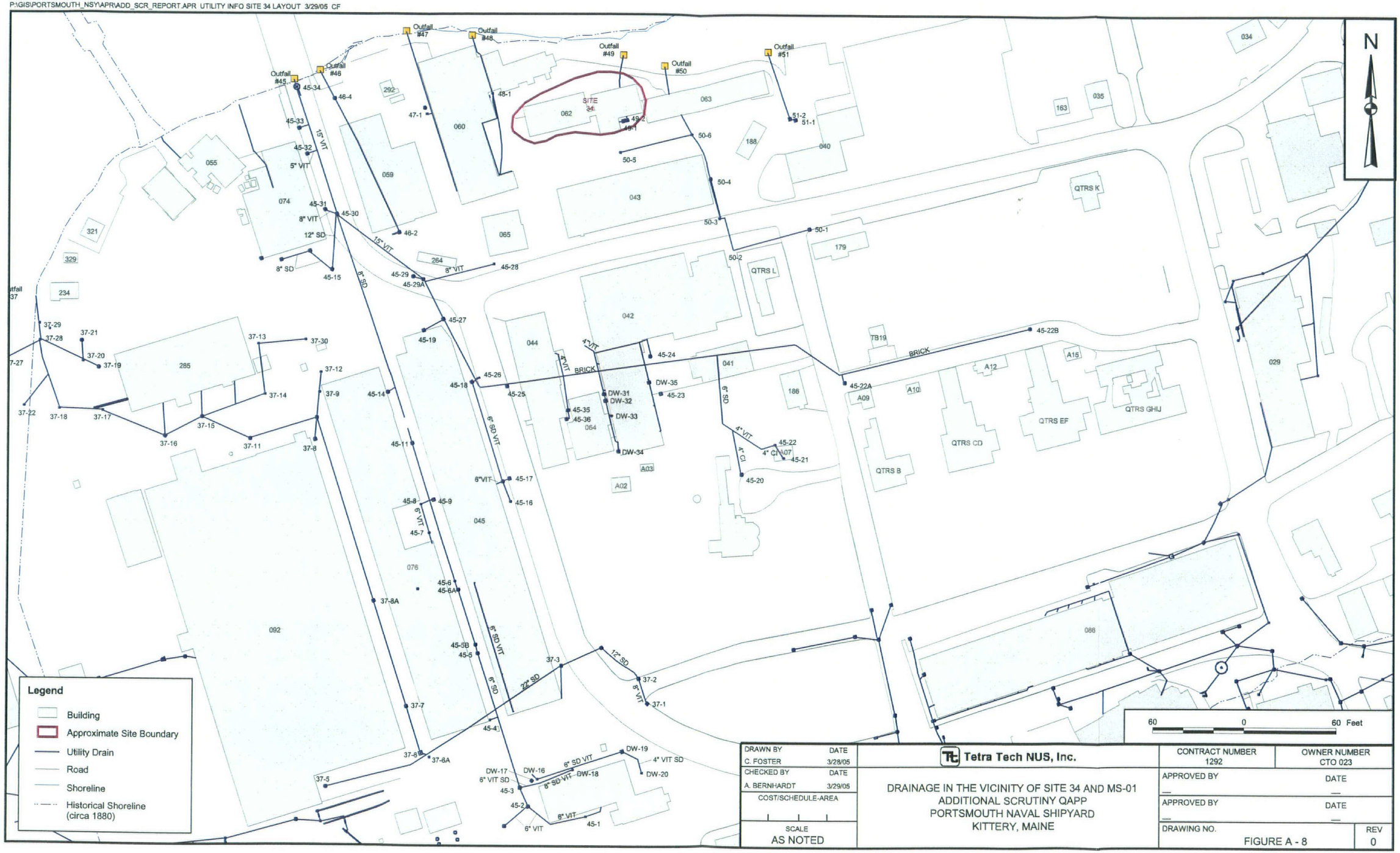
- Interim Offshore Monitoring Program Station Location
- Sediment Sample Location
- Approximate Site Boundary

- Former Building/Tank
- Fence
- Shoreline
- Historical Shoreline (circa 1880)
- Road
- Railroad
- Topographic Contour (PNS 2002 datum - feet)
- Storm Sewer Inlet
- Utility Drain
- Sewer Utility

Note: This figure only presents the results of the soil samples collected in vegetated areas; soil samples collected under asphalt are not shown on this figure.

DRAWN BY C. FOSTER	DATE 1/18/05	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
CHECKED BY A. BERNHARDT	DATE 3/29/05	4,4' - DDT CONCENTRATIONS IN SOIL AND SEDIMENT AT MS-01 AND SITE 34 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY —	DATE —
COST/SCHEDULE-AREA			APPROVED BY —	DATE —
SCALE AS NOTED			DRAWING NO. FIGURE A - 7	REV 0

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR UTILITY INFO SITE 34 LAYOUT 3/29/05 CF



DRAWN BY	DATE
C. FOSTER	3/28/05
CHECKED BY	DATE
A. BERNHARDT	3/29/05
COST/SCHEDULE-AREA	
SCALE	AS NOTED

Tetra Tech NUS, Inc.

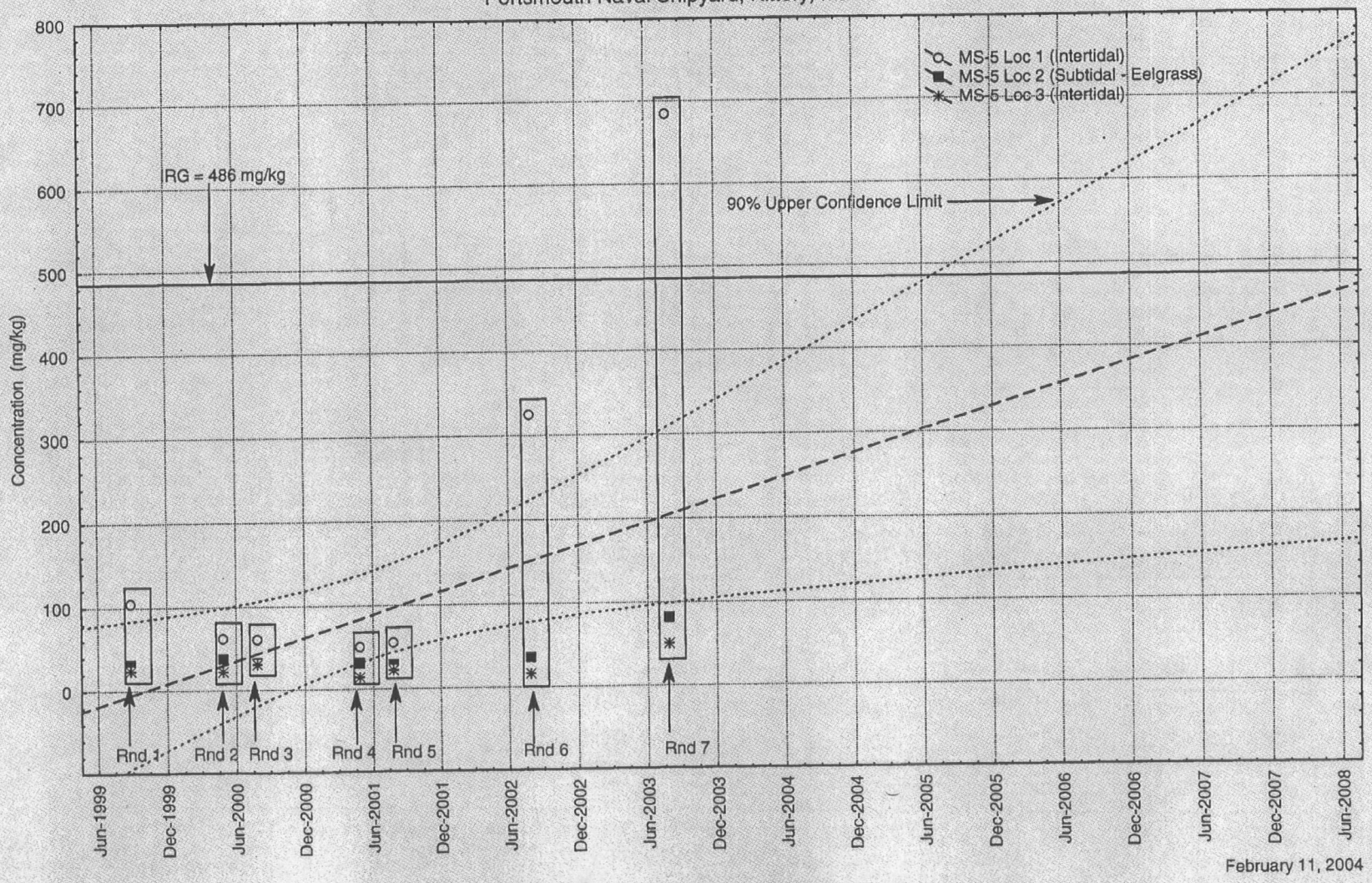
DRAINAGE IN THE VICINITY OF SITE 34 AND MS-01
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD
KITTERY, MAINE

CONTRACT NUMBER	OWNER NUMBER
1292	CTO 023
APPROVED BY	DATE
APPROVED BY	DATE
DRAWING NO. FIGURE A - 8	REV 0

APPENDIX A-2

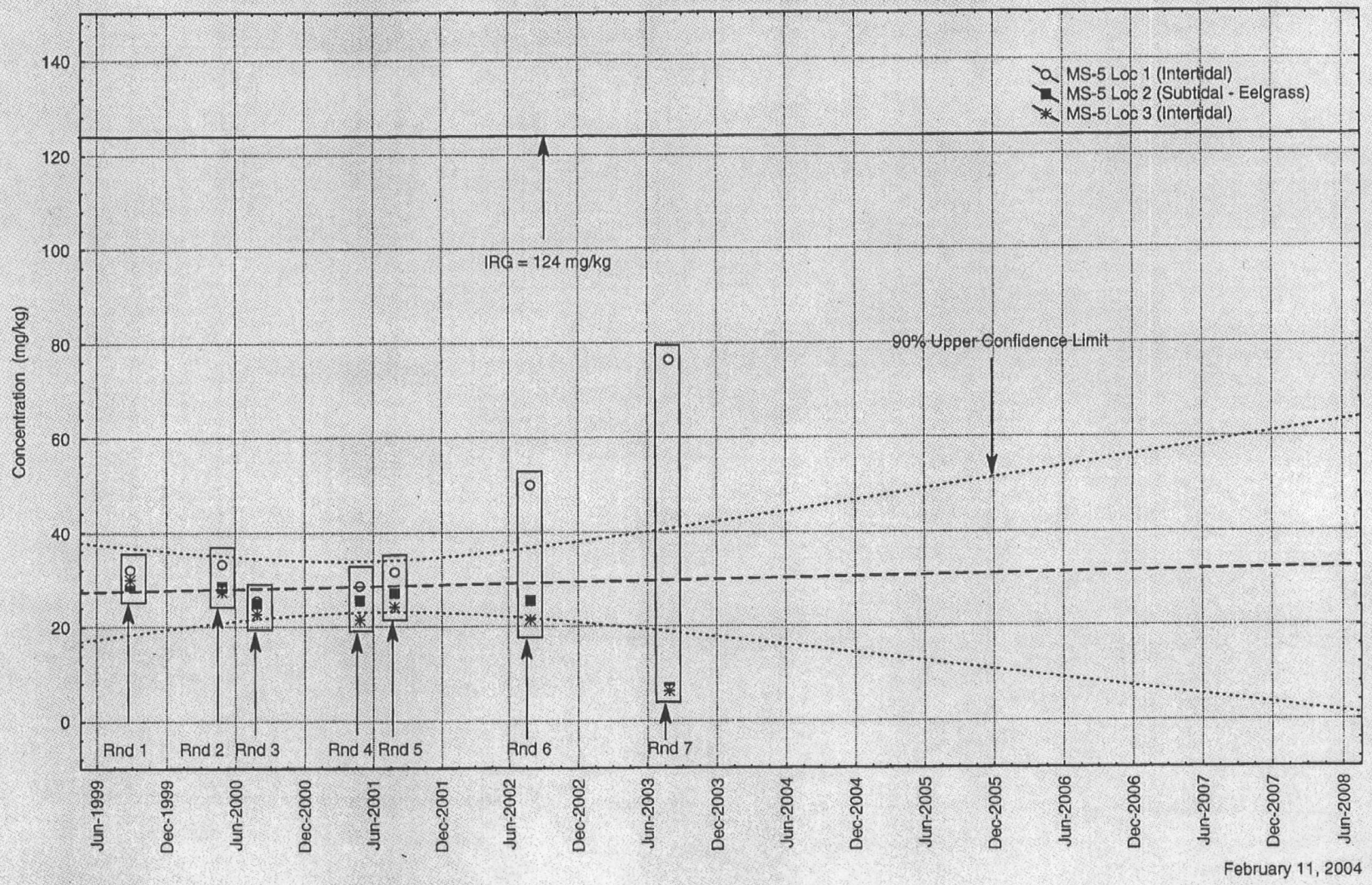
CONCENTRATION TREND PLOTS FOR MS-05 AND MS-09, PHOTOGRAPHS OF THE TURBIDITY CURTAINS, AND RECENT AERIAL PHOTOGRAPH

Monitoring Station 5 - Sediment
Copper Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



February 11, 2004

Monitoring Station 5 - Sediment
Nickel Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine

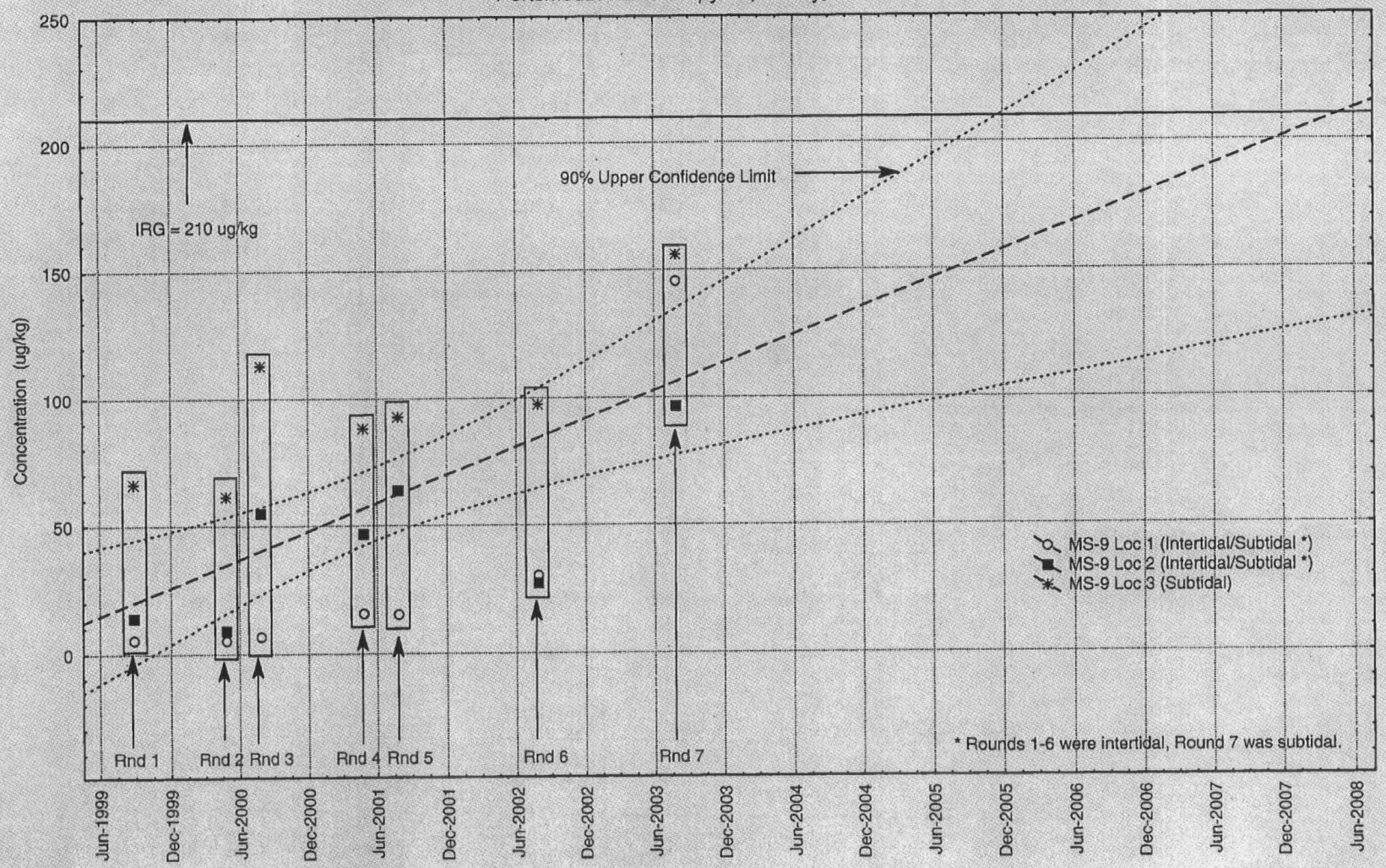


February 11, 2004

Monitoring Station 9 - Sediment
Acenaphthylene Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine

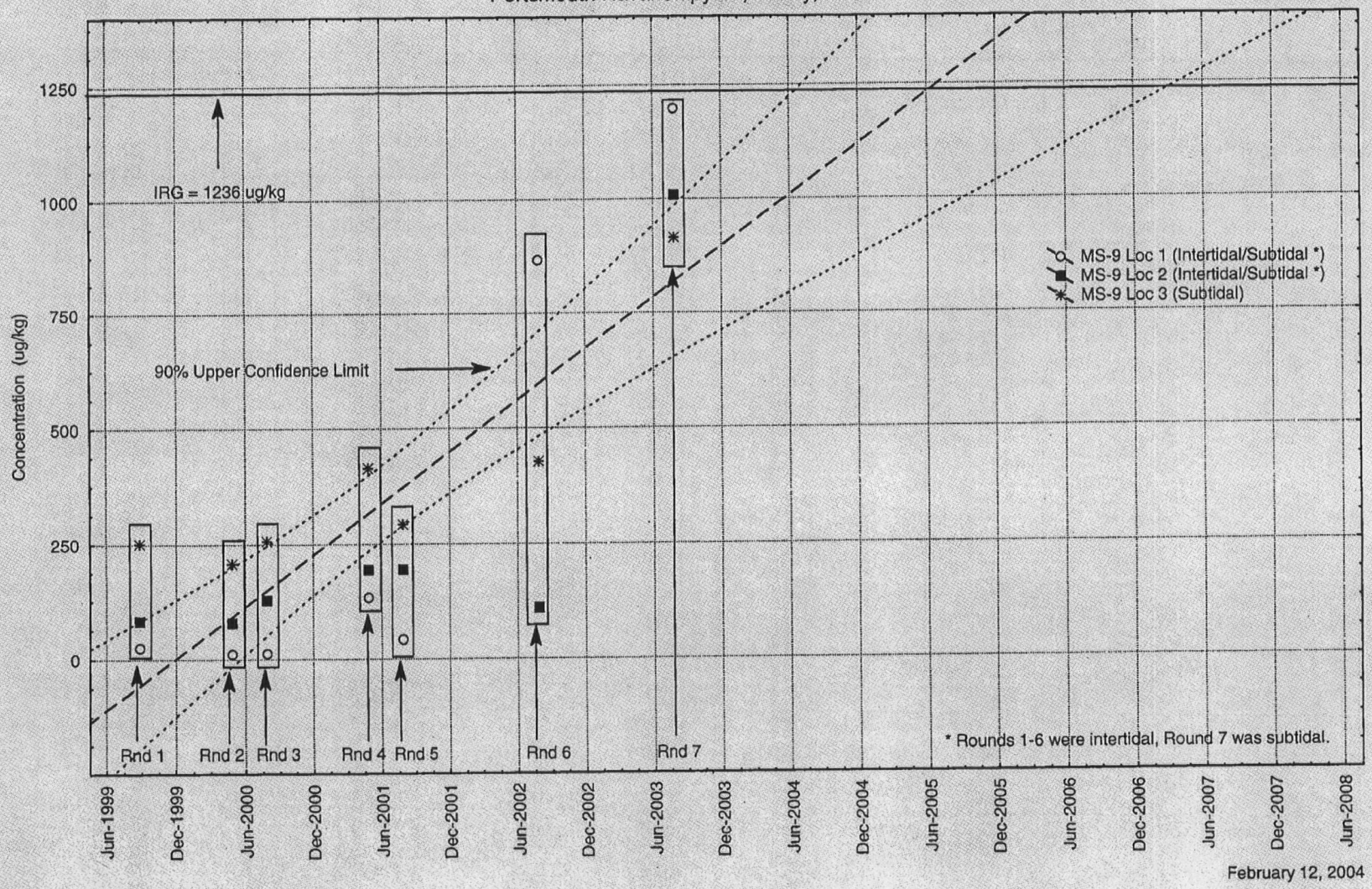
February 12, 2004

Monitoring Station 9 - Sediment
Acenaphthylene Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



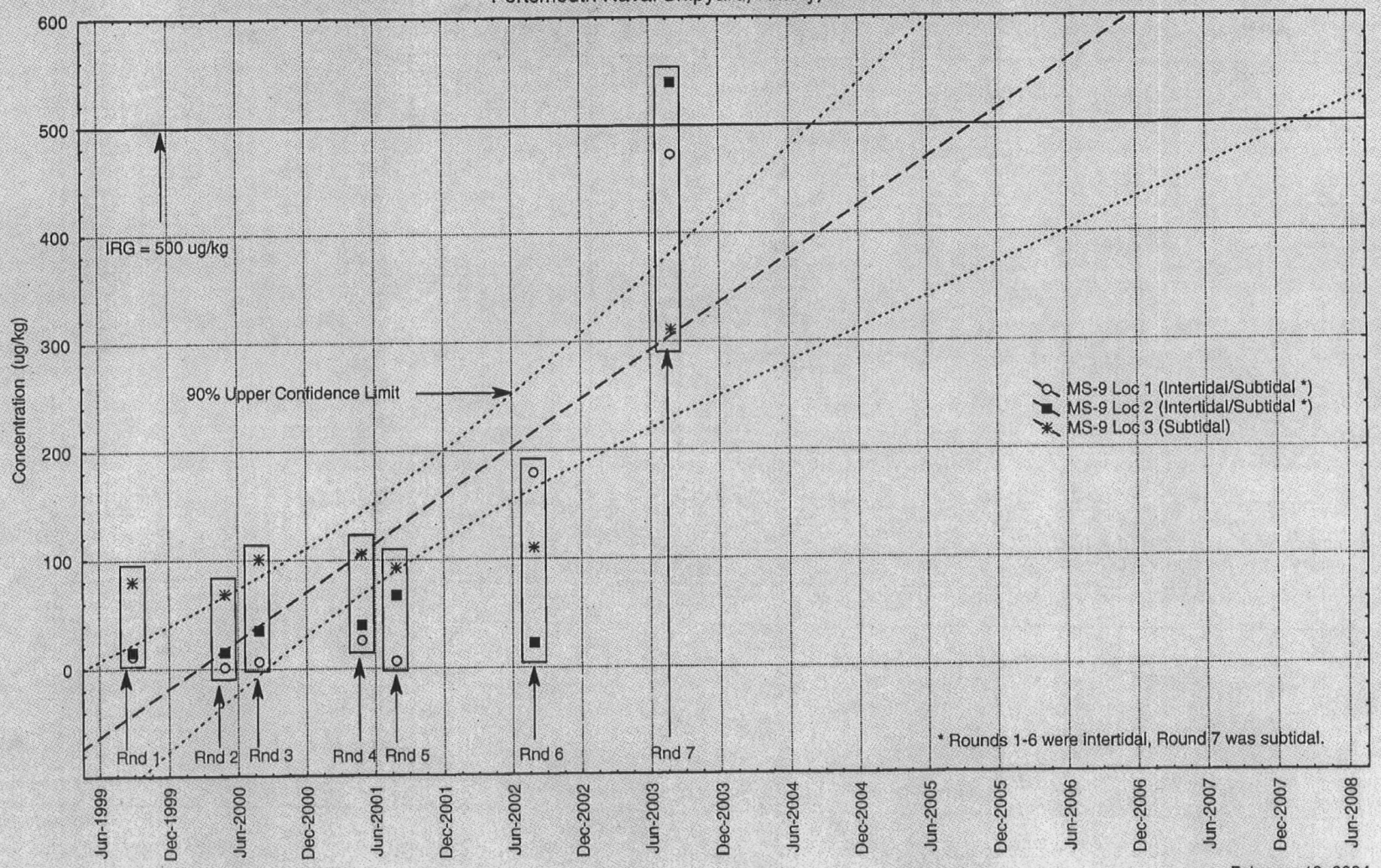
February 12, 2004

Monitoring Station 9 - Sediment
Anthracene Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



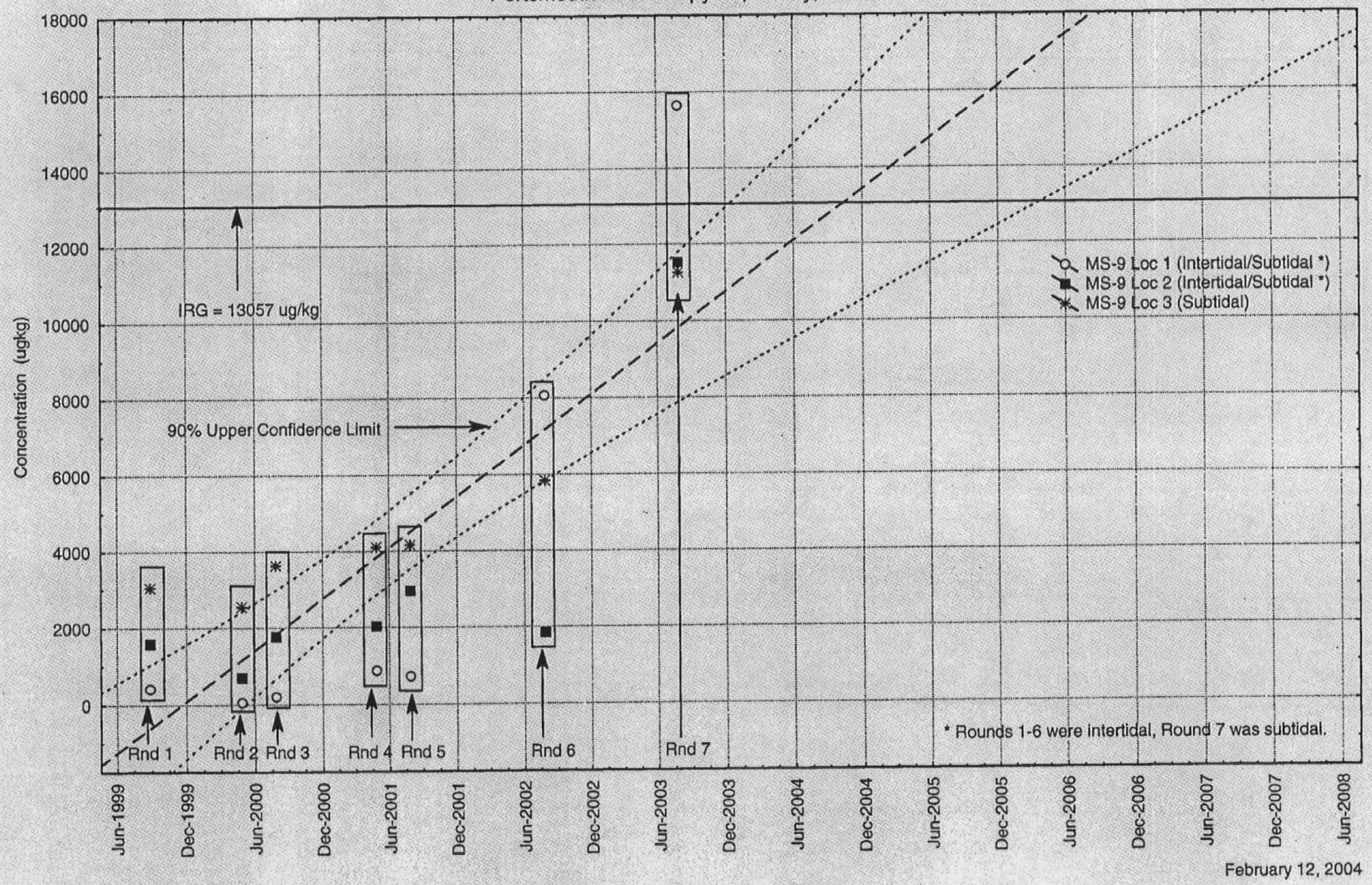
February 12, 2004

Monitoring Station 9 - Sediment
Fluorene Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



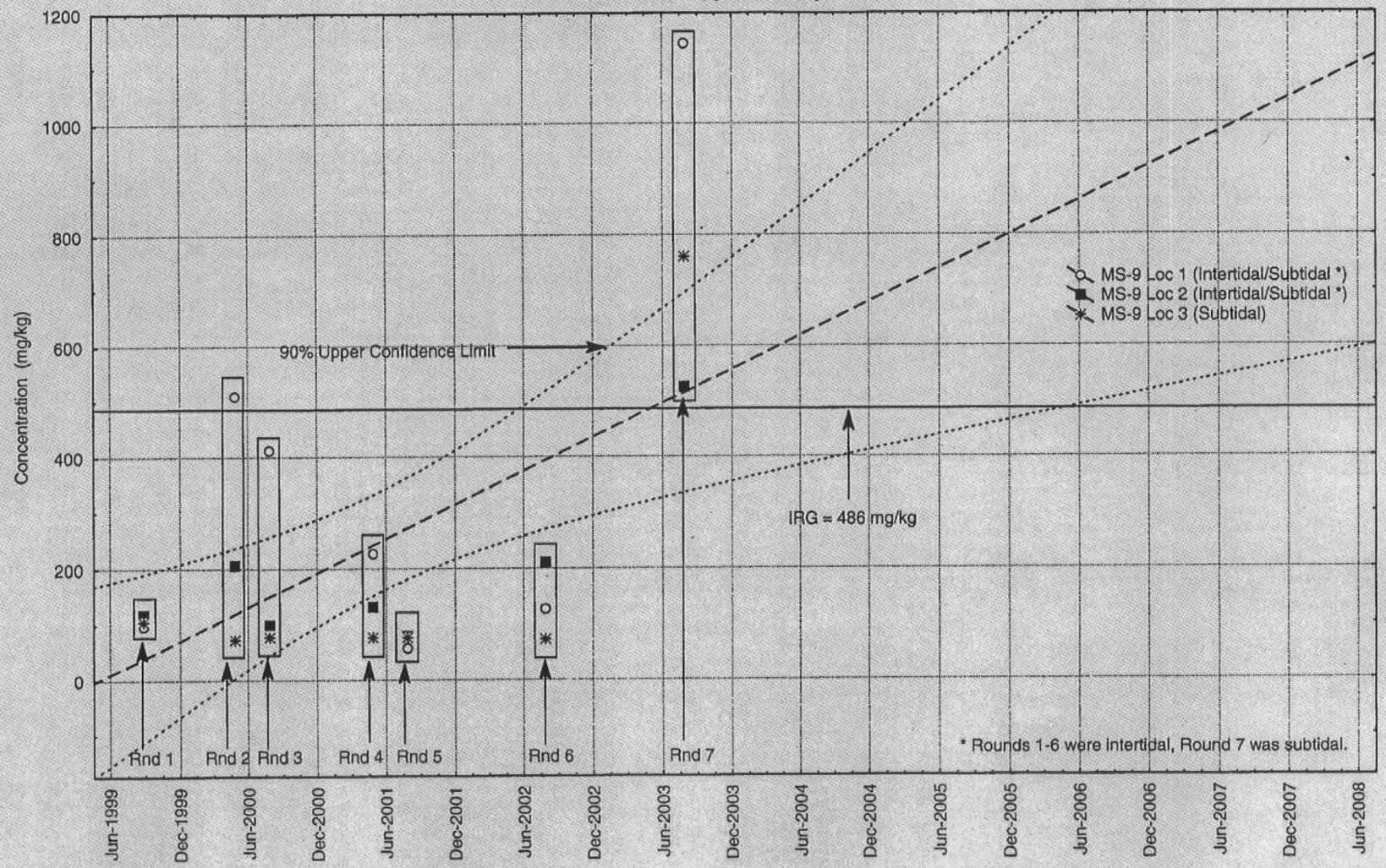
February 12, 2004

Monitoring Station 9 - Sediment
High Molecular Weight PAH Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



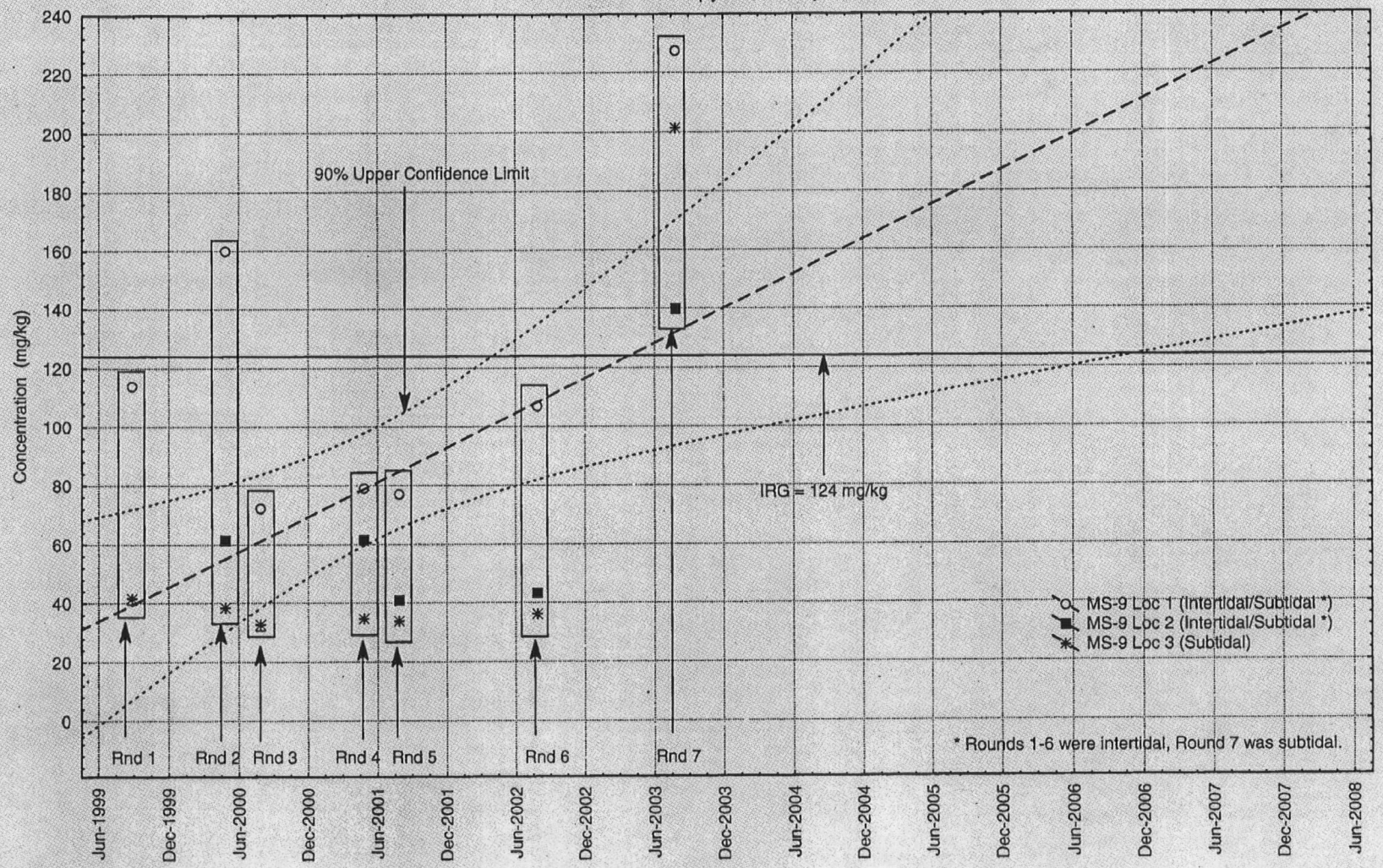
February 12, 2004

Monitoring Station 9 - Sediment
Copper Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



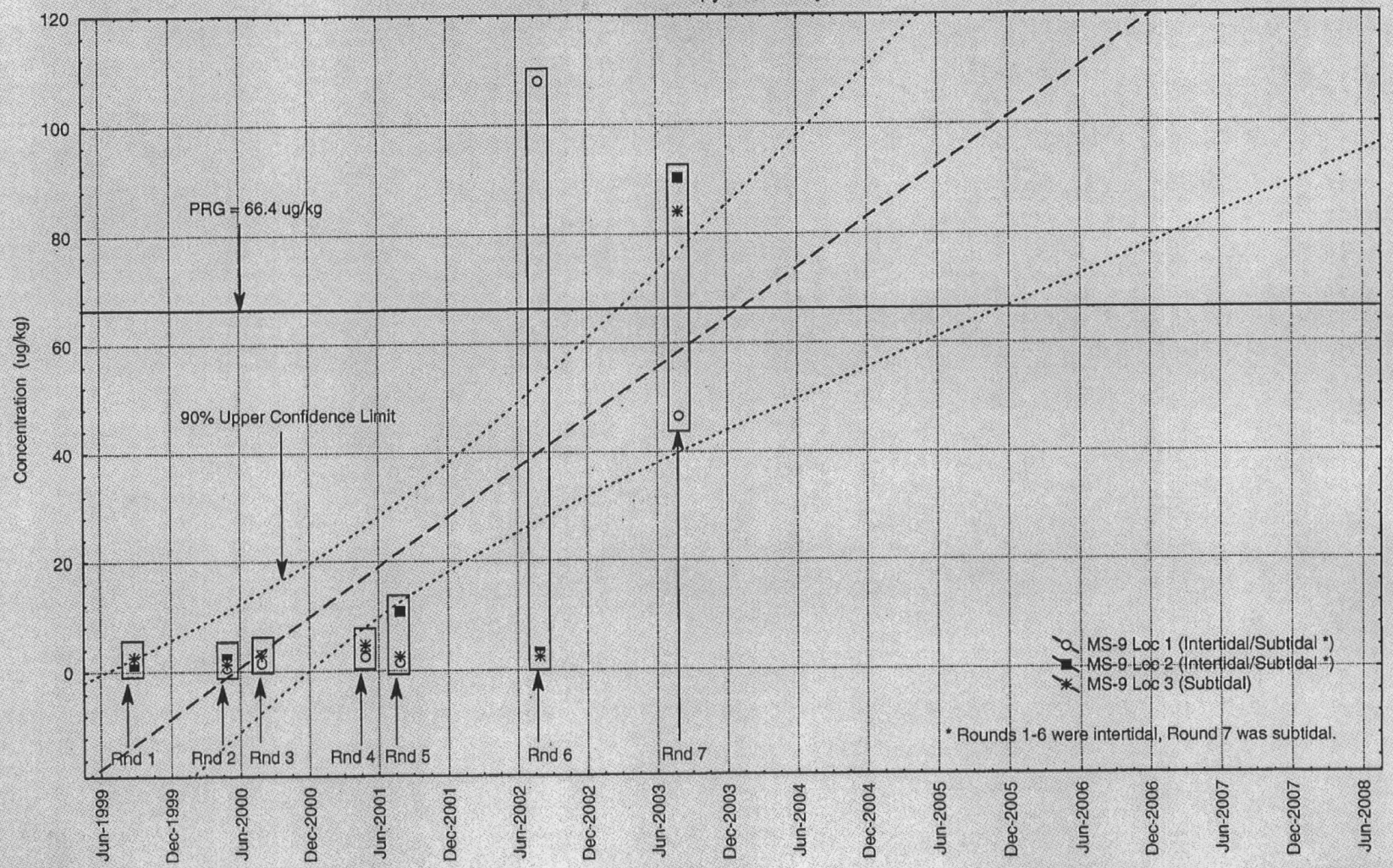
February 12, 2004

Monitoring Station 9 - Sediment
Nickel Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine

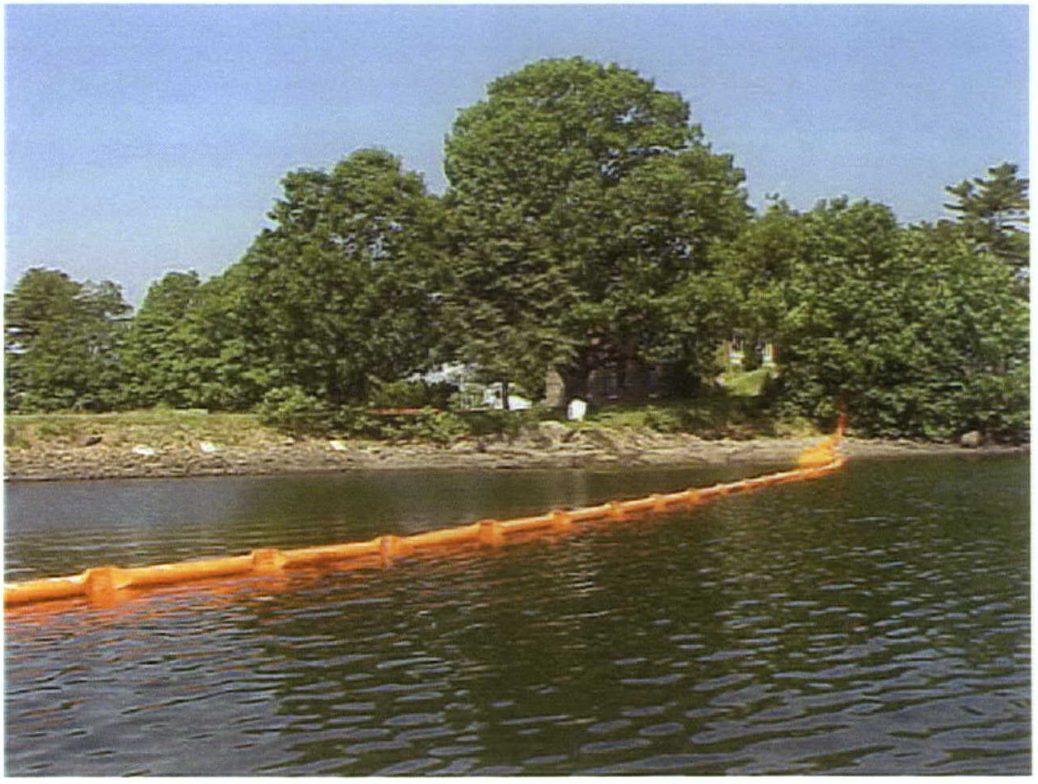


February 12, 2004

Monitoring Station 9 - Sediment
4,4'-DDT Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



February 12, 2004



PHOTOGRAPHS OF TURBIDITY CURTAIN IN JAMAICA COVE
DURING THE OU3 CONSTRUCTION ACTIVITIES
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

PHOTOGRAPH OF TURBIDITY CURTAIN IN CLARK COVE BY MS-09
DURING THE OU3 CONSTRUCTION ACTIVITIES
ADDITIONAL SCRUTINY QAPP
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

P:\GIS\PORTSMOUTH_NSY\APR\ADD_SCR_REPORT.APR AERIAL_SPRING2003 8/15/05 KMP

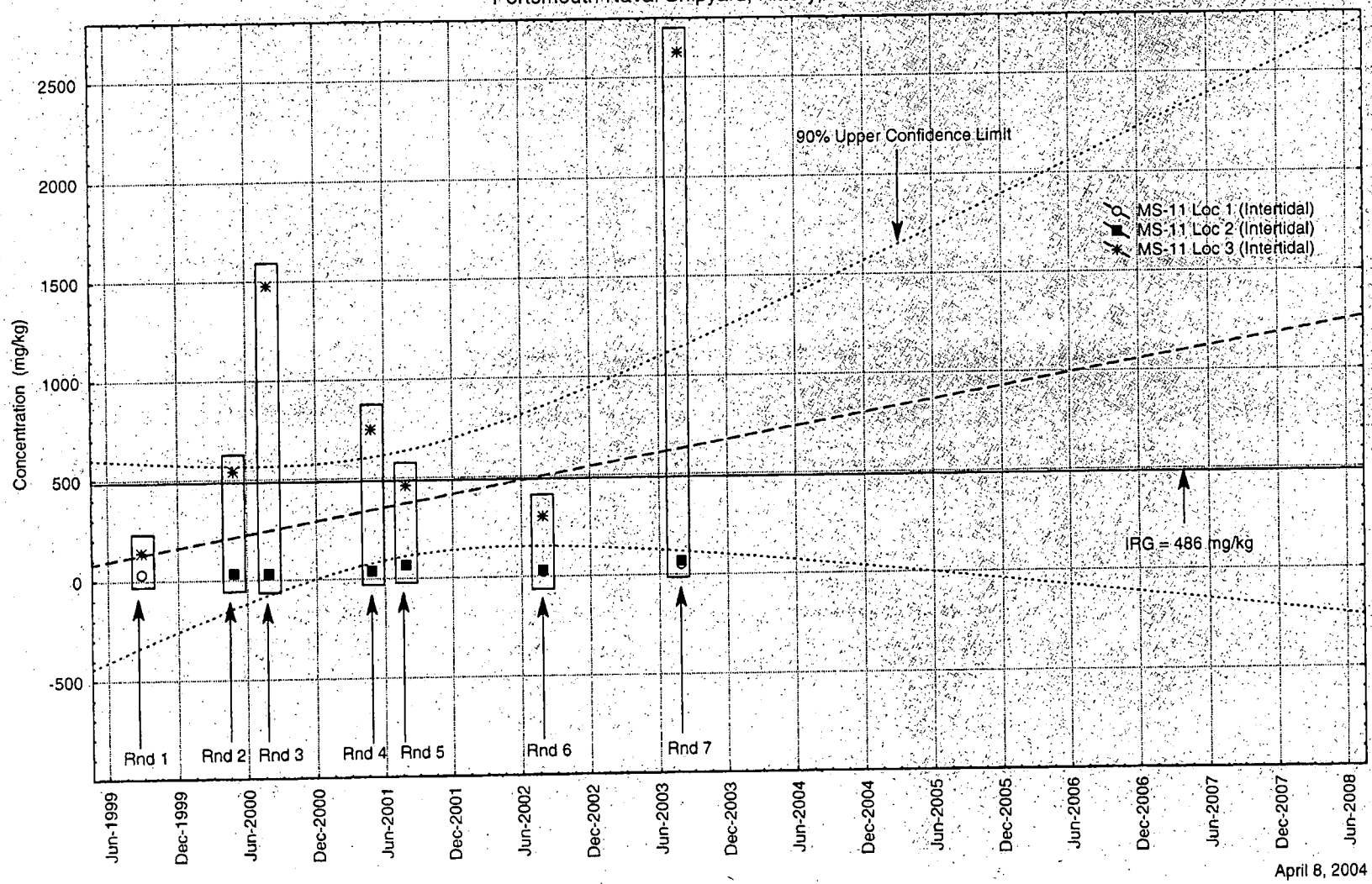
Aerial Photo Source:
Imagery is from the Maine Office of Geographic Information Systems, et. al.
Photo taken in Spring 2003.

DRAWN BY K. PEILA	DATE 8/15/05	Tetra Tech NUS, Inc.	CONTRACT NUMBER 1292	OWNER NUMBER CTO 023
CHECKED BY A. BERNHARDT	DATE 8/15/05	AERIAL PHOTOGRAPH OF PORTSMOUTH NAVAL SHIPYARD SPRING 2003 ADDITIONAL SCRUTINY QAPP PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY AMB	DATE 8-15-05
COST/SCHEDULE-AREA			APPROVED BY	DATE
SCALE AS NOTED			DRAWING NO.	REV 0

APPENDIX A-3

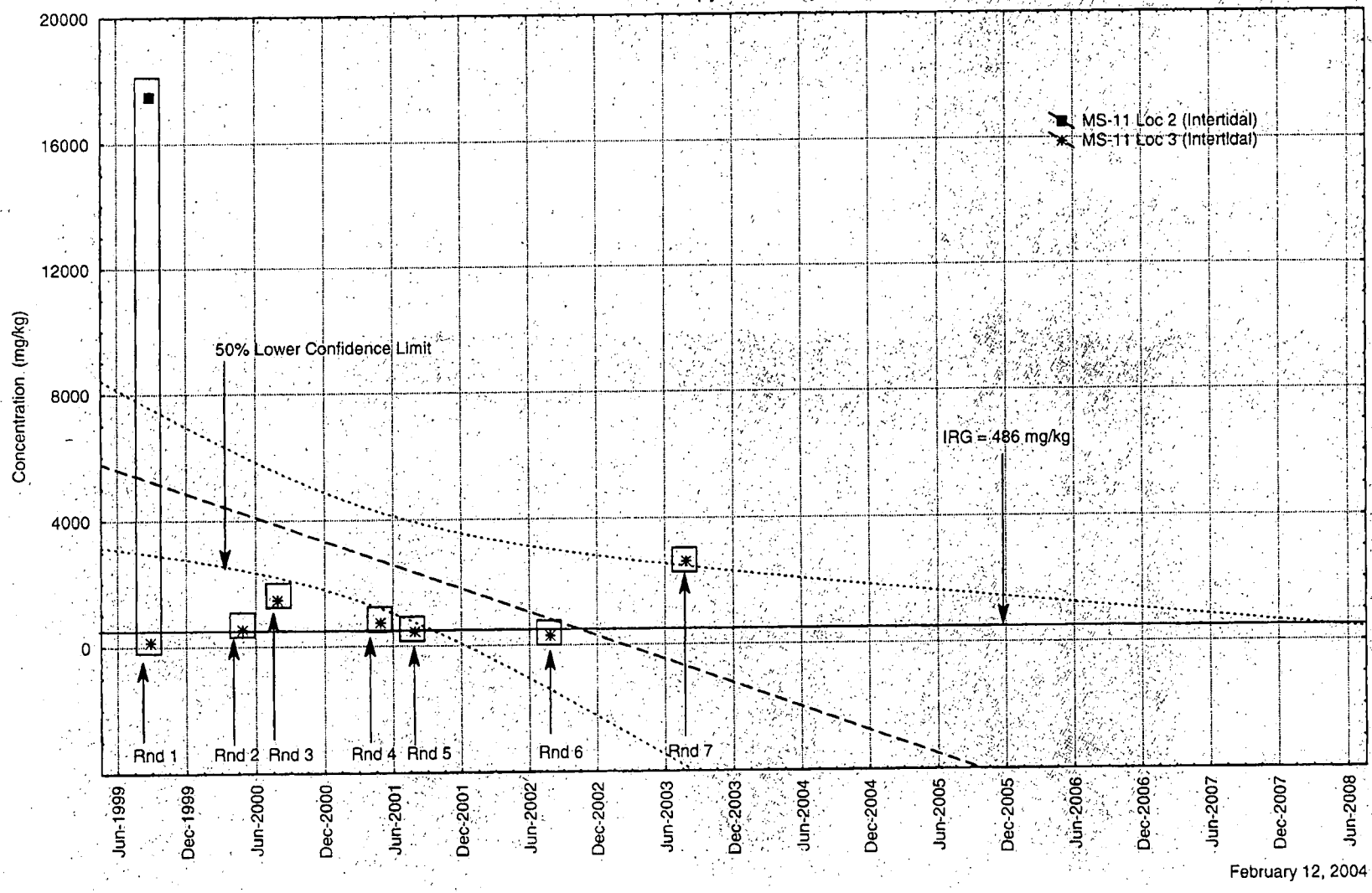
CONCENTRATION TREND PLOTS FOR MS-11 AND SHORELINE EVALUATION MEMORANDUM

Monitoring Station 11 - Sediment
Copper Results by Round All Locations (Locs 1 and 2 calculated)
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



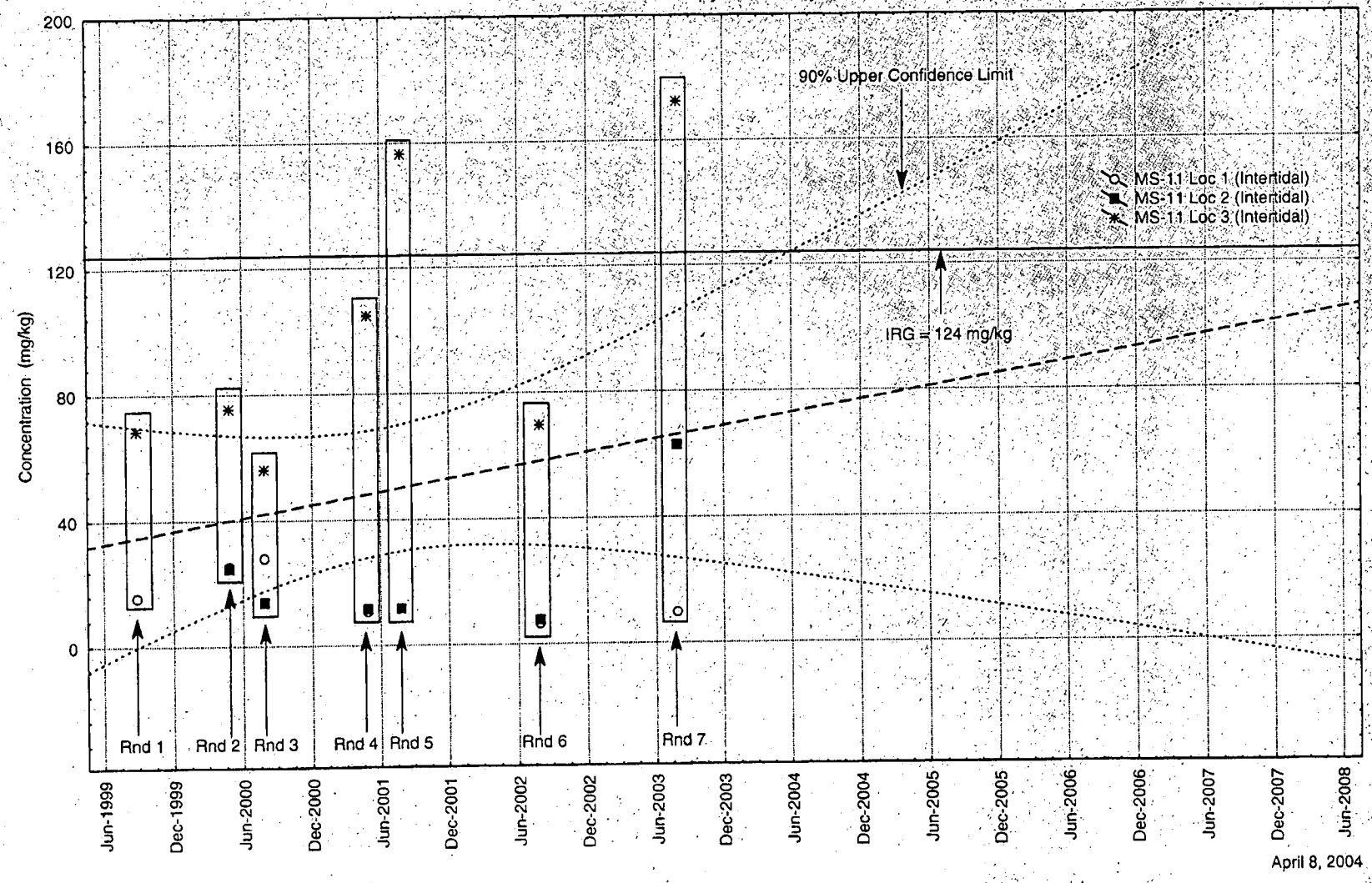
April 8, 2004

Monitoring Station 11 - Sediment
Copper Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



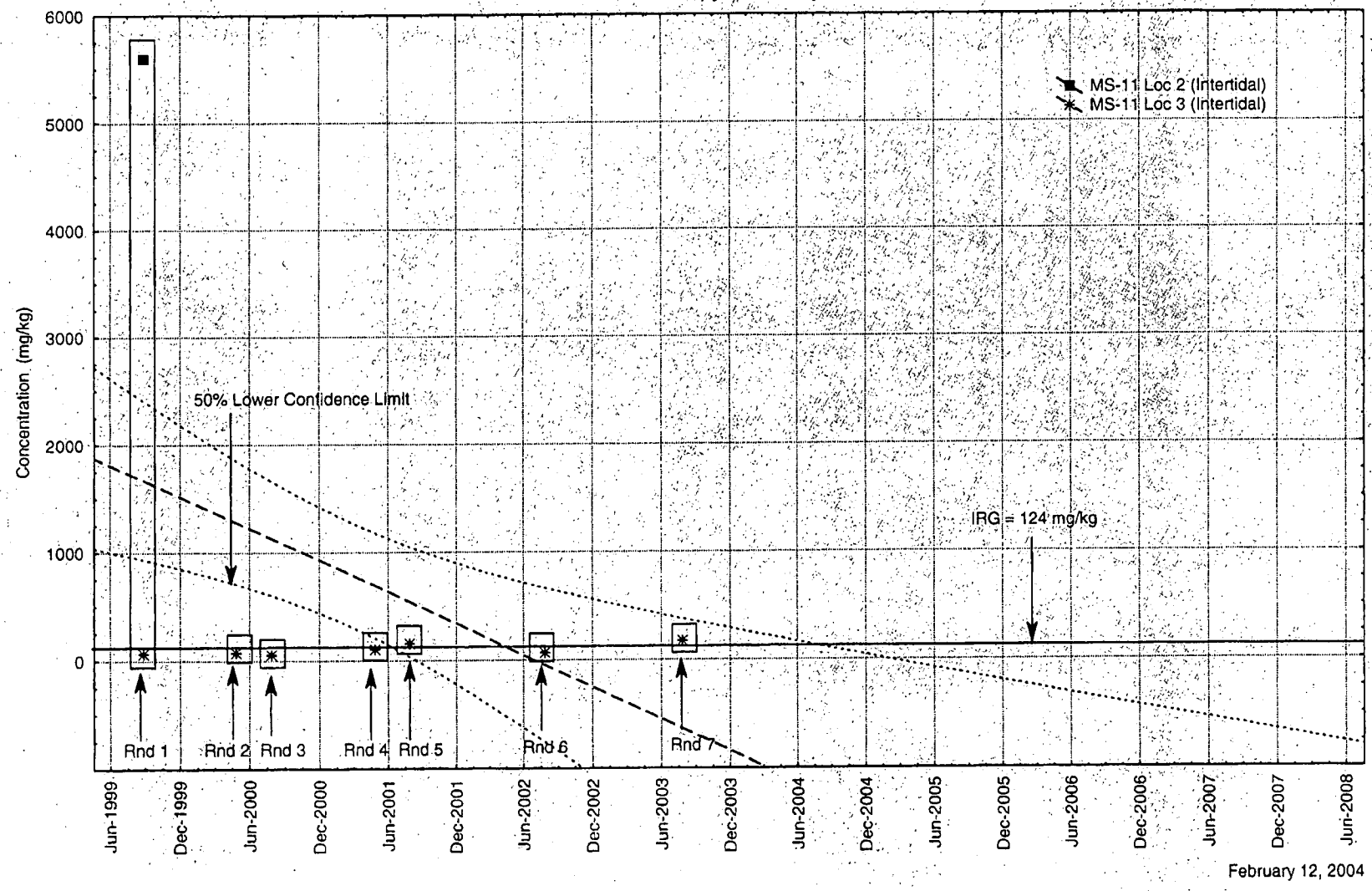
February 12, 2004

Monitoring Station 11 - Sediment
Nickel Results by Round All Locations (Locs 1 and 2 calculated)
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



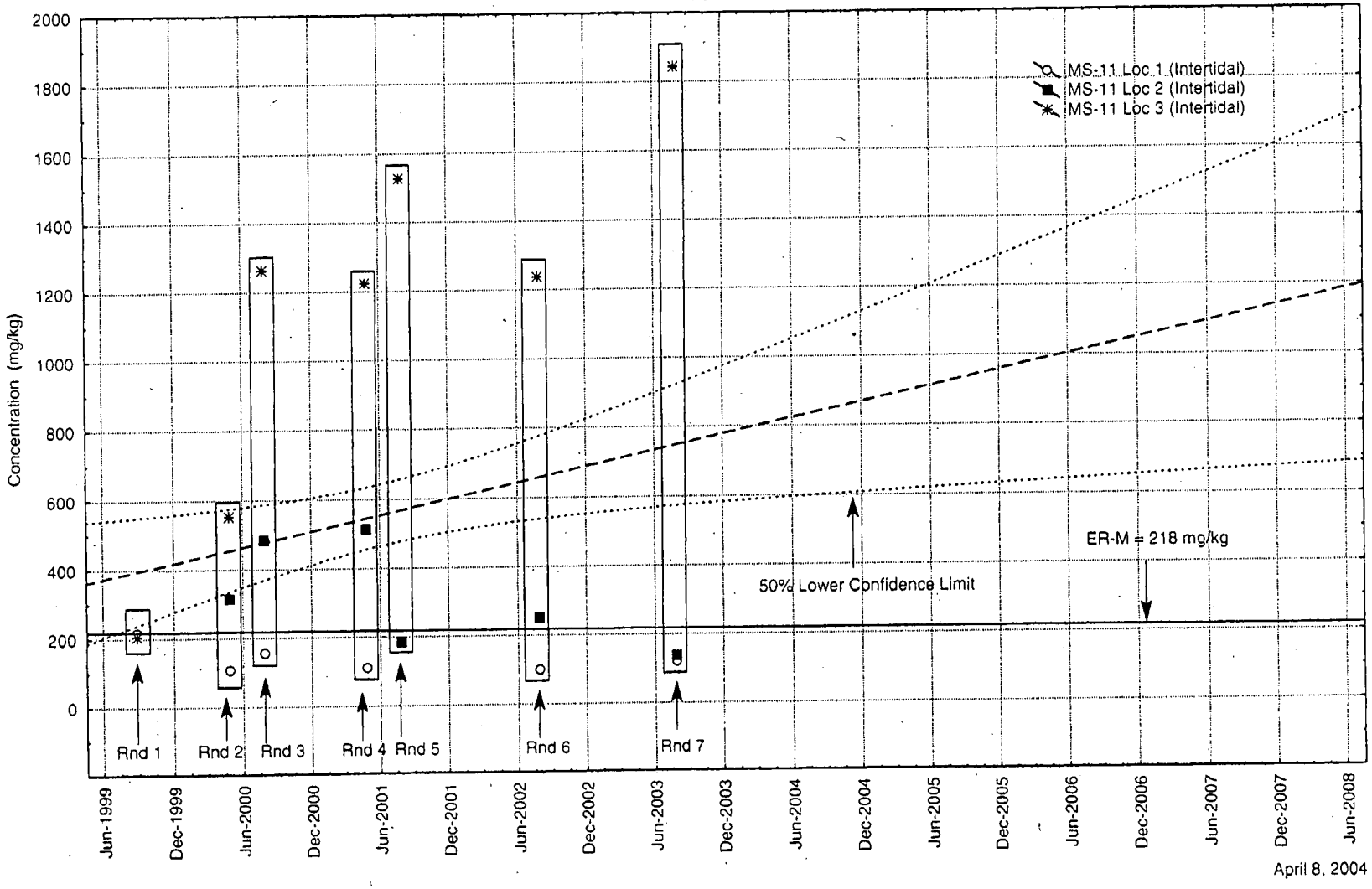
April 8, 2004

Monitoring Station 11 - Sediment
Nickel Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine

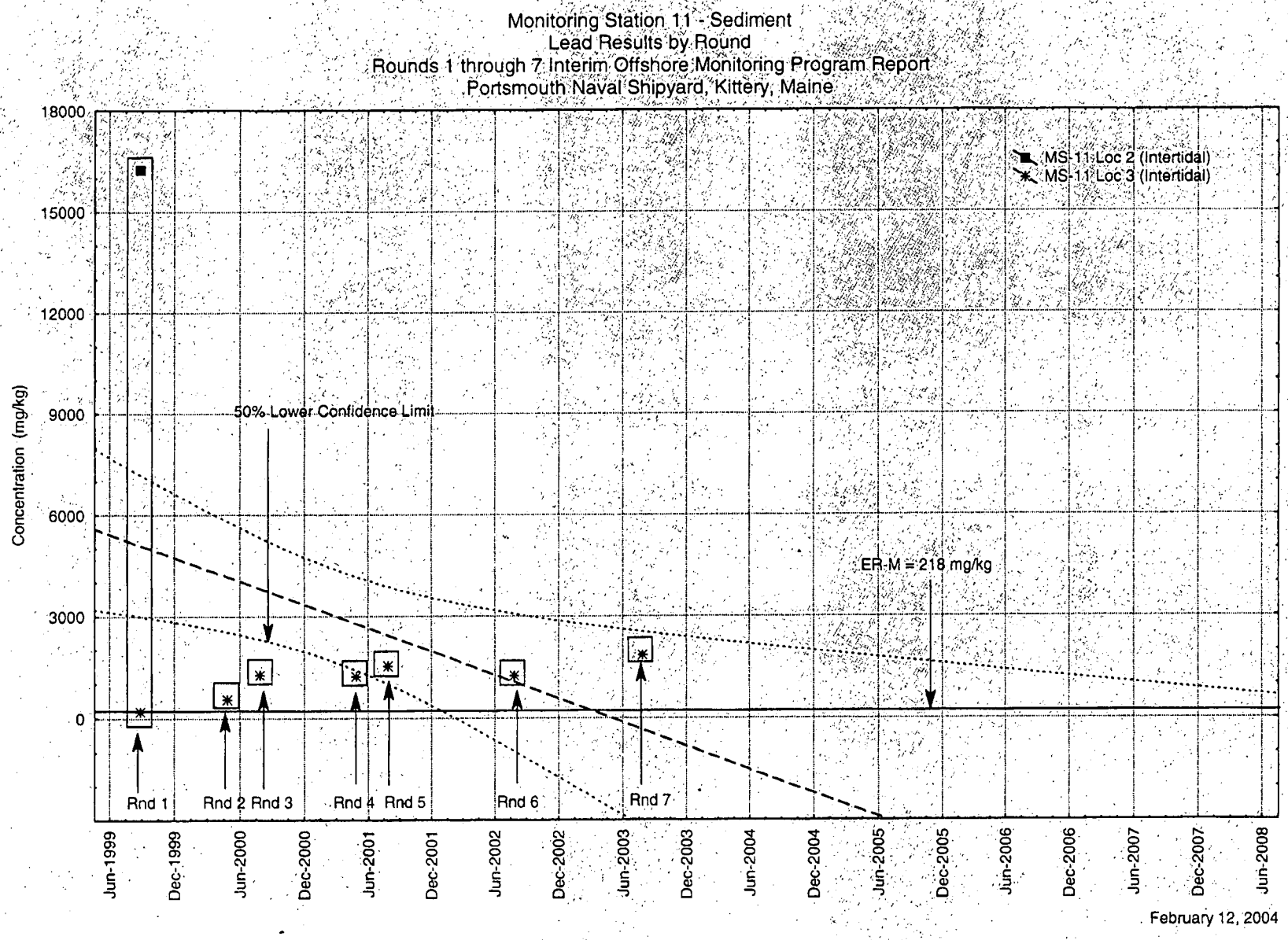


February 12, 2004

Monitoring Station 11 - Sediment
Lead Results by Round All Locations (Locs 1 and 2 calculated)
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



April 8, 2004



February 12, 2004

SHORELINE EVALUATION AT MS-11
OU4 ADDITIONAL SCRUTINY
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

The purpose of this memorandum is to summarize observations made by Tetra Tech NUS (TtNUS) during two separate site reconnaissance visits to evaluate the condition of the shoreline adjacent to monitoring station MS-11 that is being sampled as part of the Interim Offshore Monitoring Program. The primary objective of the site visits was to determine the potential for soil to erode to the offshore area in support of the additional scrutiny for Operable Unit (OU) 4. However, observations and notes that could be used to support the feasibility study (FS) for OU2, including the alternatives presented in the FS, also are included in this memorandum.

Monitoring station MS-11 is located adjacent to OU2, along the south end of Seavey Island in the Piscataqua River. OU2 includes Site 6, which encompasses the operating DRMO Area and Site 29, the former incinerator area that includes an area that was backfilled with ash and other waste. The Site 6 shoreline features an existing revetment system, while most of the Site 29 shoreline is protected by a retaining wall. A portion of the Site 29 shoreline, between the Site 6 revetment and the wall is unprotected.

The first visit was a walking tour conducted on August 20, 2004 by George Gardner and Jim Forrelli (TtNUS) accompanied by Marty Raymond (PNS). At the time of the visit, approximately 9:00 to 10:45 AM, the tide was rising and the weather was partly cloudy with the temperature in the low 80Fs. The DRMO area was closed at the time of the visit. The north half of the DRMO shoreline stabilization area was viewed by walking along the level area between the fence and the shoreline slope. Because of safety and security concerns, the walking tour did not continue along the southern half of the shoreline stabilization area. The southern section could not be observed from the other side of the fence because the DRMO area was closed. The Site 29 shoreline was viewed by walking along the existing seawall that runs along this area of the shore. The DRMO was also observed at an overlook from the topographically high location adjacent to the north-eastern part of Site 6.

The second site reconnaissance was conducted on October 25, 2004 consisted of a walking tour as well as a boat tour and included Deborah Cohen, Aaron Bernhardt, George Gardner (only for the boat tour) and Jim Forrelli (TtNUS). Navy personnel included Ken Plaisted (PNS) (only for the boat tour) and Amanda Kittelson (EFANE), and two boat operators. The tour was conducted during outgoing tide conditions from approximately 1:30 to 2:30 PM. The weather was partly cloudy with the temperature in the 50Fs. The purpose of the boat tour was to inspect the shoreline from the waterside perspective to obtain an unobstructed view of the current conditions along the existing revetment, seawall and unprotected shoreline. The walking tour was also conducted during this visit because the DRMO was closed during the August 20, 2004.

A summary of the site visits, including observations or evaluations conducted, follows.

Site 6 (DRMO) Shoreline

According to the DRMO shoreline stabilization action memorandum (FWENC 2001), the DRMO shoreline stabilization action consisted of regrading of the existing embankment rock and the placement of a multi-layer protective revetment system. The revetment consists of a variable-thickness stone (1/2-inch) layer, a non-woven geotextile layer, a minimum 6-inch layer of stone (1½-inch) bedding, an intermediate 6-inch minimum rip-rap layer and a surface rock rip-rap layer placed on a maximum slope of 1.5 horizontal: 1 vertical (1.5H:1V). The geotextile provides durability and filtering characteristics as it is permeable to water but prevents migration of lead-contaminated soil. Observations made during the walking tour of the north Site 6 shoreline stabilization area and the boat tour are presented below.

The surface rock (armor) rip-rap appears to be one layer thick. The steeply sloped shoreline (approx. 1.5H:1V according to the post construction survey) stabilization area appeared to be in reasonable good condition considering no maintenance had been performed, according to Marty Raymond, since its construction in 1999. However, local instability of the main armor layer or rip-rap was observed in this multilayer structure, particularly at the apparent high water zone where several broad areas of oversteepened or displaced rip-rap were observed. If left unattended, the downslope rip-rap displacement in these areas will continue, exposing the geotextile and resulting in subsequent erosion of the underlayer.

During the first visit, two rip-rap displacement areas were observed in the portion of shoreline viewed. At monitoring station MS-11, Loc 2 (approximate) an area was observed where "sculpting" from erosion or displacement of surface rock down slope below the high water level. Approximately 50 feet from monitoring station MS-11, Loc 2, an area was observed where more of the surface rock had moved down the slope exposing a 3-foot diameter area of geotextile at the high water level. In addition, three pipes, assumed to be storm water outfalls, were observed protruding from the middle section of the stabilization area. None were discharging at the time of the visit. No significant erosion of the rip-rap was observed below the pipes.

As the boat tour was made during outgoing tide conditions when current was fairly strong. For safety purposes a distance of approximately 100 feet had to be maintained by the boat from the shore. The depth finder on the boat indicated the depth of water was about 50 feet. Because of the distance, the evidence of the rip-rap displacement was not as apparent as when viewed from the shore on August 20, 2004; however, one area where the geotextile was exposed was observed.

Ken Plaisted (PNS) stated that fishing boats traveling this section of the river generate significant waves that impact the Site 6 shoreline.

Based on the fact that there are areas of local instability where small portions of the rip-rap slope had been displaced exposing the underlying geotextile and there are other areas where the geometry of the rip-rap slope showed "sculpting" from erosion, it can be expected that these areas will further deteriorate and expose the underlayers to potential erosion. In the short term maintenance consisting of repositioning in the displaced surface stones is required.

Site 29 Shoreline

A 12 to 18-foot high wall runs along most of the Site 29 shoreline. Based on discussions with PNS engineering staff no design and construction records exists for the Site 29 wall. It appears to be constructed of base layers of granitic blocks upon which a concrete wall was poured. Based on photocopies of historical photographs, the wall was built before 1951 as it appears in a photograph of that date (Dolph 1997). These photographs show the placement of fill on the landside of the wall. Previous sampling of the fill indicates it is contaminated, possibly from the incinerator and/or other waste disposal activities that occurred near the site. Building 310 is built over this fill. Portions of Building 298 may also be over this fill. Observations made during the walking tour of the Site 29 shoreline area and the boat tour are presented below.

The top of the wall consists of poured concrete several feet thick and apparently poured directly on the top of the underlying granite blocks. Fence posts for the chain-link fence situated on top of the wall are embedded in the concrete. The retaining wall appears to be constructed of layers of large granitic blocks ranging in size from about 6 to 8 feet long to 3 to 4 feet wide and 3 to 4 feet high. There appear to be about six to seven layers of blocks visible, and it is assumed but not known that the wall is founded on granitic blocks that are buried below the visible layers to an unknown depth. It is unknown if the wall is founded on bedrock, natural rock rubble or sediments. The natural bedrock at this location appears to be gray, low metamorphic grade schist. The seaward side of the retaining wall is composed of large boulders and blocks of the schist. The boulders and blocks of natural rock in front of the wall would tend to dissipate erosional wave and

flow action from the river. At mid-morning the day of the boat tour near high tide the waterline was observed to be approximately halfway up the wall, with the rocky beach covered.

The eastern two-thirds section of the wall appears to be in good condition considering its age and exposure. The blocks forming this portion of the wall appear reasonably tightly situated with little evidence of significant displacement. However, the western end of the wall adjacent to Building 298 appears to be structurally distressed. Erosion of the bank beyond the end of the wall has extended behind a portion of this part of the wall. Pieces of metal debris, some of which appeared to be possibly lead mesh from batteries, were observed during the site visit. Soil from this area appears to be eroding directly into the river and possible into an adjacent storm drain that discharges into the river. A number of the granitic blocks at the base of the wall have become dislodged and one block was observed on the rock beach below. The wall should be considered unstable at this localized area. There is a long rectangular gap estimated being at least 10 feet long where an steel pipeline, assumed to be a storm water discharge line (inactive at the time of the visit and estimated at 24-inch diameter), protrudes at the base of the wall near the western end.

In the wooded area at the eastern side of the wall, metal debris was observed in the soil near monitoring station MS-11, Loc 3. The soil in this area is likely to erode to the offshore area during rain events because the slope of the bank was relatively steep.

References

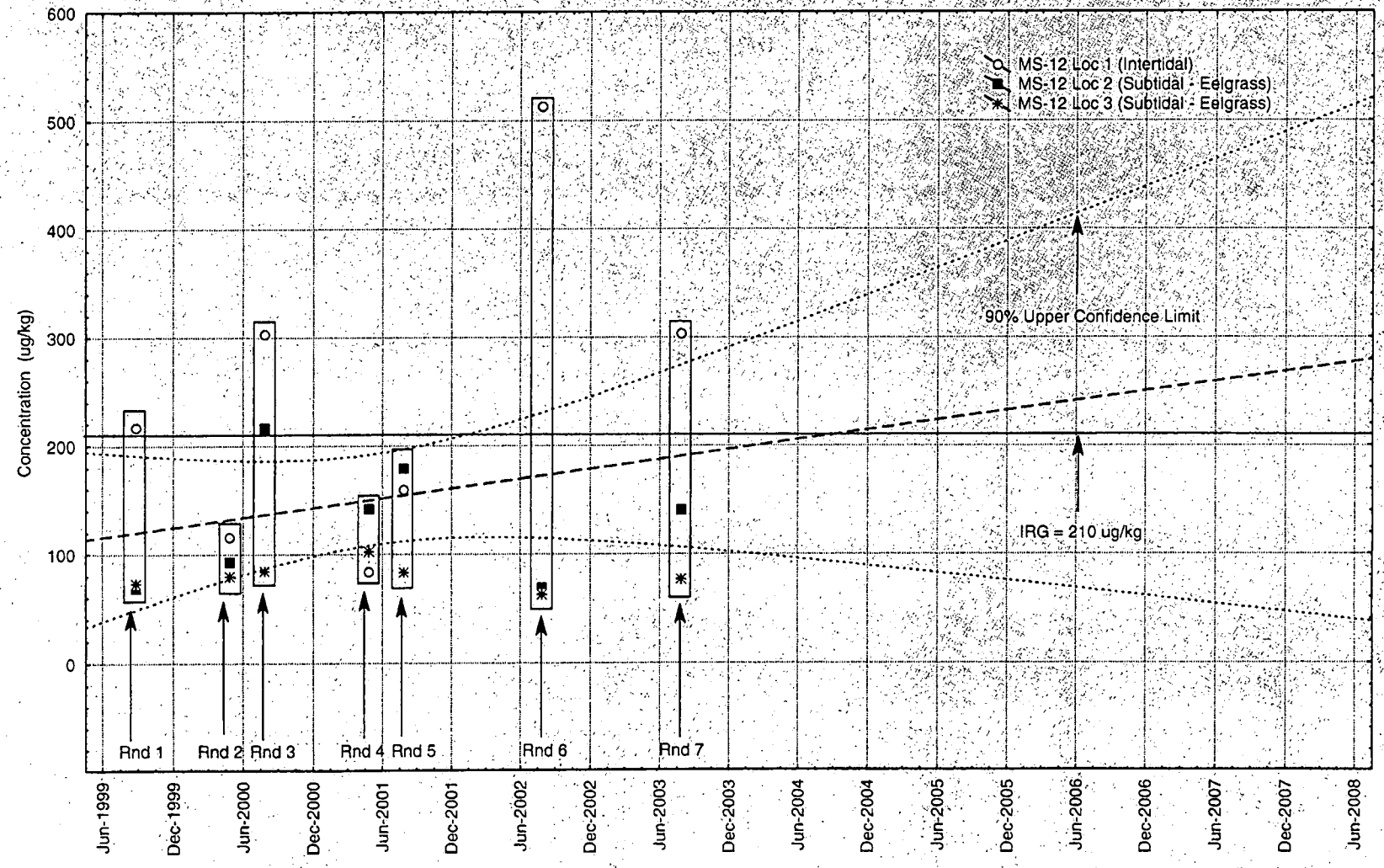
Dolph, James (Shipyard Historian) and others. 1997. Investigation of the Defense Reutilization and Marketing Office (Salvage Yard), Portsmouth Naval Shipyard, Kittery, Maine.

Foster Wheeler Environmental Corporation, Inc. 2001. DRMO Shoreline Stabilization Action Memorandum, Portsmouth Naval Shipyard, Kittery, Maine.

APPENDIX A-4

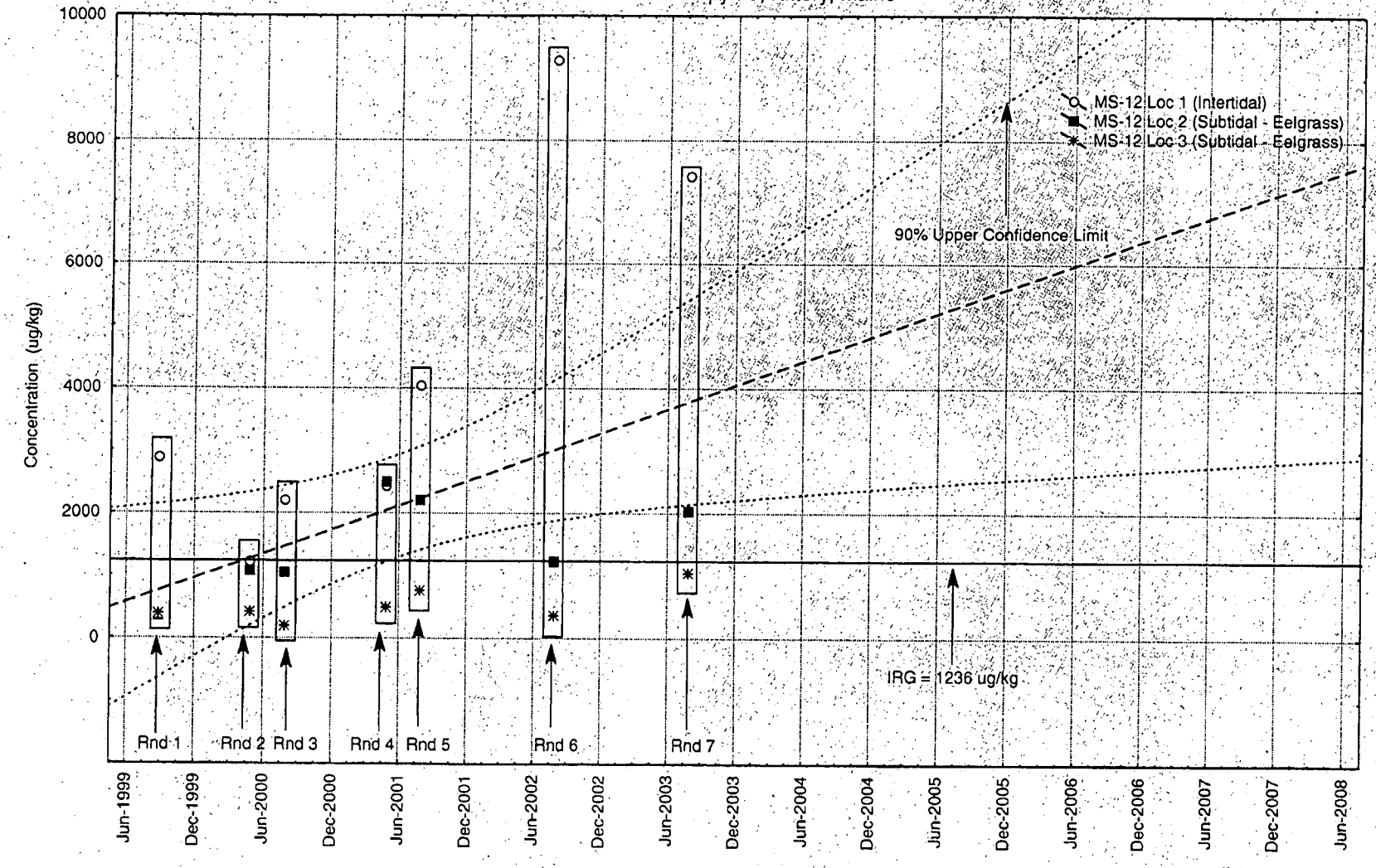
CONCENTRATION TREND PLOTS FOR MS-12

Monitoring Station 12 - Sediment
Acenaphthylene Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



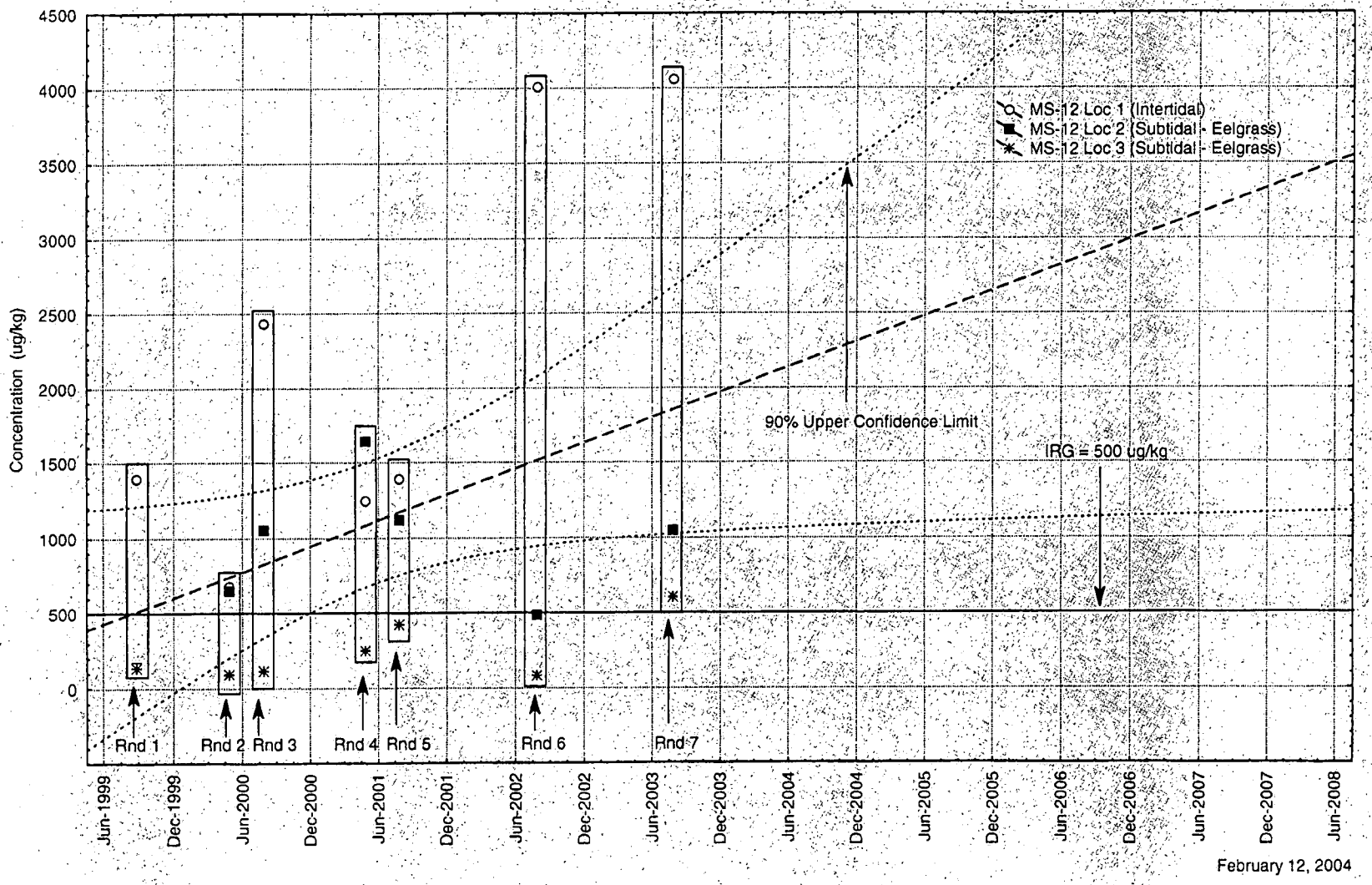
February 12, 2004

Monitoring Station 12 - Sediment
Anthracene Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



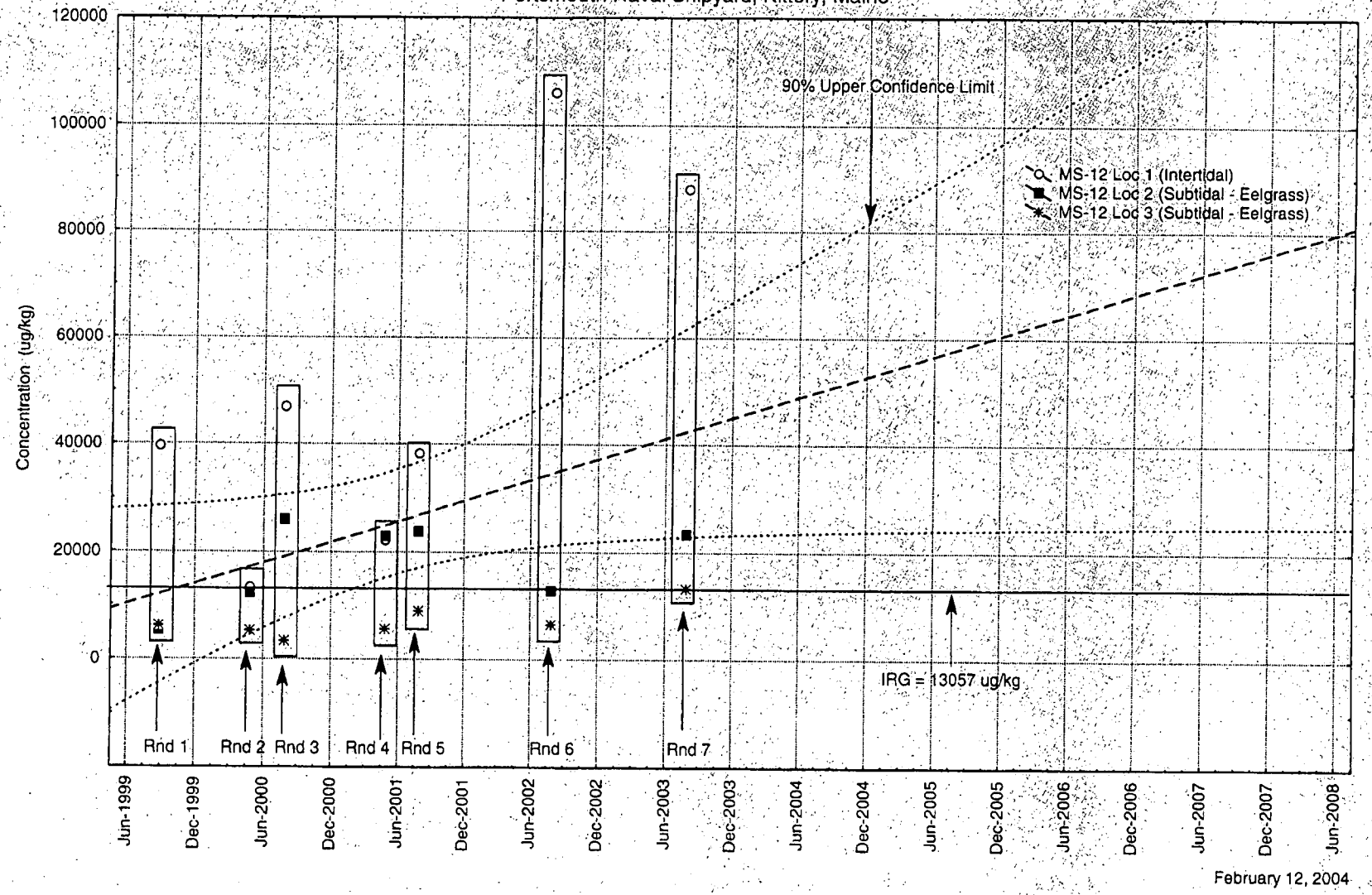
February 12, 2004

Monitoring Station 12 - Sediment
Fluorene Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



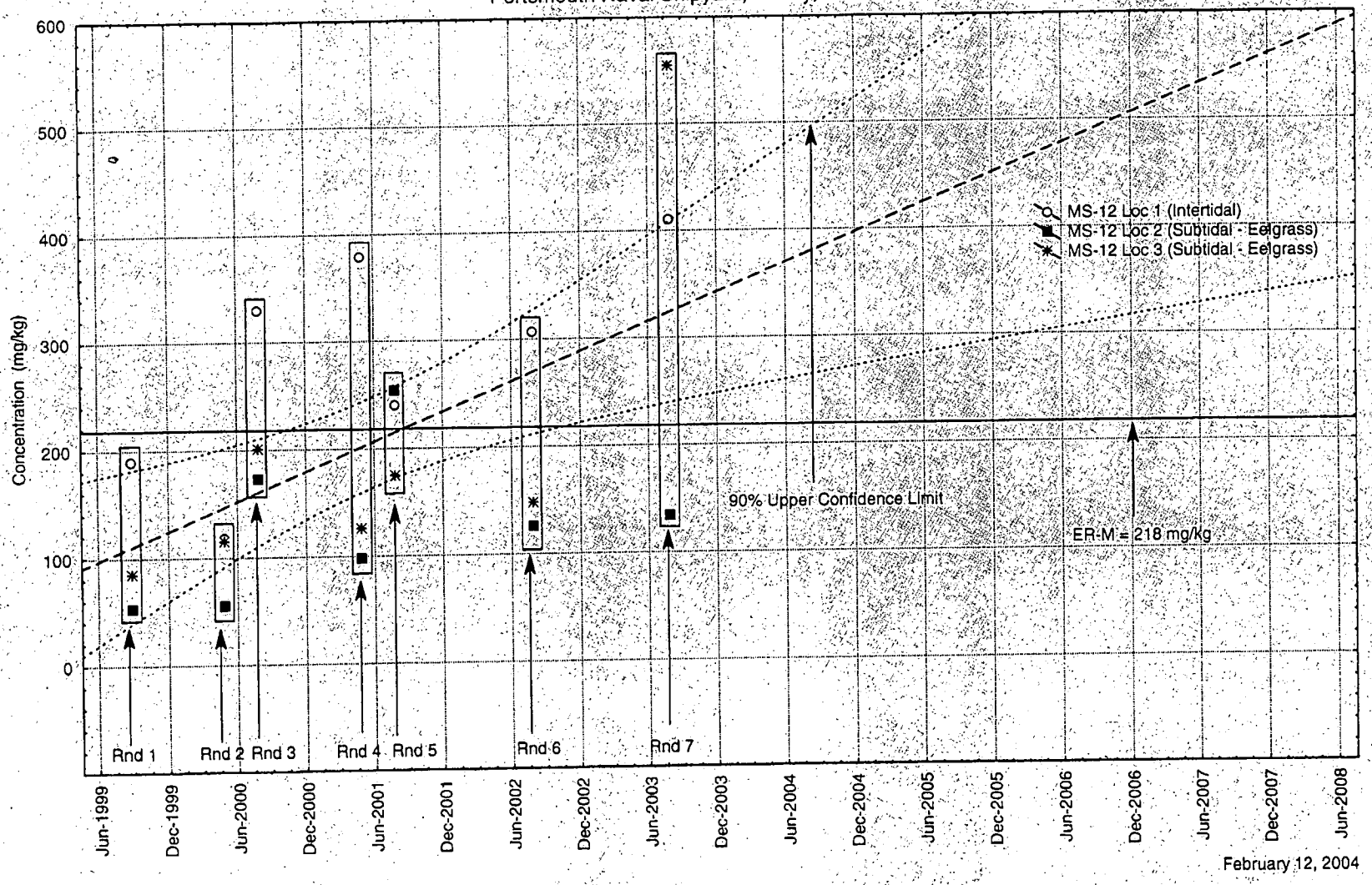
February 12, 2004

Monitoring Station 12 - Sediment
High Molecular Weight PAH Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



February 12, 2004

Monitoring Station 12 - Sediment
Lead Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



February 12, 2004

APPENDIX B

TECHNICAL MEMORANDA AND RESPONSES TO COMMENTS

- Additional Scrutiny Technical Memoranda
- Analytical Methods Technical Memorandum
- Response to Comments on the Technical Memoranda

ADDITIONAL SCRUTINY TECHNICAL MEMORANDA

Technical Memorandum

Recommended Additional Scrutiny at Monitoring Stations M05, M08, and M09

Portsmouth Naval Shipyard, Kittery, Maine

As indicated in the cover letter dated February 27, 2004 for the Round 7 Data Package for the Interim Offshore Monitoring Program for Operable Unit (OU) 4, the Navy has prepared this technical memorandum describing the additional scrutiny that is recommended for monitoring stations M05, M08, and M09. Monitoring station M05 is located in Jamaica Cove and monitoring stations M08 and M09 are located in Clark Cove at Portsmouth Naval Shipyard, Kittery, Maine (see Figure 1). All three monitoring stations are located adjacent to OU3, and as a result of the construction activities associated with the OU3 remedial action, chemical concentrations at these three monitoring stations were greater in Round 6 (M05) and Round 7 (M08 and M09) of the Interim Offshore Monitoring Program, than previous rounds. The following sections describe the additional scrutiny that is recommended, or has already been conducted, at each of these monitoring stations. The recommendations presented in this memorandum for additional sampling in August 2004 (or as close to August 2004 as possible) are based on the availability of funding.

Monitoring Station M05

This monitoring station is located in Jamaica Cove, adjacent to the wetland that was constructed as part of the remedy for OU3 (see Figure 1). During the construction activities at OU3, a turbidity curtain was placed in Jamaica Cove, approximately 30 to 40 feet from the northern edge of the saltmarsh. One of the three sample locations at this station, location 1, was within the turbidity curtain; the other two sample locations at this station were outside of the turbidity curtain. The concentrations of metals and some organic chemicals were greater at location 1 in Round 6 than previous rounds, and the concentrations were still elevated in Round 7. The majority of the construction activities related to OU3 in this area occurred between Round 5 and Round 6, but some construction activities related to OU3 may have impacted this area between Rounds 6 and 7. None of the construction activities related to OU3 are expected to significantly impact Jamaica Cove after Round 7. The following additional scrutiny is recommended for this monitoring station:

- Collect sediment samples in August 2004 (or as close to August 2004 as possible) at all three locations at M05 in accordance with the Interim Offshore Monitoring Plan (TtNUS, October 1999). The sediment samples will be analyzed for the same list of parameters using the same analytical methods as was done for Round 7 (TtNUS, February 2004). The purpose of these samples is to obtain data from this monitoring station to re-establish the concentration trend lines after onshore activities were completed.
- Collect 15 additional sediment samples adjacent to location 1 at M05 to determine the extent of contamination in the area within and outside of the turbidity curtain (see Figure 2). These samples will be analyzed for copper, nickel, and lead. Copper and nickel are the only chemicals that were detected at concentrations greater than the IRGs; the levels of polycyclic aromatic hydrocarbons in the sediment

at M05 were less than the IRGs. Also lead was detected at concentrations above the Effects-Range Median (ER-M) (Long et al., 1995) during Round 7. The 15 samples will be collected in a ring pattern, with samples approximately 25 feet apart. The first ring will consist of three samples 25 feet away from location 1 (locations 4 through 6), the second ring will be 25 feet away from the first ring and will consist of six samples (locations 7 through 12), and the third ring will be 25 feet away from the second ring and will consist of six samples (locations 13 through 18) (see Figure 1). All of the sediment samples will be collected during the same sampling event. Initially, the samples in the first ring will be analyzed, and the samples in the second and third rings will be held for analysis. If the concentrations of the metals in the samples from the first ring are greater than the IRGs (or ER-M for lead), then the samples from the second ring will be analyzed. If the concentrations of the metals in the samples from the second ring are greater than the IRGs (or ER-M for lead), then the samples from the third ring will be analyzed. All of the samples in the second and third rings may not be analyzed; the samples for analysis will be selected in order to bound the samples with elevated chemical concentrations.

Monitoring Station M08

This monitoring station is located in Clark Cove, adjacent to OU3 (see Figure 1). During the 2003 construction activities at OU3, a turbidity curtain was placed in Clark Cove, approximately 30 to 40 feet from the edge of the shoreline. Locations 1 and 3 at this station were located within the turbidity curtain; it is not known whether location 2 was within the turbidity curtain. The concentrations of metals and organic chemicals were greater at M08 in Round 7 than previous rounds, after a majority of the construction activities related to OU3 in this area occurred. The Navy further investigated this area after Round 7 and found additional waste in the intertidal area that was not removed during the initial construction activities at OU3. The waste was removed in April 2004 and replaced with clean sediment.

The Navy proposes collecting sediment samples in August 2004 (or as close to August 2004 as possible) at all three locations at M08. The sediment samples will be analyzed for the same list of parameters using the same analytical methods as was done for Round 7 (TtNUS, February 2004). The reason for this recommendation is that based on the Round 7 sampling results, the Navy conducted additional scrutiny at this monitoring station by removing additional waste in the area and replacing the sediment that was removed with clean sediment. Therefore, the only activity that needs to be conducted at this station is to re-establish the concentration trend lines.

Monitoring Station M09

This monitoring station is located south of M08 in Clark Cove, adjacent to OU3 (see Figure 1). During the construction activities at OU3, a turbidity curtain was placed in Clark Cove, approximately 30 to 40 feet from the edge of the shoreline. Locations 1 and 2 at this station were located within the turbidity curtain; it is not known whether the location 3 was within the turbidity curtain. The concentrations of metals and organic chemicals were greater at M09 in Round 7 than previous rounds, after the majority of the

construction activities related to OU3 in this area occurred. The following additional scrutiny is recommended for this monitoring station:

- Collect sediment samples in August 2004 (or as close to August 2004 as possible) at all three locations at M09 in accordance with the Interim Offshore Monitoring Plan (TtNUS, October 1999). The sediment samples will be analyzed for the same list of parameters using the same analytical methods as was done for Round 7 (TtNUS, February 2004). The purpose of these samples is to obtain data from this monitoring station to re-establish the concentration trend lines after onshore activities were completed. All activities that may impact the chemical concentrations in the sediment will be completed prior to collecting samples in August 2004.
- Collect three additional sediment samples at this station to determine the extent of contamination in the area. The three additional samples are spaced throughout the monitoring station to obtain better spatial coverage and variability information for the area (see Figure 1). The sediment samples will be analyzed for the same list of parameters using the same analytical methods as was done for Round 7 (TtNUS, February 2004).

Summary of Recommendations for Additional Scrutiny

In summary, the following additional scrutiny is recommended for monitoring stations M05, M08, and M09:

- **M05, M08, and M09:** Collect sediment samples in August 2004 (or as close to August 2004 as possible) at all three locations at the stations to re-establish the trend lines.
- **M05:** Collect additional sediment samples in Jamaica Cove to determine the extent of elevated metals concentrations in the area near location 1 at this station.
- **M09:** Collect additional sediment samples in Clark Cove to determine the extent of elevated metals and organic chemical concentrations at this monitoring station.

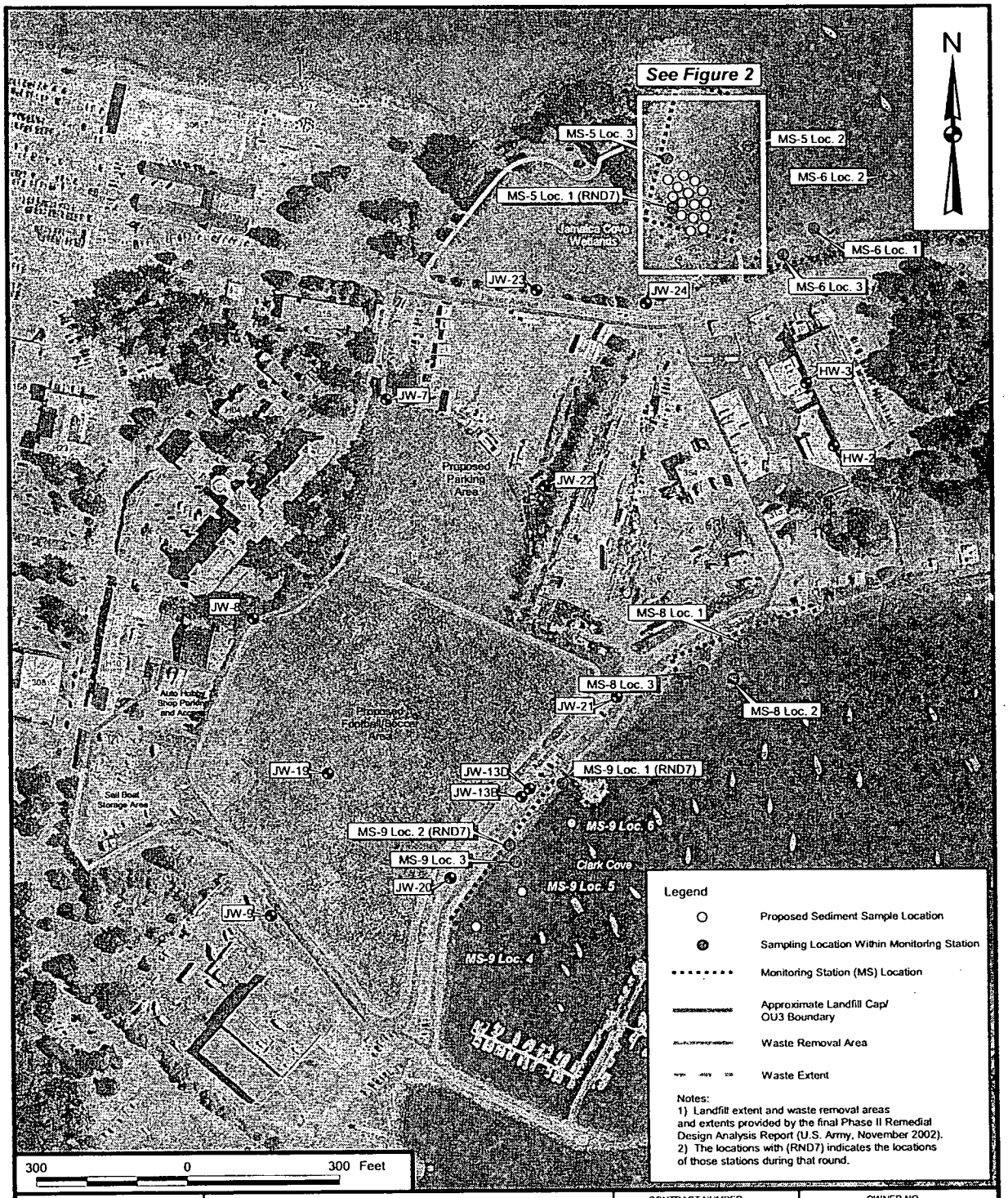
Deliverables

The analytical data from the additional scrutiny will be presented in a data package that the Navy will submit to the regulators and the restoration advisory board. A technical memorandum will be prepared after the data package is submitted and will provide an evaluation of the data.

References

TtNUS (Tetra Tech NUS, Inc), 1999. Interim Offshore Monitoring Plan Operable Unit 4 for Portsmouth Naval Shipyard, Kittery, Maine. King of Prussia, Pennsylvania, October.

TtNUS (Tetra Tech NUS, Inc), February, 2004. Interim Offshore Monitoring Program Round 7 Data Package for Portsmouth Naval Shipyard, Kittery, Maine. King of Prussia, Pennsylvania.



DRAWN BY J. LAMEY — DATE 6/16/04	Tetra Tech NUS, Inc.	CONTRACT NUMBER 2833	OWNER NO. CTO 815
CHECKED BY A. BERNHARDT — DATE 6/16/04	PROPOSED SEDIMENT SAMPLE LOCATIONS FOR ADDITIONAL SCRUTINY AT MONITORING STATIONS 5, 8, AND 9 INTERIM OFFSHORE MONITORING PROGRAM PORTSMOUTH NAVAL SHIPYARD PORTSMOUTH, MAINE	APPROVED BY — DATE —	
COST/SCHEDULE-AREA		APPROVED BY — DATE —	
SCALE AS NOTED		DRAWING NO. FIGURE 1	REV 0

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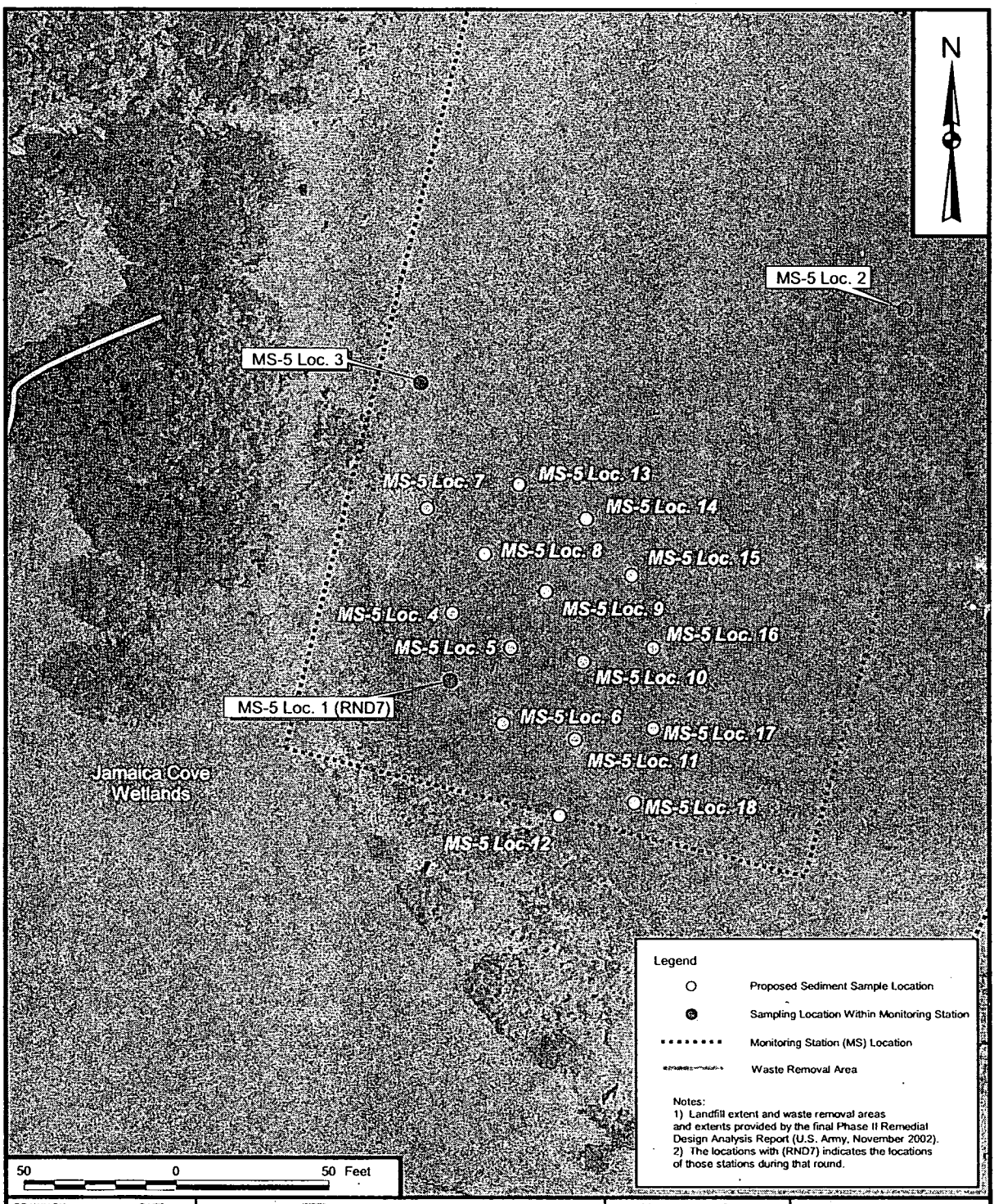

DRAWN BY J. LAMEY — DATE 6/16/04	Tetra Tech NUS, Inc.	CONTRACT NUMBER 2833	OWNER NO. CTO 815
CHECKED BY A. BERNHARDT — DATE 6/16/04	PROPOSED SEDIMENT SAMPLE LOCATIONS FOR ADDITIONAL SCRUTINY AT MONITORING STATION 5 (DETAILED VIEW) INTERIM OFFSHORE MONITORING PROGRAM PORTSMOUTH NAVAL SHIPYARD PORTSMOUTH, MAINE	APPROVED BY — DATE —	
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Technical Memorandum
Recommended Additional Scrutiny at Monitoring Stations M01, M11, and M12
Portsmouth Naval Shipyard, Kittery, Maine

As indicated in the Rounds 1 through 7 Interim Offshore Monitoring Program Report for Portsmouth Naval Shipyard (PNS), Kittery Maine, additional scrutiny was recommended for the following monitoring stations: M01, M03, M04, M05, M08, M09, M11, and M12. The proposed additional scrutiny for monitoring stations M05, M08, and M09 were presented a technical memorandum submitted to the regulators and RAB on June 21, 2004. The additional scrutiny needed at monitoring stations M03 and M04 for PAHs will be evaluated as part of the planning for the Site 32 Phase 2 remedial investigation. This technical memorandum presents the additional scrutiny the Navy is recommending for monitoring stations M01, M11, and M12 (MS-1, MS-11, and MS-12).

MS-1 is located in the Back Channel, MS-11 is located in the Main Channel of the Piscataqua River, and MS-12 is located in the dry docks area at Portsmouth Naval Shipyard, Kittery, Maine (see Figure 1). The following sections describe the additional scrutiny that is recommended at each of these monitoring stations. The additional scrutiny that is proposed for each monitoring station is designed to answer several questions. The questions are listed below and are followed by the additional scrutiny that is proposed to address each question. Several of the evaluations are very qualitative and it may be difficult, if even possible, to answer some of the questions.

Monitoring Station M01

This monitoring station is located in the Back Channel, offshore of Site 34 and adjacent to the bridge leading to Gate No. 1. Additional scrutiny was recommended for this station because the concentrations of PAHs exceeded their respective interim remediation goals (IRGs), and the trend lines indicated that the concentrations are increasing. Also, the concentration of 4,4'-DDT exceeded the preliminary remediation goal (PRG) at MS-1 and is projected to exceed the PRG for the next 5 years.

1. ***Are the concentrations of PAHs in sediment actually increasing at MS-1, or are the increases observed in the trend lines being caused by an anomaly/variation in the data?***
   - Plot PAH sediment concentrations normalized to total organic carbon (TOC) and grain size (percent silt).
   - Plot PAH data from individual sample locations at MS-1 to determine if trend lines are similar for the different locations. If they are not similar, try to determine why (i.e., location, intertidal vs subtidal, data more variable, etc.).
   - Evaluate coefficient of variation at each location to determine heterogeneity of PAH concentrations in sediment to determine if the variability in the data may be influencing the trend line.

- Review field notes/sediment descriptions to determine if there may be factors that are influencing chemical concentrations in sediment (i.e., had to move locations because of difficulty collecting a sample, heterogeneous sediment).

2. ***Is Site 34 the source of PAHs in the sediment at MS-1, and if not, what are the potential sources of PAHs in the sediment in this area?***
   - Evaluate source signature of PAHs in Site 34 soil and ash and compare to signatures observed in sediment at MS-1.
   - Evaluate storm water discharges near MS-1 and their potential impact on PAH concentrations observed at MS-1.
   - Evaluate upgradient and reference station PAH signatures found in sediment and compare to signatures observed in sediment at MS-1.

3. ***Is Site 34 the source of DDT in the sediment at MS-1, and if not, what are the potential sources of DDT in the sediment in this area?***
   - Evaluate on-shore DDT data to determine if there is a link to the DDT levels in the offshore area.
   - Evaluate the concentrations of other pesticides in the on-shore and off-shore area.
   - Evaluate background/regional data.
   - Evaluate concentrations based on normalization to TOC.

4. ***What is the variability of elevated levels of PAHs and DDT in the sediment?***
   - Collect additional sediment samples around the existing MS-1 locations (PAH forensic and pesticide analysis), storm water catch basin and/or storm water outfall sediment samples, and at least one sample from each of four reference stations (PAH forensic analysis only).
   - Evaluate the information from Question Nos.1 and 3 above.

Monitoring Station M11

This monitoring station is located in the Main Channel, just offshore of OU2 (Site 6-Defense Reutilization and Marketing Office [DRMO] and Site 29-Teepee Incinerator). Additional scrutiny was recommended at this station because the concentrations of metals exceed their IRGs, and the trend lines indicate that the concentrations are increasing. Also, the concentration of lead exceeded the Effects-Range Median (ER-M) at this station and the trend lines indicate that the concentrations are increasing.

1. ***Is there a continuing source of metals and other chemicals from Site 6 and/or Site 29 to the offshore area?***
   - Visual inspection of shoreline to determine if soil is eroding into the river.
   - Chemical analysis of eroding soil (if present) to determine if the soil (if eroding) is the possible source of metals in the sediment.
   - Review data for onshore soils at Sites 6 and 29

2. ***Are the concentrations of metals actually increasing at MS-11 (location 3), or is the increase observed in the trend line being caused by an anomaly in the data?***
   - Plot metals data normalized to grain size (i.e., percent silt) and aluminum for samples from MS-11 (location 3).

Monitoring Station M12

This monitoring station is located in the dry docks area offshore of Site 10 and Building 178. Additional scrutiny is recommended at this station because the concentrations of PAHs exceed their IRGs, and the trend lines indicate that the concentrations are increasing. Also, the concentration of lead exceeded the ER-M at this station and the trend lines indicate that the concentrations are increasing.

1. ***Are the concentrations of PAHs and lead in sediment actually increasing at MS-12, or are the increases observed in the trend lines being caused by an anomaly in the data?***
   - Plot PAH sediment concentrations normalized to total organic carbon (TOC) and grain size (percent silt).
   - Plot lead data normalized to grain size (i.e., percent silt) and aluminum.
   - Plot data from individual sample locations at MS-12 to determine if there are differences in trend lines across locations.
   - Review/plot historical data from Estuarine Ecological Risk Assessment, or other data, if available.

2. ***Is Building 178 the source of PAHs in the sediment at MS-12, and if not, what are the potential sources of PAHs in the sediment in this area?***
   - Evaluate source signature of PAHs in floor in Building 178 and compare to signatures observed in sediment at MS-12.
   - Evaluate storm water discharges near MS-12 and their potential impact on PAH concentrations observed at MS-12.
   - Evaluate reference station PAH signatures found in sediment and compare to signatures observed in sediment at MS-12.

3. ***Is Site 10 the source of lead in the sediment at MS-12, and if not, what are the potential sources of lead in the sediment in this area?***
   - Review available historical data.
   - Collect sediment samples offshore by Site 10 to determine if lead concentrations are similar in the area.

4. ***What is the extent of elevated levels of lead and PAHs in the sediment?***
   - Collect additional sediment samples for extent.

Deliverables

The Navy will submit the following documents to the regulators and the Restoration Advisory Board as part of the additional scrutiny for MS-1, MS-11, and MS-12:

- A work plan (including data quality objectives) that presents the specific data collection and data evaluation methods.
- A data package that presents the analytical data from the additional scrutiny.
- A technical memorandum that provides an evaluation of the data. This will be prepared after the data package is submitted.

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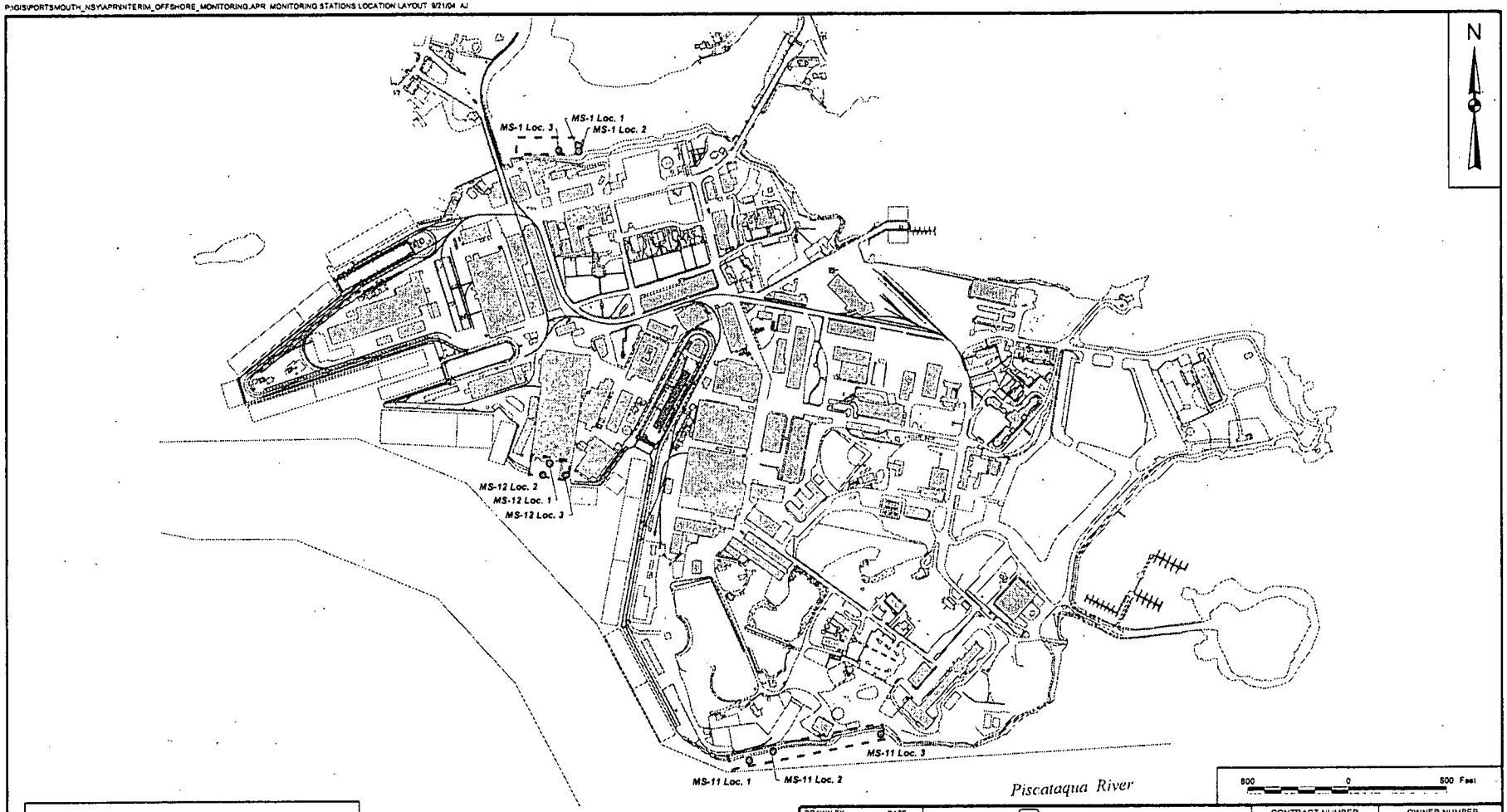

LEGEND

- Sampling Location Within Monitoring Station
- Monitoring Station (MS) Location

DRAWN BY A. JANOCHA DATE 9/21/04	Tetra Tech NUS, Inc.	CONTRACT NUMBER 2833	OWNER NUMBER CTO 0815
CHECKED BY A. BERNHARDT DATE 9/21/04	OVERVIEW OF MONITORING STATION LOCATIONS FOR MS-1, MS-11, AND MS-12 PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE	APPROVED BY — DATE —	
COST/SCHEDULE-AREA		APPROVED BY — DATE —	
SCALE AS NOTED		DRAWING NO. FIGURE 1	REV 0

ANALYTICAL METHODS TECHNICAL MEMORANDUM

Technical Memorandum

Comparison of Analytical Methods for the Interim Offshore Monitoring Program for Operable Unit 4

Portsmouth Naval Shipyard, Kittery, Maine

INTRODUCTION

For the first seven rounds of the Interim Offshore Monitoring Program at Portsmouth Naval Shipyard (PNS), Kittery Maine, sediment and tissue samples were analyzed for metals and organic chemicals [i.e., dioxins, polycyclic aromatic hydrocarbons (PAHs), pesticides, and polychlorinated biphenyls (PCBs)] using analytical methods developed for the National Oceanic and Atmospheric Administration (NOAA) Status and Trends program. These methods were selected to be consistent with methods used to analyze samples during previous investigations in the offshore area (TtNUS, 1999). In addition, these methods yield lower detection limits for some chemicals compared to standard U.S. Environmental Protection Agency (USEPA) analytical methods. However, NOAA methods are typically more expensive than standard USEPA methods and can be conducted by only a few laboratories in the United States; therefore, the analysis time is typically twice as long as it is for commercial laboratories. For these reasons, as was discussed during the January 8, 2004 technical meeting for the Round 1 through 7 Interim Offshore Monitoring Program report, and as described in the action item letter from the Navy dated March 16, 2004, the Navy has evaluated the need to continue using NOAA methods for future rounds of interim offshore monitoring.

The following two questions must be answered to determine whether the analytical methods can be changed for future rounds of monitoring:

- Will changing analytical methods yield different results, and if so, are those changes important enough to warrant not changing the methods?
- Will changing analytical methods raise the analytical detection limits so that the project objectives cannot be met?

The remainder of this memorandum answers the two questions first for analysis of metals and second for analysis of organic chemicals.

EVALUATION OF METALS ANALYTICAL METHODS

Background

Based on the analytical methods for metals, differences in the concentrations of some metals are expected by changing the analytical methods. The NOAA analytical method utilizes a complete digestion of the sediment particle using hydrofluoric acid so metals that are incorporated into the sediment matrix are included in the sample results. These typically include metals such as aluminum, iron, and other metals that may be specific to the geologic material in the area where samples were collected. The USEPA analytical method, on the other hand, utilizes a total recoverable digestion, which digests the material bound to the outer portion of the sediment particle. This is done to determine the concentration of chemicals that will be more bioavailable to human and ecological receptors. Therefore, the change in methods will yield different results for metals that are incorporated into the sediment matrix, which are not likely related to site activities.

The more critical issue, however, is whether the concentrations of the primary chemicals of concern in the offshore area [i.e., chemicals for which Interim Remediation Goals (IRGs) were developed such as copper and nickel] or other metals that may be important at some sites (such as lead) change significantly by using USEPA methods. This is an important issue because if much lower or higher concentrations were obtained for these metals using the USEPA methods, it would appear as if there was a decline or increase in the chemical concentrations over time, when the changes may be solely because of the differences in analytical methods.

Approach

To address the concerns raised above and to evaluate the differences in chemical concentrations obtained by the different analytical methods, Texas A&M University (TAMU), the laboratory that analyzed the Round 7 Interim Offshore Monitoring Program samples using the NOAA methods, shipped the Round 7 sediment samples to Katahdin Analytical Services (Katahdin) in January 2004. The samples were collected from August 9 through 13, 2003. Katahdin analyzed the split samples between February 16 and 25, 2004 which is within a few days of the end of the standard six-month holding time. Metals in the sediment are expected to be stable, chemical analysis a few days past the holding time is not expected to affect the sample results for the purpose of this evaluation. Fifteen samples (plus two duplicates) were then selected for analysis by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) using USEPA Method 6020.

Mercury was not analyzed by Katahdin because the NOAA method does not utilize a complete digestion of the sediment so the mercury results obtained using the USEPA 7471A method are expected to be similar to the results obtained using the NOAA method. Also, the tissue samples were not analyzed using the USEPA method because tissue is completely dissolved using both NOAA and USEPA methods so the results obtained using the USEPA method are also expected to be similar to the results obtained using NOAA methods. TAMU analyzed aluminum, cadmium, chromium, copper, iron, manganese, nickel, and zinc using ICP-MS methodology, arsenic, lead and silver using Graphite Furnace Atomic Absorption (GFAA) methodologies. Katahdin analyzed these metals using ICP-MS.

Results

Table 1 presents the results of the samples analyzed by both the NOAA and USEPA methods. In addition to the sample results, a ratio was calculated by dividing the results from the NOAA method analysis by the results from the USEPA method analysis. Table 2 is a summary of the maximum, minimum, average, and median ratio for each chemical. A ratio of 1.0 indicates that the sample results from both methods were essentially the same. A ratio of 2.0 indicates that the NOAA method result was approximately two times higher than the result obtained using the USEPA method, and so on. Ratios were not calculated for samples where a non-detected value was found for samples analyzed by either the NOAA or USEPA method. As can be seen in Table 1, most ratios ranged from 1.0 to 2.0 indicating that the samples analyzed using the NOAA methods produce detected results approximately one to two times greater than that detected results with the USEPA method.

Figures 1 through 12 present graphically the positive results of the samples that were analyzed by both NOAA and USEPA methods; non-detected data were not included in the figures. NOAA concentrations are plotted on the X-axis and the corresponding USEPA concentration for each sample analyzed is plotted on the Y-axis. The best fit line and equation of the best fit line (including the correlation coefficient, R^2) are also shown. The correlation coefficient ranged from 0 to 1.0 with an R^2 value of 1.0 indicating the best correlation and a value of 0 indicating no correlation.

IRGs have been developed for two metals, copper and nickel. Also, lead has been identified as a metal of concern at several on-shore sites. Therefore, these three metals are the primary focus of this memorandum, although the results for other metals are discussed as well. Figures 1 through 3 present the correlation plots for copper, lead, and nickel, respectively. All three metals have very good correlations, with R^2 values of 0.95, 0.91, and 0.75, for copper, lead, and nickel, respectively. The slightly poorer correlation of nickel is caused by more variability in the sample results with the two greatest nickel concentrations, which may be more indicative of the heterogeneous nature of the samples. Overall, most samples for these three metals fall close to the best fit line, especially for the concentrations close to

the IRGs or Effects-Range Median, which are footnoted on the figures. The ratios of the results using NOAA to USEPA methods for these three metals ranged from 0.5 to 2.6 for copper, 0.4 to 2.6 for lead, and 0.5 to 3.1 for nickel, with average ratios of 1.4, 1.4, and 1.3, respectively. A review of the ratios in Table 1 for the individual samples indicates that most of the ratios for copper and nickel ranged from 1.0 and 1.3, which indicates that very little of these metals are incorporated into the sediment matrix. For lead, the ratios were slightly higher with most of them ranging from 1.2 to 1.4, so slightly more lead may be incorporated into the sediment matrix. Also, in the samples with the greater chemical concentrations, some of the variability may be caused by the heterogeneous nature of the sediment as evident when evaluating the duplicate samples. For example, as seen in Table 1, the copper results at M04-1 using the NOAA methods ranged from 6,421 mg/kg in the original sample and 7,725 mg/kg in the duplicate sample. Using the USEPA methods the concentrations ranged from 6,070 mg/kg in the original sample and 6,490 mg/kg in the duplicate sample, which are similar to the results in the original sample.

Figures 4 through 12 present the correlation plots for the remainder of the metals. These plots were evaluated to understand the differences in the analytical results using these two methods.

The correlation coefficients for aluminum (Figure 4), cadmium, (Figure 6), and manganese (Figure 10) are low (especially aluminum) compared to the R^2 values for the other metals (the low R^2 value for chromium will be discussed in the next paragraph). The NOAA/USEPA ratios are also the greatest for these metals, with average ratios of 4.5 for aluminum, 5.1 for cadmium, and 2.6 for manganese. As discussed above, metals with higher NOAA/USEPA ratios have a larger percentage of these metals are incorporated into the sediment matrix because the NOAA method extracts that portion of the metal from the sediment particle.

For chromium, two correlation plots were generated; one with all the data and one with the data from monitoring station M03-2 removed. The chromium concentration for M03-2 using NOAA methods was 925 mg/kg, which was much higher than the chromium concentrations at that location during the previous six rounds. During previous rounds, chromium concentrations ranged from 94 mg/kg (Round 4) to 137 mg/kg (Round 2). Therefore, there may have been a small piece of metal in the sample aliquot that was analyzed using the NOAA methods but was not present in the aliquot that was analyzed using the USEPA methods which had a chromium concentration of 58.1 mg/kg. If a value of between 94 and 137 mg/kg was used instead of the 925, the NOAA/USEPA ratio for that sample would be 1.6 to 2.4, which is in-line with the NOAA/USEPA ratio for the other samples. After removing that data point, the R^2 values increased to 0.72, which shows relatively good correlation. The average NOAA/USEPA ratio for chromium after removing that sample was 1.8, indicating that a larger amount of chromium is incorporated into the sediment matrix compared to some of the other metals such as copper, lead, and nickel.

Finally, arsenic, iron, silver, and zinc had relatively high R^2 values of 0.88, 0.70, 0.80, and 0.92, respectively. The average NOAA/USEPA ratios for these metals were 1.3, 1.3, 1.4, and 1.2.

Summary

As indicated from Table 1, there were very few non-detections in this data set, but a review of the non-detect values for the USEPA method indicates that any slight difference in the detection limits between the two methods should not impact the project objectives because the detection limits are below the IRGs.

For the primary metals of concern for OU4, copper, nickel, and to a lesser extent lead, the results of this evaluation show that there is a good correlation of sample results between the NOAA and USEPA analytical methods. NOAA results were consistently greater than USEPA results, suggesting, some percentage of these metals are bound up in the sediment matrix, which is extracted in the complete digestion using NOAA method that is not extracted in the recoverable digestion used in the USEPA method.

Although the Navy could realize some cost savings by switching to the USEPA analytical methods for the Interim Offshore Monitoring Program, the cost savings are not significant to warrant changing methods at this time based on the uncertainties in the data as follows:

- If the Navy decided to switch analytical methods for the sampling program, a slight adjustment to the chemical concentrations obtained using the USEPA method would need to be made when conducting a trend analysis, which would slightly increase the chemical concentration in the sediment samples. This adjustment would be done to account for the portion of chemical that is bound to the sediment matrix and not digested using the USEPA method. There would be uncertainty in the adjustment factor because it would only be based on a limited number of samples.

- As presented in the draft Rounds 1 through 7 Interim Offshore Monitoring Program report, metals are only proposed for analysis at three monitoring stations during the next two rounds (Rounds 8 and 9), and at all of the monitoring stations for Round 10. Therefore, compared to the costs for the overall monitoring program, the cost savings involved in switching analytical methods for metals are low, because of the small numbers of samples involved and the lower cost for metals analysis compared to the analysis for the organic chemicals.

Therefore, because of the uncertainty in the adjustment factors that would be needed, and the relatively low cost savings at this time, the Navy is not recommending changing analytical methods for analysis of metals in sediment as part of the Interim Offshore Monitoring Program. The continued use of the NOAA analytical methods for sediment as part of the Interim Offshore Monitoring Program is being recommended primarily because the data are being plotted on trend plots and the first seven rounds were analyzed using NOAA methods. However, the Navy believes that it is appropriate to use USEPA analytical methods for samples that will not be used for trending because of the similarity in the results between the two analytical methods. Also, the Navy is recommending using USEPA analytical methods for the analysis of mussels in future rounds because as discussed above, similar analytical results are expected using the NOAA and USEPA methods.

EVALUATION OF ORGANIC CHEMICAL ANALYTICAL METHODS

Background/Approach

Both NOAA and USEPA methods for analysis of organic chemicals in tissue and sediment samples are similar in instrumentation, technique, and quantification. Therefore, the results obtained using the two methods are expected to yield similar results so chemical analysis for the organic chemicals using the USEPA methods was not conducted for the Round 7 samples. However, an evaluation of the differences in the methods is included herein. The following bullets list the items that were included in this evaluation:

- Method detection limits (MDLs)
- Parameter lists included in analytical methods
- Analytical methods

Results

The following sections present the results of the evaluation of each of the items listed above.

Method Detection Limits

MDLs were obtained from Columbia Analytical Services, Inc. (CAS), Severn Trent Laboratories, Inc. (STL), and TAMU. These MDLs are presented in Tables 3 through 9 for PAHs (Tables 3 and 4), PCBs (Tables 5 and 6), pesticides (Tables 7 and 8), and dioxins in sediment and tissue (Table 9). The target MDLs from the Interim Offshore Monitoring Plan (TtNUS, October 1999) are also presented on the tables. CAS and STL do not have current MDLs for some of the chemical groups that are included in the standard analyte list. The MDLs for sediment and dioxin tissue results are presented on a dry weight

basis; other tissue results are presented on a wet weight basis. The MDLs for the tissue samples from CAS (with the exceptions of dioxins) are presented on a wet weight basis. The MDLs listed in the tables are similar for the three laboratories, indicating the low detections limits that meet the project objectives can be obtained using standard USEPA methods.

Parameter Lists

There are some differences in the compound lists between the laboratories and the analytical methods. The following bullets present a summary of these differences:

- **PAHs:** All of the PAHs and alkylated PAHs can be obtained using the SW-846 8270 SIM analytical method; however, CAS and STL do not have established MDLs for all the parameters as presented in Tables 3 and 4. The MDLs would need to be calculated by the laboratory selected for the chemical analysis before sampling. Also, the Navy is considering eliminating alkylated PAHs from the Interim Offshore Monitoring Program, so MDLs for those parameters may not be needed.

- **PCBs:** All of the 28 PCB congeners being analyzed for as part of the Interim Offshore Monitoring program can be analyzed for using USEPA method SW-846 method 8082.

- **Pesticides:** The majority of the pesticides being analyzed for as part of the Interim Offshore Monitoring program can be analyzed for using USEPA method SW-846 method 8081. STL would analyze chloropyrifos by SW-846 Method 8141 and CAS would analyze pentachloroanisole by SW-846 Method 8151. STL would analyze pentachloroanisole, pentachlorobenzene, 1,2,3,4-tetrachlorobenzene, and 1,2,4,5- tetrachlorobenzene by SW-846 Method 8270, the same method they would use for the PAHs. Therefore, at least two different analytical methods would be needed to obtain results for all of the pesticides, if NOAA methods were not used. However, the five pesticides listed above that are included in "typical" analytical lists were not identified as chemicals of concern (COCs) in the Interim Record of Decision (ROD) for OU4 (Navy, 1999), do not have IRGs established for them, and are not currently being used to make any decisions for OU4. Therefore, the Navy proposes removing those pesticides from the list of analytical procedures for future sampling events if USEPA methods are used.

- **Dioxins/Furans:** All of the dioxins/furans being analyzed for as part of the Interim Offshore Monitoring program can be analyzed for using USEPA Method 1613 with similar detection limits as the NOAA methods.

Analytical Methods

In general, the extraction and analytical methods are similar between the NOAA and USEPA methods. The methods used by TAMU are presented as Standard Operating Procedures (SOPs) adapted from the technical memorandum on the sampling and analytical methods of the Mussel Watch Project (NOAA, 1998). The methods used by STL and CAS are based on Test Methods for Evaluating Solid Waste; Physical/Chemical Methods (SW-846), 3rd edition, up to and including Update III, Office of Solid Waste and Emergency Response, Washington, DC., and Chemical Analyses of Water and Wastewater. The following bullets summarize the USEPA analytical methods and the SOPs for each group of parameters:

- PAHs: TAMU SOP 9733; CAS and STL SW-846 8270 SIM.
- PCBs: TAMU SOP 9810; CAS and STL SW-846 8082.
- Pesticides: TAMU SOP 9810; CAS and STL SW-846 8081.
- Dioxins: TAMU SOP 9722; CAS and STL USEPA 1613.

Summary

The proposed USEPA analytical methods can obtain similar MDLs as the NOAA methods and any differences in the MDLs will not impact the project objectives. Therefore, the impact of MDLs should have no bearing on whether USEPA analytical methods can be used in future sampling rounds.

All of the parameters being analyzed as part of the Interim Offshore Monitoring Program can be analyzed using USEPA methods; however, additional analytical methods will need to be utilized to obtain the current list of pesticides. The Navy proposes removing five pesticides from the parameter list (chloropyrifos, pentachloroanisole, pentachlorobenzene, 1,2,3,4-tetrachlorobenzene, and 1,2,4,5-tetrachlorobenzene) for future rounds because the pesticides are not typically included in the standard SW-846 Method 8081 list, are not listed as COCs in the Interim ROD for OU4, and no decisions for OU4 are being made based on these chemicals:

All of the other parameters can be measured using standard USEPA analytical methods, although laboratory specific MDLs would need to be obtained for some of the parameters before selecting the laboratory for analysis. Also, the Navy is considering eliminating alkylated PAHs from the Interim Offshore Monitoring Program.

The USEPA analytical methods proposed by CAS and STL are similar to the SOPs provided by TAMU. The analytical methods should not impact the quality of data produced and the project objectives will be achieved using USEPA methodology.

OVERALL RECOMMENDATIONS

The following bullets summarize the overall recommendations for this memorandum:

- Use NOAA analytical methods for metals analysis of sediment samples at the monitoring and reference stations as part of the Interim Offshore Monitoring Program stations for data that will be used for chemical trend plots; consider using USEPA analytical methods for sediment samples that will not be included in the trend plots (i.e., extent samples).
- Use USEPA analytical methods for metals analysis of mussel samples at the monitoring and reference stations as part of the Interim Offshore Monitoring Program stations.
- Use USEPA analytical methods for organic chemical analysis of sediment and mussel samples at the monitoring and reference stations as part of the Interim Offshore Monitoring Program stations provided that the detection limits are low enough to meet project objectives.
- Remove chloropyrifos, pentachloroanisole, pentachlorobenzene, 1,2,3,4-tetrachlorobenzene, and 1,2,4,5-tetrachlorobenzene from the parameter list for future Interim Offshore Monitoring Program sampling rounds.

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TABLE 1

METALS RESULTS USING NOAA AND USEPA ANALYTICAL METHODS
EVALUATION OF ANALYTICAL METHODS MEMORANDUM
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

	Aluminum			Arsenic			Cadmium			Chromium		
Station	NOAA (mg/kg)	USEPA (mg/kg)	Ratio	NOAA (mg/kg)	USEPA (mg/kg)	Ratio	NOAA (mg/kg)	USEPA (mg/kg)	Ratio	NOAA (mg/kg)	USEPA (mg/kg)	Ratio[1]
M01-1	48,335	5,040	9.6	7.2	4.9	1.5	0.45 U	0.08 B	NA	97.4	30.8	3.2
M03-2	64,801	9,060	7.2	17.7	10.6	1.7	0.46 U	0.8	NA	925	58.1	15.9
M04-1	38,231	7,870	4.9	26.3	36.2	0.7	0.57 J	1.2	0.5	206	157	1.3
M04-1D	39,400	10,100	3.9	25.4	23.8	1.1	1.0	1	1.0	210	111	1.9
M05-1	80,242	20,300	4.0	59.6	49	1.2	1.5 J	1.5	1.0	155 J	68.4	2.3
M08-1	39,664 J	19,100	2.1	21.2	17.6	1.2	8.5	3	2.8	188	133	1.4
M08-1D	39,768 J	17,100	2.3	21.5	16.2	1.3	9.0	2.7	3.3	182	118	1.5
M08-2	45,646 J	12,600	3.6	13.6	10.9	1.2	3.1	0.71	4.3	115	74.3	1.5
M09-1	54,927 J	18,400	3.0	24.2	20.6	1.2	5.6	1.2	4.7	138	103	1.3
M09-2	34,866 J	7,960	4.4	13	11.7	1.1	4.3	0.63	6.8	94	47.5	2.0
M09-3	39,764 J	16,600	2.4	21.2	19.2	1.1	5.8	1.2	4.8	138	93	1.5
M11-3	32,113 J	9,460	3.4	22.6	14.2	1.6	8.1	2.4	3.4	215	83.7	2.6
M12-1	45,717 J	10,500	4.4	18.0	11.9	1.5	5.6	0.5	11.2	145	63	2.3
M13-1	62,366	14,200	4.4	15.9	12.1	1.3	0.47 U	0.68	NA	137 J	67.8	2.0
R01-2	30,335 J	3,750	8.1	5.0	3.3	1.5	1.7	0.07 B	NA	31.5	16.2	1.9
R01-4	38,200 J	5,540	6.9	7.2	4.8	1.5	1.9	0.12	15.7	38.3	24.4	1.6
R03-1	23,119 J	13,400	1.7	7.4	8.3	0.9	2.3	0.36	6.3	48.0	43.8	1.1
Minimum	23,119	3,750	1.7	4.99	3.3	0.7	0.45	0.07	0.5	31.5	16.2	1.1
Maximum	80,242	20,300	9.6	59.6	49	1.7	9.0	3.0	15.7	925	157	15.9
Average	44,558	11,822	4.5	19.2	16.2	1.3	3.5	1.1	5.1	180	76.1	1.8
Median	39,764	10,500	4.0	18.0	12.1	1.2	2.3	0.8	4.3	138	68.4	1.7

TABLE 1

METALS RESULTS USING NOAA AND USEPA ANALYTICAL METHODS
EVALUATION OF ANALYTICAL METHODS MEMORANDUM
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

	Copper			Iron			Lead			Manganese		
Station	NOAA (mg/kg)	USEPA (mg/kg)	Ratio	NOAA (mg/kg)	USEPA (mg/kg)	Ratio	NOAA (mg/kg)	USEPA (mg/kg)	Ratio	NOAA (mg/kg)	USEPA (mg/kg)	Ratio
M01-1	68.3	29.7	2.3	15,562	9,540	1.6	63	53.9	1.2	641	88.6	7.2
M03-2	732	1,580	0.5	34,919	31,500	1.1	180	229	0.8	460	185	2.5
M04-1	6,421	6,070	1.1	76,871	141,000	0.5	747	521	1.4	1,576	522	3.0
M04-1D	7,725	6,490	1.2	75,344	87,000	0.9	834	575	1.5	966	615	1.6
M05-1	685 J	553	1.2	41,758	37,900	1.1	694 J	541	1.3	589	385	1.5
M08-1	1,958	1,880	1.0	56,465	43,300	1.3	2,187	1,690	1.3	554	350	1.6
M08-1D	1,878	1,690	1.1	58,158	40,200	1.4	1,976	1,560	1.3	537	315	1.7
M08-2	446	349	1.3	34,024	21,600	1.6	439	372	1.2	394	175	2.2
M09-1	1,145	1,100	1.0	50,716	36,200	1.4	762	614	1.2	771	595	1.3
M09-2	526	517	1.0	31,909	22,800	1.4	519	382	1.4	720	491	1.5
M09-3	785	608	1.3	39,955	30,700	1.3	704	568	1.2	689	466	1.5
M11-3	2,628	1,020	2.6	56,674	40,300	1.4	1,843	774	2.4	509	262	1.9
M12-1	421	322	1.3	52,818	32,400	1.6	410	372	1.1	492	251	2.0
M13-1	111 J	46.8	2.4	24,602	20,900	1.2	97.7 J	60.4	1.6	408	212	1.9
R01-2	5.1	5.7 U	NA	11,502	5,830	2.0	23.6	9	2.6	417	62.8	6.6
R01-4	6.3	8.1 U	NA	12,855	8,680	1.5	27.2	13.7	2.0	251	68.5	3.7
R03-1	13.1	21.1 U	NA	13,731	16,500	0.8	37.8	95.4	0.4	316	152	2.1
Minimum	5.1	5.7	0.5	11,502	5,830	0.5	23.6	9	0.4	251	62.8	1.3
Maximum	7,725	6,490	2.6	76,871	141,000	2.0	2187	1,690	2.6	1,576	615	7.2
Average	1,503	1,311	1.4	40,462	36,844	1.3	679	496	1.4	605	306	2.6
Median	685	553	1.2	39,955	31,500	1.4	519	382	1.3	537	262	1.9

TABLE 1

METALS RESULTS USING NOAA AND USEPA ANALYTICAL METHODS
EVALUATION OF ANALYTICAL METHODS MEMORANDUM
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

	Nickel			Silver			Zinc		
Station	NOAA (mg/kg)	USEPA (mg/kg)	Ratio	NOAA (mg/kg)	USEPA (mg/kg)	Ratio	NOAA (mg/kg)	USEPA (mg/kg)	Ratio
M01-1	18.8 J	12	1.6	0.28	0.21	1.3	128	64.2	2.0
M03-2	315 J	103	3.1	1.4	1.4	1.0	535	629	0.8
M04-1	385 J	500	0.8	1.4	0.62	2.2	1,629	1,520	1.1
M04-1D	287 J	284	1.0	1.3	0.82	1.6	1,755	1,540	1.1
M05-1	76.5	75.3	1.0	1.5	1.4	1.1	698	638	1.1
M08-1	197	179	1.1	3.7	3.4	1.1	1581	1530	1.0
M08-1D	190	173	1.1	3.9	3.7	1.0	1506	1290	1.2
M08-2	64.1	51.4	1.2	1.5	1.1	1.3	365	323	1.1
M09-1	228	217	1.0	2.5	2.6	1.0	695	733	0.9
M09-2	140	153	0.9	2.1	1.2	1.7	515	465	1.1
M09-3	208	175	1.2	3.0	2.5	1.2	618	569	1.1
M11-3	172	89.8	1.9	9.4	4.5	2.1	1,659	840	2.0
M12-1	101	98.5	1.0	0.78	0.36	2.2	1,937	1,800	1.1
M13-1	28.0	22.1	1.3	0.33	1.2	0.3	180	116	1.6
R01-2	9.0	6 U	NA	0.09 U	0.06 B	NA	25.9	22.7	1.1
R01-4	11.8	8	1.5	0.09 U	0.1	NA	35.7	33.2	1.1
R03-1	11.7	22.9	0.5	0.12 J	0.08 B	NA	49.9	59.2	0.8
Minimum	9.0	6.0	0.5	0.1	0.1	0.3	25.9	22.7	0.8
Maximum	385	500	3.1	9.4	4.5	2.2	1,937	1,800	2.0
Average	144	128	1.3	2.0	1.5	1.4	818	716	1.2
Median	140	98.5	1.1	1.4	1.2	1.3	618	629	1.1

1 - The average and median ratios for chromium do not include the ratio of 15.9.

NOAA - National Oceanic and Atmospheric Administration (Method referenced in NOS ORCA 130)
USEPA - United States Environmental Protection Agency (Analytical Method SW-846, Method 7471A)
Ratio = [NOAA]/[USEPA]

NA - Ratios were not calculated for samples where one value was not detected
U - Nondetected
B - Validated as nondetected
J - Estimated value

TABLE 2

SUMMARY OF RATIOS OF NOAA/USEPA ANALYTICAL RESULTS
EVALUATION OF ANALYTICAL METHODS MEMORANDUM
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Metal	*Minimum Ratio*	*Maximum Ratio*	*Average Ratio*	*Median Ratio*
ALUMINUM	1.7	9.6	4.5	4.0
ARSENIC	0.7	1.7	1.3	1.2
CADMIUM	0.5	15.7	5.1	4.3
CHROMIUM(1)	1.1	15.9	1.8	1.7
COPPER	0.5	2.6	1.3	1.1
IRON	0.5	2.0	1.3	1.4
LEAD	0.4	2.6	1.4	1.3
MANGANESE	1.3	7.2	2.6	1.9
NICKEL	0.5	3.1	1.3	1.1
SILVER	0.3	2.2	1.4	1.3
ZINC	0.8	2.0	1.2	1.1

1 - The average and median ratios for chromium do not include the ratio of 15.9.

Ratio = [NOAA]/[USEPA] (see Table 1)
NOAA - National Oceanic and Atmospheric Administration (Method referenced in NOS ORCA 130)
USEPA - United States Environmental Protection Agency (Analytical Method SW-846, Method 7471A)

TABLE 3

MDLs AND LABORATORY REPORTING LIMITS - PAHs IN TISSUE
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Target MDL[1] (µg/kg dry weight	TAMU MDL[2] (µg/kg dry weight)	CAS MDL[2,3] (µg/kg wet weight)	STL MDL[2,4] (µg/kg dry weight)
Analytical Method		GERG SOP 9733	SW-846 8270 SIM	SW-846 8270 SIM
1-Methylnaphthalene	20	3.15	0.13	--
1-Methylphenanthrene	20	3.16	0.053	--
2-Methylnaphthalene	20	4.05	0.15	--
2,6-Dimethylnaphthalene	20	2.88	0.11	--
1,6,7-Trimethylnaphthalene	20	3.48	0.074	--
Acenaphthene	20	3.85	0.074	--
Acenaphthylene	20	2.84	0.05	--
Anthracene	20	2.77	0.055	--
Biphenyl	20	3.35	0.068	--
Dibenzothiophene	20	1.88	0.14	--
Fluorene	20	3.88	0.054	--
Naphthalene	20	4.73	0.26	--
Phenanthrene	20	3.07	0.066	--
Benz(a)anthracene	20	2.09	0.054	--
Benzo(a)pyrene	20	4.15	0.076	--
Benzo(b)fluoranthene	20	6.80	0.045	--
Benzo(e)pyrene	20	4.66	0.012	--
Benzo(g,h,i)perylene	20	5.70	0.097	--
Benzo(k)fluoranthene	20	3.83	0.081	--
Chrysene	20	2.75	0.08	--
Dibenz(a,h)anthracene	20	5.90	0.079	--
Fluoranthene	20	2.68	0.053	--
Indeno(1,2,3-c,d)pyrene	20	10.7	0.073	--
Perylene	20	9.50	0.10	--
Pyrene	20	2.61	0.070	--
Alkylated PAHs				
C1-Naphthalenes	20	7.20	--	--
C2-Naphthalenes	20	5.76	--	--
C3-Napthalenes	20	6.96	--	--
C4-Naphthalenes	20	6.96	--	--
C1-Fluorenes	20	7.76	--	--
C2-Fluorenes	20	7.76	--	--
C3-Fluorenes	20	7.76	--	--

TABLE 3

MDLs AND LABORATORY REPORTING LIMITS - PAHs IN TISSUE
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Target MDL(1) (µg/kg dry weight	TAMU MDL(2) (µg/kg dry weight)	CAS MDL(2,3) (µg/kg wet weight)	STL MDL(2,4) (µg/kg dry weight)
C1-Phenanthrenes/Anthracenes	20	5.54	--	--
C2-Phenanthrenes/Anthracenes	20	5.54	--	--
C3-Phenanthrenes/Anthracenes	20	5.54	--	--
C4-Phenanthrenes/Anthracenes	20	5.54	--	--
C1-Dibenzothiophenes	20	3.76	--	--
C2-Dibenzothiophenes	20	3.76	--	--
C3-Dibenzothiophenes	20	3.76	--	--
C1-Fluoranthenes/Pyrenes	20	5.22	--	--
C1-Chrysenes	20	5.50	--	--
C2-Chrysenes	20	5.50	--	--
C3-Chrysenes	20	5.50	--	--
C4-Chrysenes	20	5.50	--	--

1 The Target MDLs are from the QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations: Chemical Evaluations U.S. EPA, Office of Water, Office of Science and Technology. EPA 823-B-95-001. 1995.
2 All positive results will be reported by the laboratory.
3 CAS does not currently have MDLs for alkylated PAHs by SW-846 Method 8270 SIM.
4 STL does not currently have MDLs for PAHs or alkylated PAHs by SW-846 Method 8270 SIM.

Abbreviations:
TAMU = Texas A&M University
CAS = Columbia Analytical Services
STL = Severn Trent Laboratory
GERG = Geochemical and Environmental Research Group
SOP = Standard Operating Procedure
SIM = Selected Ion Monitoring
MDL = Method Detection Limit
PAH = Polycyclic Aromatic Hydrocarbon

TABLE 4

MDLs AND LABORATORY REPORTING LIMITS - PAHs IN SEDIMENT
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE
PAGE 1 OF 2

Compound	Target Sediment MDL(1) (µg/kg dry weight)	TAMU MDL(2) (µg/kg dry weight)	CAS MDL(2) (µg/kg dry weight)	STL MDL(2,3) (µg/kg dry weight)
Analytical Method		GERG SOP 9733	SW-846 8270 SIM	SW-846 8270 SIM
1-Methylnaphthalene	20	2.35	0.20	0.0962
1-Methylphenanthrene	20	0.77	0.11	0.120
2-Methylnaphthalene	20	3.21	0.21	0.125
2,6-Dimethylnaphthalene	20	2.09	0.13	0.0822
1,6,7-Trimethylnaphthalene	20	1.30	0.18	0.0941
Acenaphthene	20	0.52	0.21	0.141
Acenaphthylene	20	0.78	0.16	0.0799
Anthracene	20	0.52	0.19	0.132
Biphenyl	20	0.83	0.18	0.0886
Dibenzothiophene	20	0.75	0.19	0.113
Fluorene	20	0.80	0.17	0.157
Naphthalene	20	3.64	0.21	0.111
Phenanthrene	20	2.96	0.15	0.416
Benz(a)anthracene	20	0.94	0.13	0.314
Benzo(a)pyrene	20	2.55	0.14	0.207
Benzo(b)fluoranthene	20	1.31	0.14	0.668
Benzo(e)pyrene	20	1.23	0.12	0.188
Benzo(g,h,i)perylene	20	2.46	0.10	0.680
Benzo(k)fluoranthene	20	0.49	0.15	0.540
Chrysene	20	0.40	0.15	0.634
Dibenz(a,h)anthracene	20	0.99	0.18	1.18
Fluoranthene	20	1.18	0.17	0.558
Indeno(1,2,3-c,d)pyrene	20	1.33	0.15	0.921
Perylene	20	2.46	0.18	0.470
Pyrene	20	1.96	0.11	0.547
Alkylated PAHs				
C1-Naphthalenes	20	5.56	2.5	--
C2-Naphthalenes	20	4.18	2.5	--
C3-Naphthalenes	20	2.60	2.5	--
C4-Naphthalenes	20	2.60	2.5	--
C1-Fluorenes	20	1.60	2.5	--
C2-Fluorenes	20	1.60	2.5	--

TABLE 4

MDLs AND LABORATORY REPORTING LIMITS - PAHs IN SEDIMENT
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Target Sediment MDL(1) (µg/kg dry weight)	TAMU MDL(2) (µg/kg dry weight)	CAS MDL(2) (µg/kg dry weight)	STL MDL(2,3) (µg/kg dry weight)
C3-Fluorenes	20	1.60	2.5	--
C1-Phenanthrenes/Anthracenes	20	1.54	2.5	--
C2-Phenanthrenes/Anthracenes	20	1.54	2.5	--
C3-Phenanthrenes/Anthracenes	20	1.54	2.5	--
C4-Phenanthrenes/Anthracenes	20	1.54	2.5	--
C1-Dibenzothiophenes	20	1.50	2.5	--
C2-Dibenzothiophenes	20	1.50	2.5	--
C3-Dibenzothiophenes	20	1.50	2.5	--
C1-Fluoranthenes/Pyrenes	20	3.14	2.5	--
C1-Chrysenes	20	0.80	2.5	--
C2-Chrysenes	20	0.80	2.5	--
C3-Chrysenes	20	0.80	2.5	--
C4-Chrysenes	20	0.80	2.5	--

1 The Target MDLs are from the QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluaitons: Chemical Evaluations U.S. EPA, Office of Water, Office of Science and Technology. EPA 823-B-95-001. 1995
2 All positive results will be reported by the laboratory.
3 STL does not currently have MDLs for alkylated PAHs by SW-846 Method 8270 SIM.

Abbreviations:
TAMU = Texas A&M University
CAS = Columbia Analytical Services
STL = Severn Trent Laboratory
GERG = Geochemical and Environmental Research Group
SOP = Standard Operating Procedure
SIM = Selected Ion Monitoring
MDL = Method Detection Limit
PAH = Polycyclic Aromatic Hydrocarbon

TABLE 5

MDLs AND LABORATORY REPORTING LIMITS - PCBs IN TISSUE
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Target Tissue MDL(1) (µg/kg dry weight)	TAMU MDL(2) (µg/kg dry weight)	CAS MDL(2) (µg/kg wet weight)	STL MDL(2) (µg/kg dry weight)
Analytical Method		GERG SOP 9810	SW-846 Method 8082	SW-846 Method 8082
PCB 8	2	2.02	0.14	0.4952
PCB 18	2	3.27	0.11	0.4380
PCB 28	2	0.99	0.31	0.4394
PCB 44	2	0.73	0.063	0.3760
PCB 52	2	0.85	0.080	0.4903
PCB 66	2	1.20	0.073	0.3237
PCB 77	2	1.0	0.092	0.3032
PCB 81	2	1	0.082	0.2699
PCB 101	2	1.07	0.065	0.3248
PCB 105	2	0.97	0.21	0.1722
PCB 114	2	1	0.32	0.2167
PCB 118	2	1.77	0.10	0.2117
PCB 123	2	1	0.11	0.3423
PCB 126	2	1.0	0.12	0.1929
PCB 128	2	0.96	0.091	0.3247
PCB 138	2	1.80	0.23	0.1426
PCB 153	2	1.27	0.15	0.3941
PCB 156	2	1	0.13	0.1571
PCB 157	2	1	0.082	0.4841
PCB 167	2	1	0.22	0.2519
PCB 169	2	1.0	0.085	0.0611
PCB 170	2	10.4(3)	0.080	0.1943
PCB 180	2	1.33	0.11	0.4585
PCB 187	2	0.88	0.18	0.2407
PCB 189	2	1	0.089	0.0750
PCB 195	2	1.04	0.095	0.1211
PCB 206	2	1.08	0.077	0.5385
PCB 209	2	1.41	0.095	0.1977

1 The Target MDLs are from the QA/QC Guidance for Sampoing and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations: Chemical Evaluations U.S. EPA, Office of Water, Office of Science and Technology. EPA 823-B-95-001. 1995.
2 All positive results will be reported by the laboratory.
3 Interference from phthalate.

Abbreviations:
TAMU = Texas A&M University
CAS = Columbia Analytical Services
STL = Severn Trent Laboratory
GERG = Geochemical and Environmental Research Group
SOP = Standard Operating Procedure
SIM = Selected Ion Monitoring
MDL = Method Detection Limit
PCB = Polychlorinated biphenyl

TABLE 6

MDLs AND LABORATORY REPORTING LIMITS - PCBs IN SEDIMENT
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Target Sediment MDL(1) (µg/kg dry weight)	TAMU MDL(2) (µg/kg dry weight)	CAS MDL(2) (µg/kg dry weight)	STL MDL(2) (µg/kg dry weight)
Analytical Method		GERG SOP9810	SW-846 Method 8082	SW-846 Method 8082
PCB 8	1	0.095	0.087	0.0598
PCB 18	1	0.071	0.029	0.0639
PCB 28	1	0.028	0.25	0.0613
PCB 44	1	0.052	0.18	0.0677
PCB 52	1	0.113	0.047	0.1315
PCB 66	1	0.050	0.037	0.0901
PCB 77	1	0.050	0.065	0.0573
PCB 81	1	0.05	0.030	0.0774
PCB 101	1	0.064	0.030	0.0860
PCB 105	1	0.049	0.040	0.3975
PCB 114	1	0.05	0.075	0.0912
PCB 118	1	0.096	0.039	0.0845
PCB 123	1	0.05	0.034	0.0897
PCB 126	1	0.050	0.039	0.0708
PCB 128	1	0.099	0.25	0.1584
PCB 138	1	0.042	0.030	0.0844
PCB 153	1	0.073	0.039	0.0941
PCB 156	1	0.05	0.043	0.0747
PCB 157	1	0.05	0.035	0.0858
PCB 167	1	0.05	0.033	0.0866
PCB 169	1	0.050	0.032	0.0760
PCB 170	1	0.443(3)	0.033	0.1205
PCB 180	1	0.031	0.031	0.0795
PCB 187	1	0.046	0.036	0.0872
PCB 189	1	0.05	0.030	0.0894
PCB 195	1	0.028	0.041	0.0984
PCB 206	1	0.031	0.055	0.0972
PCB 209	1	0.037	0.050	0.0908

1 The Target MDLs are from the QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations: Chemical Evaluations U.S. EPA, Office of Water, Office of Science and Technology. EPA 823-B-95-001. 1995.
2 All positive results will be reported by the laboratory.
3 Interference from phthalate.

Abbreviations:
TAMU = Texas A&M University
CAS = Columbia Analytical Services
STL = Severn Trent Laboratory
GERG = Geochemical and Environmental Research Group
SOP = Standard Operating Procedure
SIM = Selected Ion Monitoring
MDL = Method Detection Limit
PCB = Polychlorinated biphenyl

TABLE 7

MDLs AND LABORATORY REPORTING LIMITS - PESTICIDES IN TISSUE
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Target Tissue MDL[1] (µg/kg dry weight)	TAMU MDL[2] (µg/kg dry weight)	CAS MDL[2] (µg/kg wet weight)	STL MDL[2] (µg/kg dry weight)
Analytical Method		GERG SOP 9810	SW-846 Method 8081	SW-846 Method 8081
2,4' DDD	10	0.89	0.18	0.2377
2,4' DDE	10	1.38	0.096	0.2818
2,4' DDT	10	1.01	0.22	0.0861
4,4'-DDD	10	1.01	0.13	0.4649
4,4'-DDE	10	1.71	0.12	0.1817
4,4'-DDT	10	1.26	0.38	0.2522
Aldrin	10	1.05	0.20	0.1252
Alpha Chlordane	10	0.90	0.36	0.1809
Alpha HCH	10	1.29	0.16	0.1874
Beta HCH	10	1.58	0.21	0.2192
Chlorpyrifos	10	4.09	0.17	--[5]
Cis-Nonachlor	10	0.76	0.12	0.1618
Delta HCH	10	0.58	0.34	0.1810
Dieldrin	10	1.24	0.11	0.1795
Endosulfan II	10	2.03	0.35	0.0889
Endrin	10	1.95	0.099	0.1480
Gamma Chlordane	10	0.73	0.14	0.1701
Gamma HCH	10	1.15	0.28	0.2997
Heptachlor	10	1.34	0.45	0.1043
Heptachlor Epoxide	10	0.30	0.15	0.1959
Hexachlorobenzene	10	2.13	0.34	0.5389
Mirex	10	0.70	0.27	0.1340
Oxychlordane	10	0.88	0.077	0.2637
Pentachlorobenzene	10	3.33	--[4]	--[6]
Pentachloroanisole	10	1.50	--[3]	--[6]
Tetrachlorobenzene 1,2,3,4	10	2.47	--[4]	--[6]
Tetrachlorobenzene 1,2,4,5	10	8.38	--[4]	--[6]
Trans-Nonachlor	10	0.97	0.051	0.1409

1 The Target MDLs are from the QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations: Chemical Evaluations U.S. EPA, Office of Water, Office of Science and Technology. EPA 823-B-95-001. 1995.
2 All positive results will be reported by the laboratory.
3 CAS proposes analyzing pentachloroanisole by SW-846 Method 8151 but does not currently have MDLs.

4 CAS proposes doing these compounds by SW-846 Method 8081 but does not currently have MDLs.
5 STL proposes doing chlorpyrifos by SW-846 Method 8141 but does not currently have MDLs.
6 STL proposes doing these compounds by SW-846 Method 8270 but does not currently have MDLs.

Abbreviations:
TAMU = Texas A&M University
CAS = Columbia Analytical Services
STL = Severn Trent Laboratory
GERG = Geochemical and Environmental Research Group
SOP = Standard Operating Procedure
SIM = Selected Ion Monitoring
MDL = Method Detection Limit

TABLE 8

MDLs AND LABORATORY REPORTING LIMITS - PESTICIDES IN SEDIMENT
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	Target Sediment MDL[1] (µg/kg dry weight)	TAMU MDL[2] (µg/kg dry weight)	CAS MDL[2] (µg/kg dry weight)	STL MDL[2] (µg/kg dry weight)
Analytical Method		GERG SOP 9810	SW-846 Method 8081	SW-846 Method 8081
2,4' DDD	2	0.032	0.16	0.0307
2,4' DDE	2	0.090	0.069	0.1127
2,4' DDT	2	0.060	0.080	0.0261
4,4'-DDD	2	0.046	0.093	0.0296
4,4'-DDE	2	0.018	0.076	0.0662
4,4'-DDT	2	0.034	0.17	0.0315
Aldrin	2	0.036	0.25	0.0298
Alpha Chlordane	2	0.015	0.062	0.0265
Alpha HCH	2	0.073	0.083	0.1307
Beta HCH	2	0.088	0.22	0.0730
Chlorpyrifos	2	0.127	0.27	--[5]
Cis-Nonachlor	2	0.050	0.13	0.0280
Delta HCH	2	0.036	0.14	0.1026
Dieldrin	2	0.040	0.082	0.0274
Endosulfan II	2	0.101	0.061	0.0499
Endrin	2	0.197	0.24	0.0291
Gamma Chlordane	2	0.062	0.038	0.0297
Gamma HCH	2	0.021	0.099	0.0240
Heptachlor Epoxide	2	0.020	0.14	0.0543
Heptahclor	2	0.077	0.097	0.1134
Hexachlorobenzene	2	0.051	0.16	0.1182
Mirex	2	0.032	0.068	0.0551
Oxychlordane	2	0.019	0.15	0.0175
Pentachloroanisole	2	0.024	50[3]	--[6]
Pentachlorobenzene	2	0.234	--[4]	--[6]
Tetrachlorobenzene 1,2,3,4	2	0.134	--[4]	--[6]
Tetrachlorobenzene 1,2,4,5	2	0.331	--[4]	--[6]
Trans-Nonachlor	2	0.047	0.095	0.0197

1 The Target MDLs are from the QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations: Chemical Evaluations U.S. EPA, Office of Water, Office of Science and Technology. EPA 823-B-95-001. 1995.
2 All positive results will be reported by the laboratory.
3 CAS proposes analyzing pentachloroanisole by SW-846 Method 8151.

4 CAS proposes doing these compounds by SW-846 Method 8081 but does not currently have MDLs.
5 STL proposes doing chlorpyrifos by SW-846 Method 8141 but does not currently have MDLs.
6 STL proposes doing these compounds by SW-846 Method 8270 but does not currently have MDLs.

Abbreviations:
TAMU = Texas A&M University
CAS = Columbia Analytical Services
STL = Severn Trent Laboratory
GERG = Geochemical and Environmental Research Group
SOP = Standard Operating Procedure
SIM = Selected Ion Monitoring
MDL = Method Detection Limit

TABLE 9

MDLs AND LABORATORY REPORTING LIMITS – DIOXINS IN SEDIMENT/TISSUE PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Compound	TAMU MDL[1] (µg/kg dry weight)	CAS MDL[1] (µg/kg dry weight)	STL MDL[1] (µg/kg dry weight)
Analytical Method	GERG SOP 9722	EPA Method 1613	EPA Method 1613
2,3,7,8-TCDD	1.0	1.0	1.0
Total TCDD	1.0	1.0	1.0
2,3,7,8-TCDF	1.0	1.0	1.0
Total TCDF	1.0	1.0	1.0
1,2,3,7,8-PeCDD	5.0	2.5	5.0
Total PeCDD	5.0	2.5	5.0
1,2,3,7,8-PeCDF	5.0	2.5	5.0
2,3,4,7,8-PeCDF	5.0	2.5	5.0
Total PeCDF	5.0	2.5	5.0
1,2,3,4,7,8-HxCDD	5.0	2.5	5.0
1,2,3,6,7,8-HxCDD	5.0	2.5	5.0
1,2,3,7,8,9-HxCDD	5.0	2.5	5.0
Total HxCDD	5.0	2.5	5.0
1,2,3,4,7,8-HxCDF	5.0	2.5	5.0
1,2,3,6,7,8-HxCDF	5.0	2.5	5.0
1,2,3,7,8,9-HxCDF	5.0	2.5	5.0
2,3,4,6,7,8-HxCDF	5.0	2.5	5.0
Total HxCDF	5.0	2.5	5.0
1,2,3,4,6,7,8-HpCDD	5.0	2.5	5.0
Total HpCDD	5.0	2.5	5.0
1,2,3,4,6,7,8-HpCDF	5.0	2.5	5.0
1,2,3,4,7,8,9-HpCDF	5.0	2.5	5.0
Total HpCDF	5.0	2.5	5.0
OCDD	10.0	5.0	10.0
OCDF	10.0	5.0	10.0

1 All positive results will be reported by the laboratory.

Abbreviations:
TAMU = Texas A&M University
CAS = Columbia Analytical Services

STL = Severn Trent Laboratory
GERG = Geochemical and Environmental Research Group
SOP = Standard Operating Procedure
SIM = Selected Ion Monitoring
MDL = Method Detection Limit

Figure 1
Copper Concentrations for Samples Analyzed Using USEPA and NOAA Methods
Evaluation of Analytical Methods Memorandum
Portsmouth Naval Shipyard, Kittery, Maine

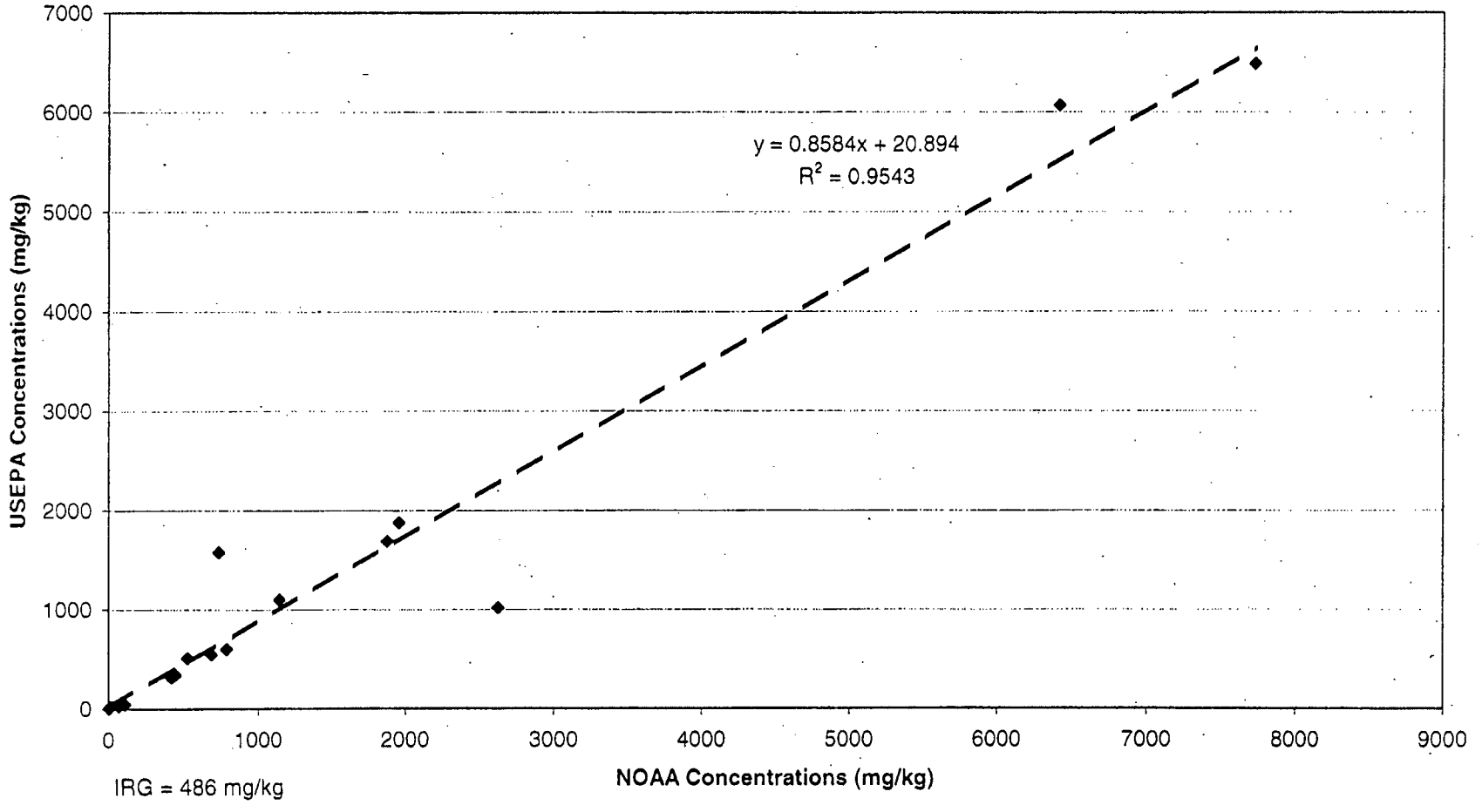


Figure 2
Lead Concentrations for Sample Analyzed Using USEPA and NOAA Methods
Evaluation of Analytical Methods Memorandum
Portsmouth Naval Shipyard, Kittery, Maine

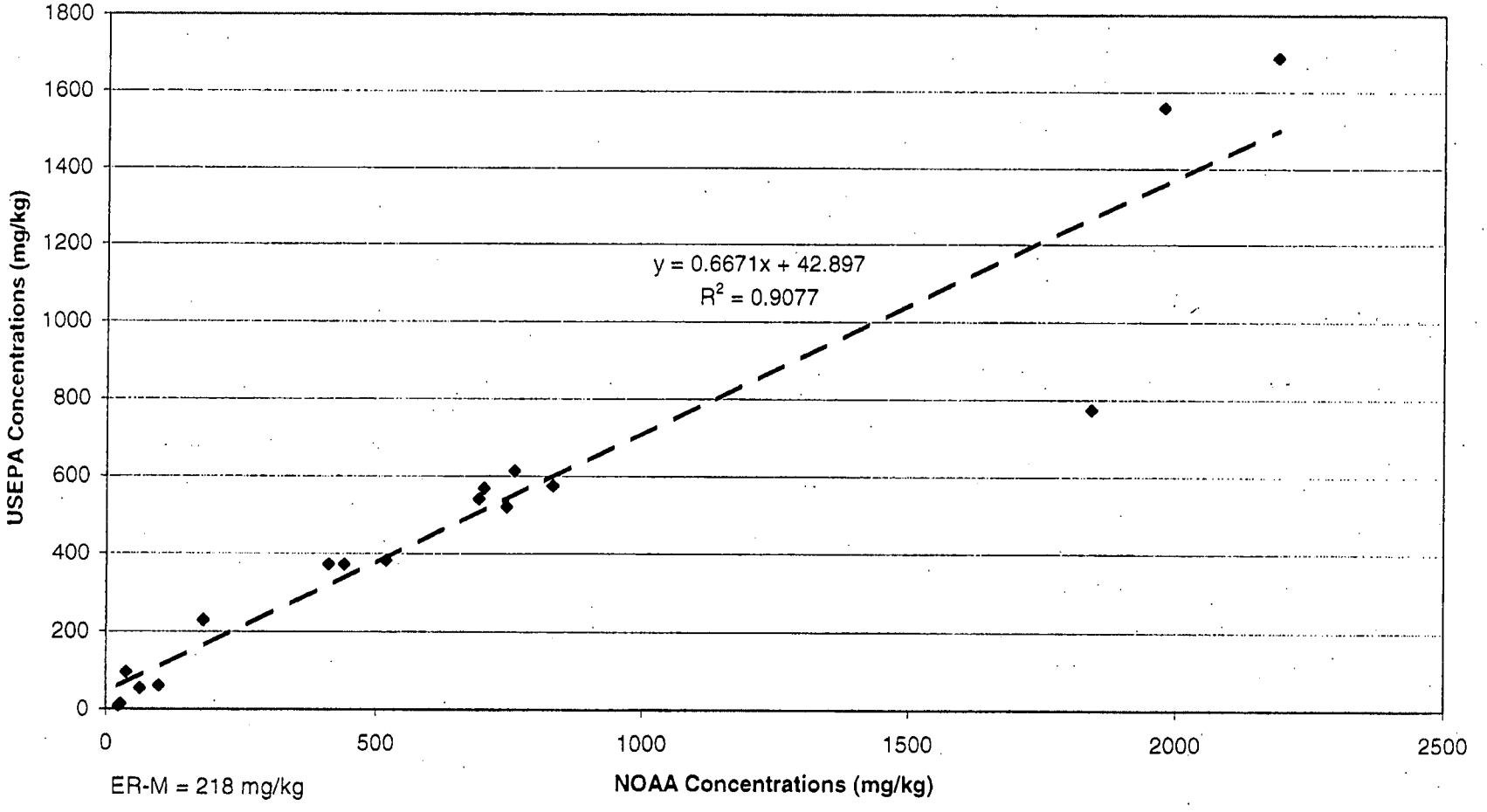


Figure 3
Nickel Concentrations for Samples Analyzed Using USEPA and NOAA Methods
Evaluation of Analytical Methods Memorandum
Portsmouth Naval Shipyard, Kittery, Maine

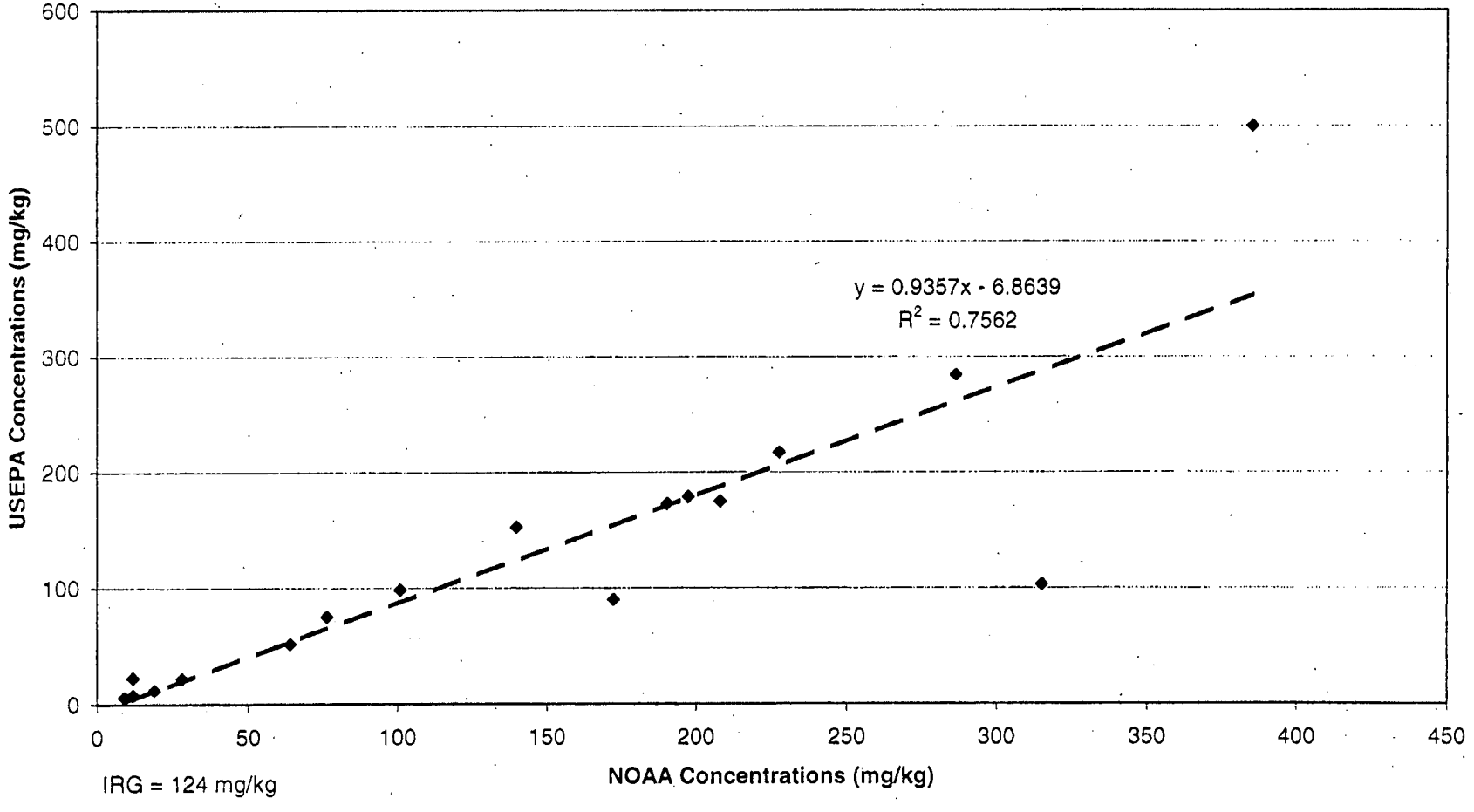


Figure 4
Aluminum Concentrations for Samples Analyzed Using USEPA and NOAA Methods
Evaluation of Analytical Methods Memorandum
Portsmouth Naval Shipyard, Kittery, Maine

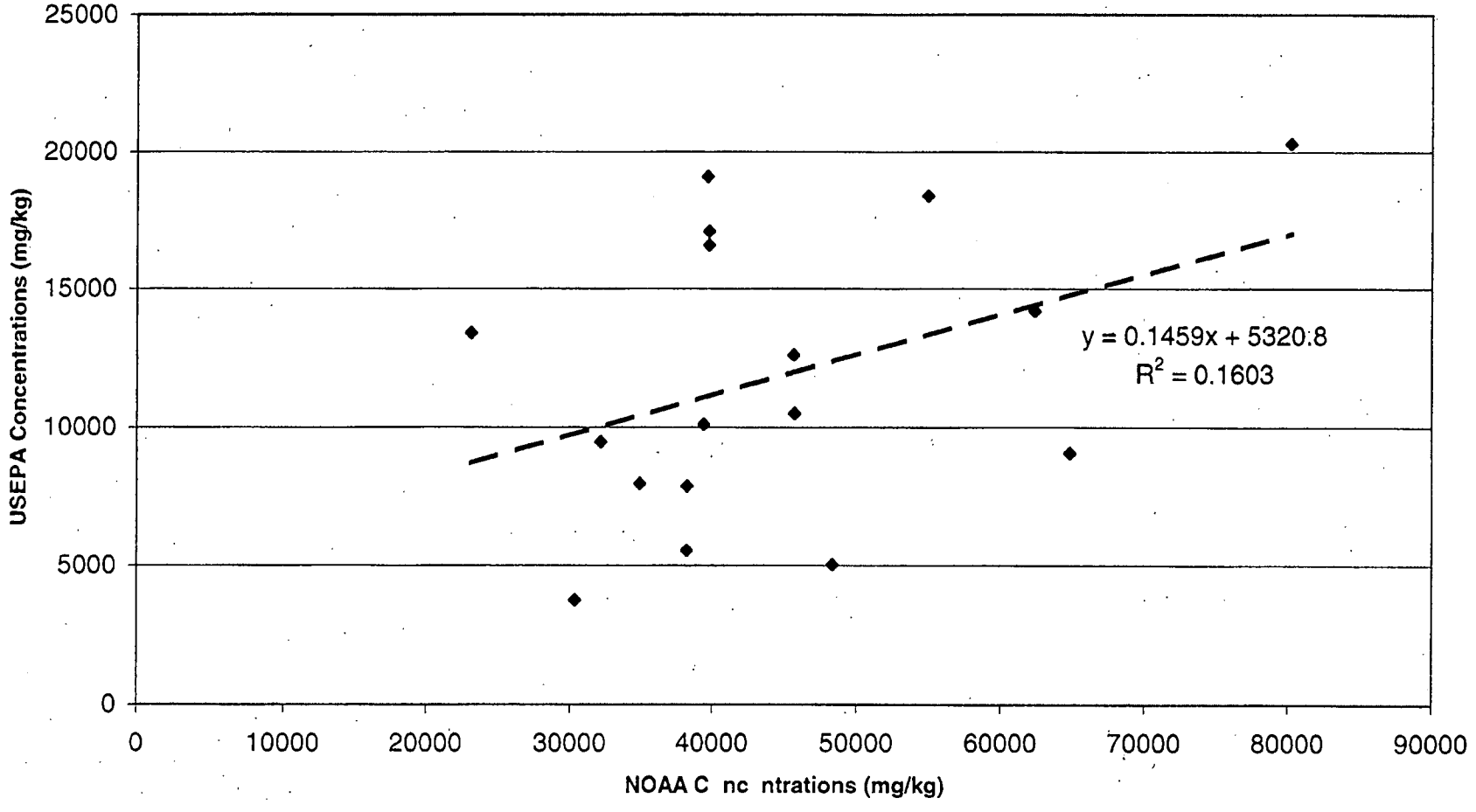


Figure 5
Arsenic Concetrations for Samples Analyzed Using USEPA and NOAA Methods
Evaluation of Analytical Methods Memorandum
Portsmouth Naval Shipyard, Kittery, Maine

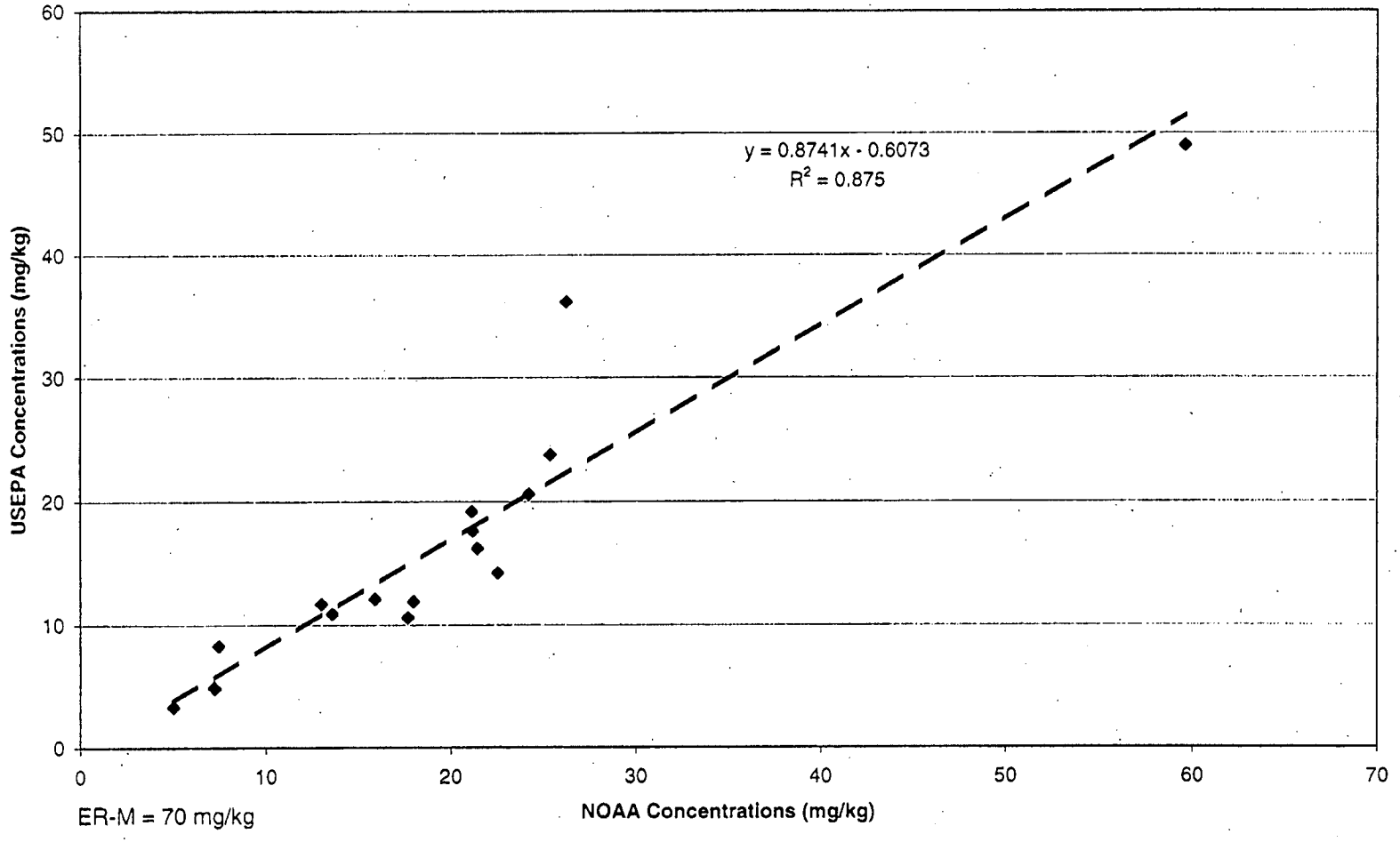


Figure 6
Cadmium Concentrations for Samples Analyzed Using USEPA and NOAA Methods
Evaluation of Analytical Methods Memorandum
Portsmouth Naval Shipyard, Kittery, Maine

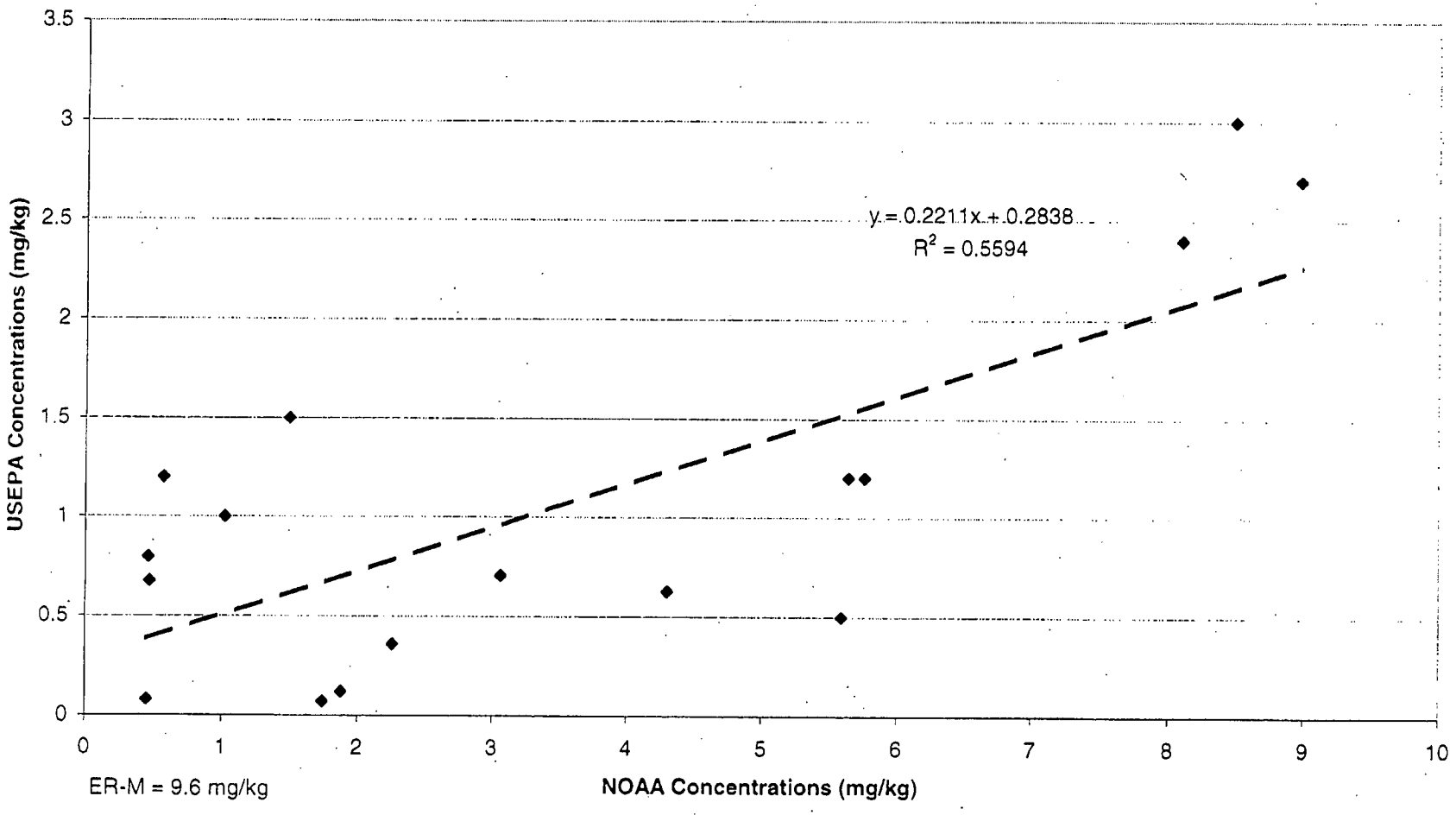


Figure 7
Chromium Concentrations for Samples Analyzed Using USEPA and NOAA Methods
Evaluation of Analytical Methods Memorandum
Portsmouth Naval Shipyard, Kittery, Maine

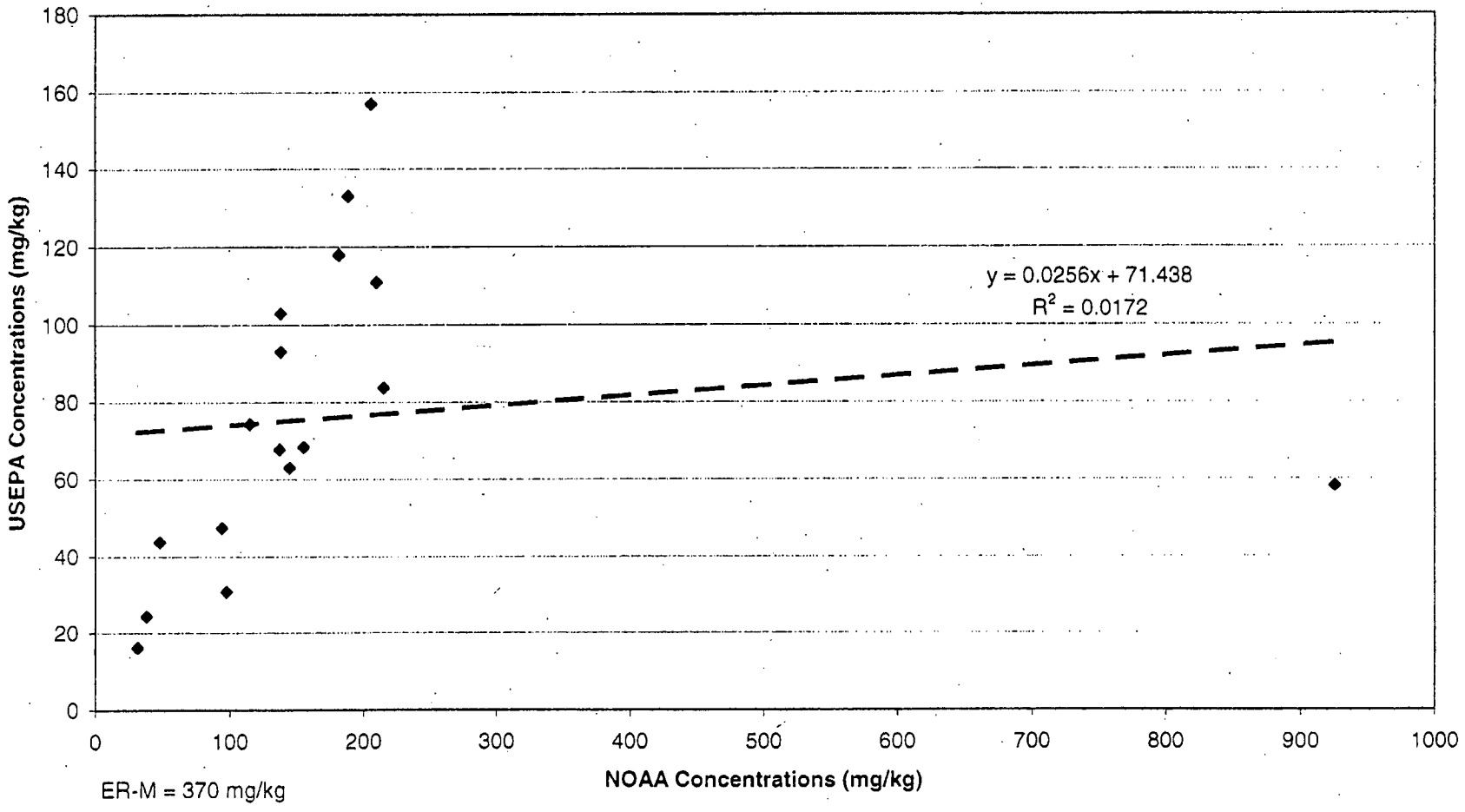


Figure 8
Chromium Concentrations for Samples Analyzed Using USEPA and NOAA Methods
(excluding sample OU4-SD-M03-203A)
Evaluation of Analytical Methods Memorandum
Portsmouth Naval Shipyard, Kittery, Maine

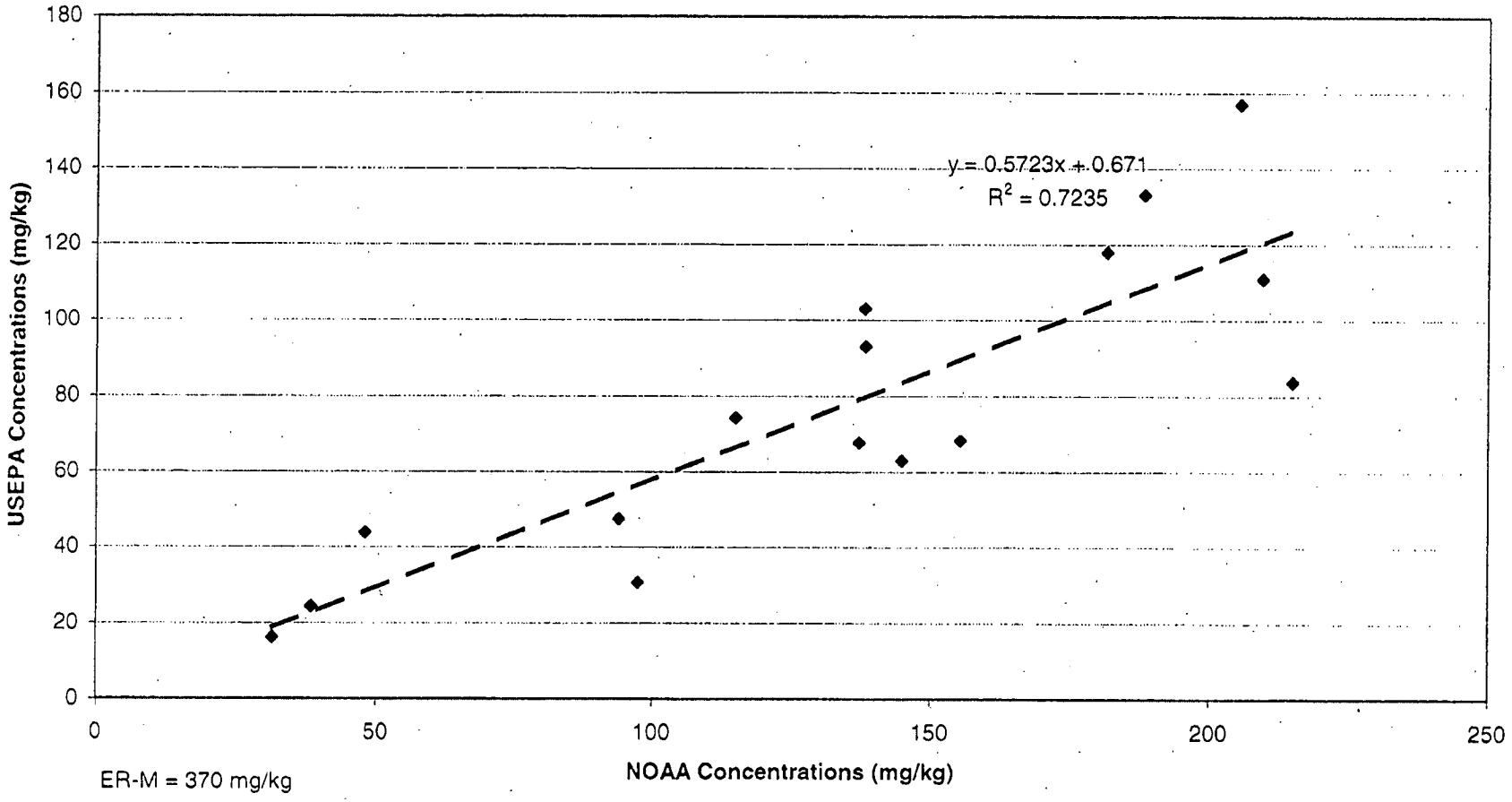


Figure 9
Iron Concentrations for Samples Analyzed Using USEPA and NOAA Methods
Evaluation of Analytical Methods Memorandum
Portsmouth Naval Shipyard, Kittery, Maine

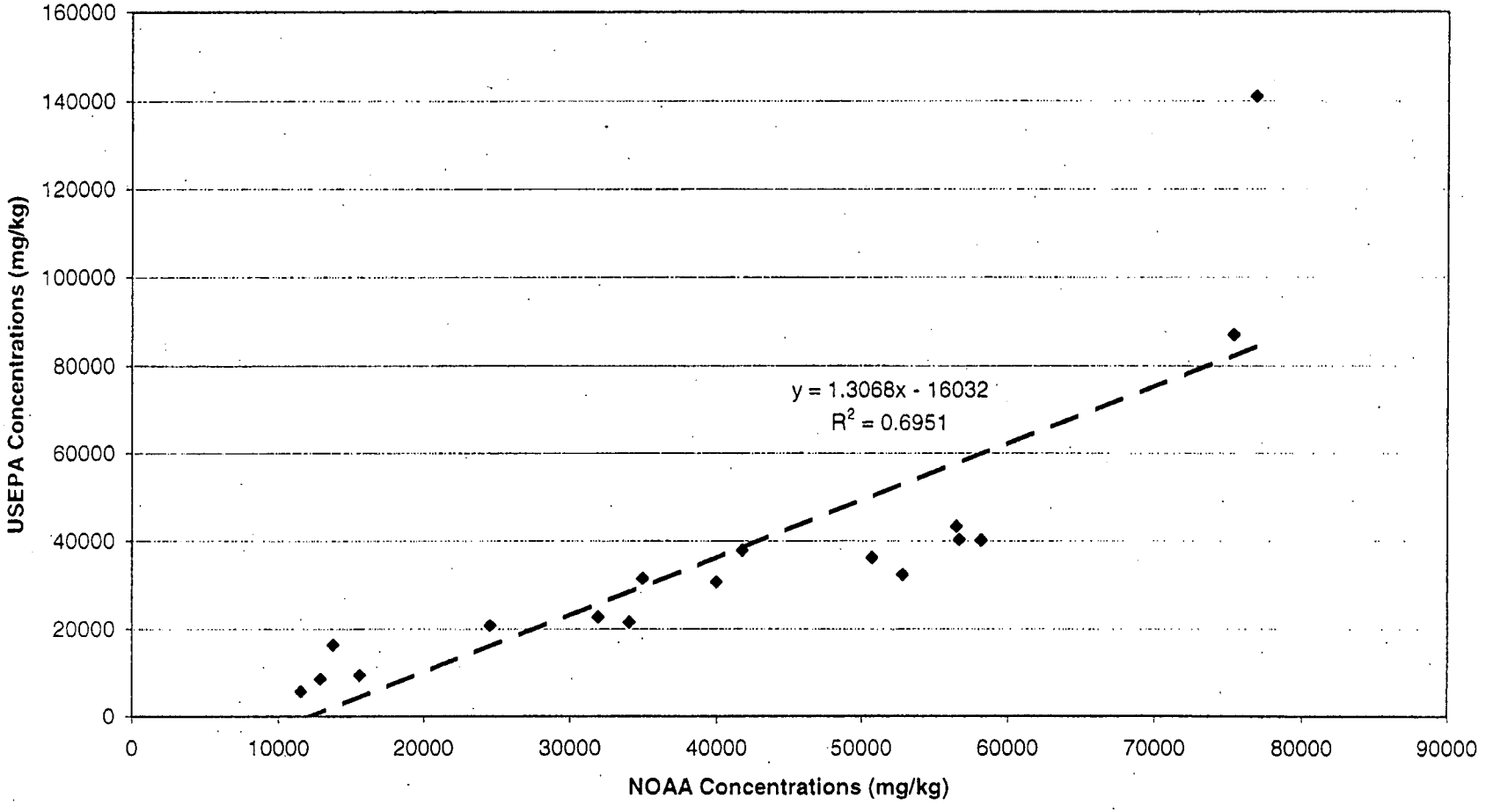


Figure 10
Manganese Concentrations for Samples Analyzed Using USEPA and NOAA Methods
Evaluation of Analytical Methods Memorandum
Portsmouth Naval Shipyard, Kittery, Maine

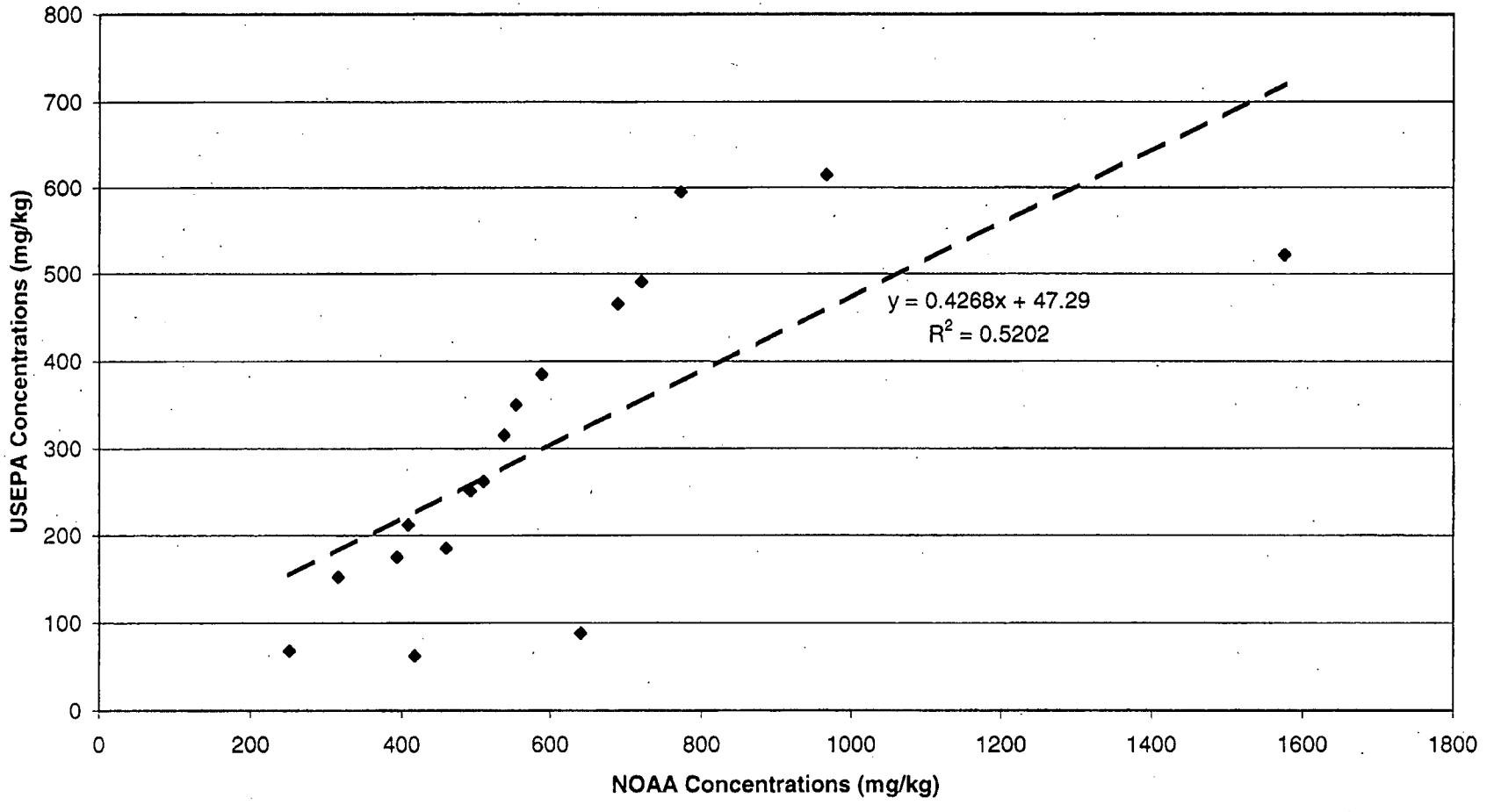


Figure 11
Silver Concentrations for Samples Analyzed Using USEPA and NOAA Methods
Evaluation of Analytical Methods Memorandum
Portsmouth Naval Shipyard, Kittery, Maine

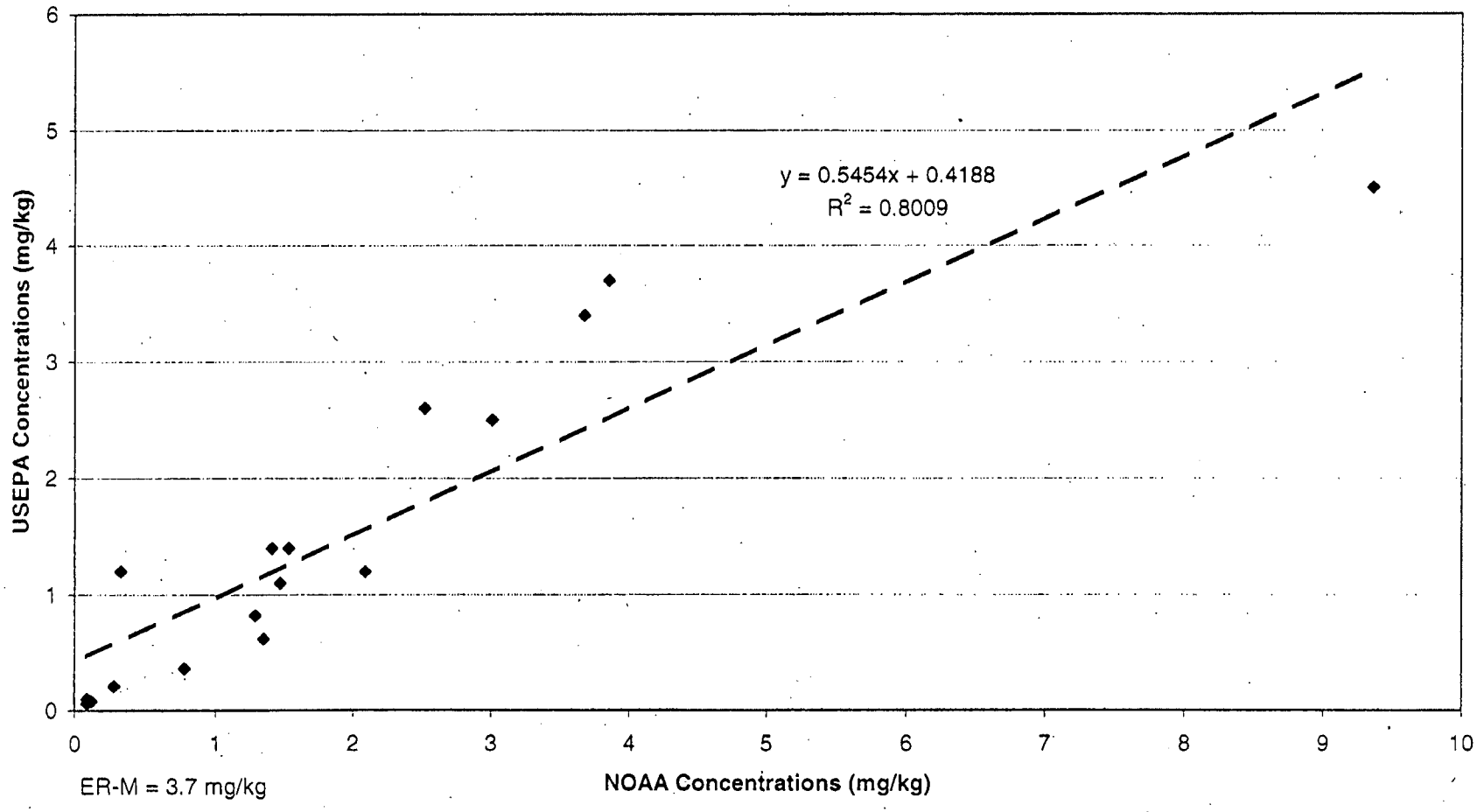
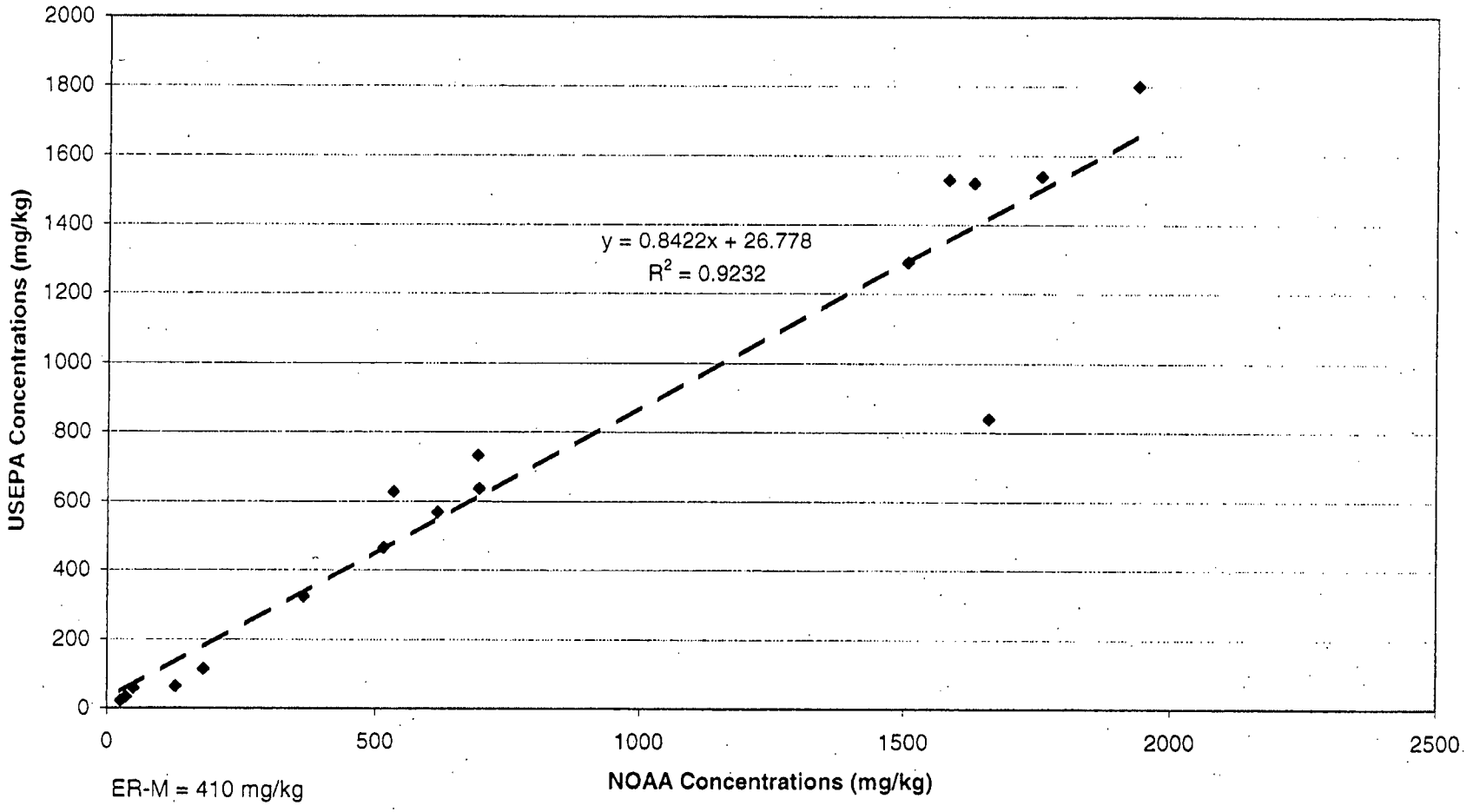


Figure 12
Zinc Concentrations for Samples Analyzed Using USEPA and NOAA Methods
Evaluation of Analytical Methods Memorandum
Portsmouth Naval Shipyard, Kittery, Maine



RESPONSE TO COMMENTS ON THE TECHNICAL MEMORANDA

RESPONSES TO MEDEP COMMENTS DATED JULY 23, 2004
TECHNICAL MEMORANDUM, RECOMMENDED ADDITIONAL SCRUTINY AT MONITORING STATIONS M05, M08, AND M09
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

1. **Comment:** The MEDEP agrees with the Navy's recommendations in this technical memorandum. We also recognize that this tech memo is specifically to address additional scrutiny for those three stations that have been affected by construction activities at OU3. However, it would be useful to point out that the "Rounds 1 through 7 Interim Offshore Monitoring Program Report" recommended other stations besides MS5, MS8 and MS9 for additional scrutiny (for different reasons). As written it seems to indicate that stations 5, 8 and 9 are the only stations recommended for additional scrutiny.

   Our July 2, 2004 comment letter on the Rounds 1 through 7 Interim Offshore Monitoring Program Report discusses the MEDEP's concerns regarding additional scrutiny at monitoring stations MS1 and MS12. However, as the subject tech memo discusses only those stations affected by OU3 construction we will not repeat those concerns here.

   Response: A technical memorandum for additional scrutiny at monitoring stations M01, M11, and M12 will be submitted. The first paragraph of the memorandum clarifies that additional scrutiny was recommended at other stations.

2. **Comment:** Monitoring Station M05

   Are the samples in the first ring (locations 4 – 6) within the former location of the silt curtain?

   Response: As discussed during the May 12, 2004 technical meeting, there was both a silt curtain and turbidity curtain present in Jamaica Cove, but the silt curtain was removed when waste excavation was completed. The locations of the silt curtain and turbidity curtain were not surveyed, so their exact location is not known. Also, the turbidity curtain moved slightly with the tides. However, based on site photographs during construction, it is likely that the samples in the first ring are within the former location of the turbidity curtain, but it is not as likely that all three samples are within the former location of the silt curtain.

3. **Comment:** Monitoring Station M09

   "...it is not known whether the location 3 was within the turbidity curtain."

   Are there any construction photos that may shed light on this?

   Response: It is not possible to determine if location 3 was within the turbidity curtain from the construction photographs of the area of Clark Cove by monitoring station M09.

RESPONSES TO NOAA COMMENTS DATED JUNE 22, 2004
TECHNICAL MEMORANDUM, RECOMMENDED ADDITIONAL SCRUTINY AT MONITORING STATIONS M05, M08, AND M09
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

1. **Comment:** Thank-you for the Technical Memorandum for Additional Scrutiny at Monitoring Stations M05, M08, and M09, PNSY, Kittery, Maine, June 18, 2004. NOAA participated in the May 12, 2004 meeting whereby the Navy, State of Maine, EPA, USF&WS and NOAA discussed these and the other eleven monitoring stations. NOAA finds the sampling plan for these three stations very adequate but questions why other stations also were not included for further scrutiny. My notes (in quotes) from the May 2004 meeting are provided below and discrepancies shown.

   Response: Comment noted. The additional scrutiny recommended for the other monitoring stations will be provided separately as discussed in the responses herein.

2. **Comment:** Station 01: "The concentration trend is above the IRG. The Navy is suggesting further scrutiny – fingerprinting the PAHs – to see if the PAHs are from the Site 34 Ash Pile or from offsite discharges into the estuary." There is no mention of this station in the document.

   Response: The Navy is recommending conducting PAHs fingerprinting as part of the additional scrutiny at monitoring station M01 to see if the PAHs are from the ash present at Site 34 or from offsite discharges into the estuary. This recommendation is provided in the technical memorandum for additional scrutiny at monitoring stations M01, M11, and M12 (dated October 4, 2004).

3. **Comment:** Station 03 and 04: "High metal concentrations from slag deposits. The modestly high PAHs are puzzling. Is this from the nearby parking lot? The Navy has offered further scrutiny of the PAHs. In addition, the metal slag is breaking down and likely becoming more and more available." Again, these two stations are not included.

   Response: Additional scrutiny for copper and nickel at monitoring stations M03 and M04 was not recommended as part of the OU4 monitoring program because additional scrutiny has occurred in the area represented by those stations as part of the Site 32 RI (Phase 1). PAHs will be evaluated in the planning for the Phase 2 RI for Site 32 to determine the additional scrutiny that is recommended for these chemicals.

4. **Comment:** Station 11. "The Station is next to DRMO. No sediment in sample locations 1 and 2. Use BAFs from mussels to estimate expected sediment concentrations. Lead was very high in the sediment from sample #3 but not in the mussels. The Navy wants to complete further scrutiny to learn if DRMO remains a source." As before, the Station is not included in the Technical Memorandum.

Response: The Navy is recommending additional scrutiny at monitoring station M11 to determine if DRMO remains a source of metals to the offshore area. This recommendation is provided in the technical memorandum for additional scrutiny at monitoring stations M01, M11, and M12 (dated October 4, 2004).

5. **Comment:** Station 12. "High PAHs at this station. The Navy wants to learn the source and plans to complete further scrutiny although the adjacent Navy facilities are the likely source." The Site is not mentioned in the Technical Memorandum.

   Response: The Navy is recommending conducting additional scrutiny at monitoring station M12 to see if the PAHs are related to activities from PNS Installation Restoration Program sites or are related to other sources. This recommendation is provided in the technical memorandum for additional scrutiny at monitoring stations M01, M11, and M12 (dated October 4, 2004).

6. **Comment:** In fairness to the Navy, these other Stations may be addressed later. But NOAA believes one plan and one mobilization are more cost-effective and may answer the remaining questions concerning the source of the contamination.

   Response: Comment noted. The Navy will need conduct the additional scrutiny in the most cost-effective manner as possible depending upon the availability of funding.

RESPONSE TO USEPA COMMENTS DATED NOVEMBER 18, 2004
TECHNICAL MEMORANDUM: RECOMMENDED ADDITIONAL SCRUTINY AT MONITORING STATIONS M01, M11, and M12
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

General Comments

The proposed additional scrutiny is generally appropriate and should provide additional information regarding the previously observed trends in OU4. However, it is not entirely clear the effort will add additional value to the current assessment regarding the nexus between off-shore sediments and on-shore contaminant source areas. It would appear that the continuation of the monitoring program would, in some instances, be more beneficial. In other instances the memorandum is vague in its description of additional sampling or inconsistent with its approach towards different monitoring stations.

1. Comment: M01

1. It is not clear what the purpose of this question is. Based on the Navy's prior trend analysis this question appears academic. Expected anomalies and variations were seemingly addressed with the establishment of a 90% confidence interval. Given this, a larger data set (i.e. continued monitoring) would provide more evidence to support trend validity than the proposed effort.

   Third Bullet. While a correlation coefficient would help determine if variability is influencing established trend lines, it is unclear what such a value would effectively mean. That is, what value of R^2 would call into question the current trend analysis?

2. *First Bullet.* Does the forensic analysis account for the differences in degradation between soils and sediments?

3. As with PAHs a simple comparison with the reference station concentrations indicates a lack of material contribution of DDT to MS-01.

Response:

1. The Navy agrees that a larger data set will provide good evidence to support the validity of the concentration trend plots, but it is important to determine if chemical concentrations are really increasing as part of the additional scrutiny because this could signify a continuing source of contamination at that station. As will be presented in the DQOs, whether the trend is increasing will be one line of evidence to determine if there is a continuing source of PAHs at MS-01. Although the trend plots are showing an increasing trend, much of the increase appears to be caused by relatively low PAHs concentrations during Round 1 and a high concentration at one location during Round 7. Based on a visual review of the data, the trend appears relatively flat, with the concentrations varying from round to round. For example, the concentrations of fluorene at MS-01, Loc 3 increase then decrease in every subsequent round and the concentration in Round 7 is slightly lower than the concentration in Round 1.

   The third bullet indicates that a coefficient of variation (CV) will be calculated, not a

correlation coefficient. Therefore, correlation coefficient (R) value will not be calculated. As part of the development of the data Quality Objectives (DQOs), it was determined that the CV would not be useful for evaluating trend lines so CVs will not be calculated as part of the additional scrutiny. The reason is that an increasing (or decreasing trend) would have a high CV, as would a flat trend with concentrations increasing and decreasing each round such as for fluorene, as discussed above. Therefore, it would be difficult to draw any conclusions based on the CV of the data.

2. As part of the PAH forensics analysis, concentrations of approximately 50 PAH analytes that are representative of hundreds of individual PAH isomers will be determined. The numerous PAH analytes will reveal a rich hydrocarbon signature that can be used to estimate weathering patterns and a wide range of PAH sources simultaneously. Weathering effects will not be confused with source signatures.

3. The reference stations were located in areas where only minimal, if any, spraying of DDT would have occurred, so low levels of DDT in the sediment were expected. Therefore, although the DDT concentrations detected in the sediment at MS-01 are greater than the concentrations in the reference stations, the DDT concentrations may be similar to concentrations in background/regional locations where significant spraying of DDT has occurred.

2. Comment: M11

1. Additional scrutiny of MS-01 involves significant work designed to assess the potential contribution of up-gradient source areas. MS-11 contains no such similar effort. The Navy should attempt to address this question of sediment transport specifically addressing the MS-12 and Site 10 area.

   Second Bullet. Has the Navy considered the collection of river water for suspended solids and analysis of total lead?

2. As with MS-01, based on the Navy's prior trend analysis this question appears academic.

   First Bullet. Again, the Navy's approach to specific monitoring stations is inconsistent. For example, there is no proposal to develop a correlation coefficient for MS-11 or plotting individual location data separately for trend analysis.

Response:

1. If Site 10 were the source of lead at MS-11, then the concentrations of lead at MS-12, which is located in a depositional area immediately adjacent to Site 10, should be much greater than the concentrations at MS-11. However, this is not the case. The concentrations of lead in the sediment at MS-12 are much lower than the concentrations at MS-11. As presented in response to comment documents on the Round 1 through 7 Interim Offshore Monitoring Program report, the Navy believes that there strong evidence that the source of elevated metals in the sediment at MS-11 is the erosion of contaminated soil from the OU2 shoreline, not contamination from Site 10. Therefore, the Navy will collect several surface soil samples in erosional areas along the shoreline

as part of the additional scrutiny to determine whether the soil from the OU2 shoreline is the likely source of metals at MS-11.

The Navy has not considered the collection of river water for suspended solids and analysis of total lead because it is not clear how that data would be used. Surface water samples were collected from the river for analysis of lead as part of the Estuarine Ecological Risk Assessment (NCCOSC, 2000), and the concentrations were much less than the water quality criteria.

2. Please see the Navy's response to USEPA Comment No. 1.

   The approach for conducting additional scrutiny for each monitoring stations is based on site-specific data so the approach may not be the same for each station. The specific data needs for each station will be detailed in the QAPP for the additional scrutiny.

3. **Comment: M12**

   1. Again, based on the Navy's prior trend analysis this question appears academic.

      Third Bullet. As with MS-11, the Navy's approach to specific monitoring stations is inconsistent. For example, there is no proposal to develop a coefficient of variability?

   2. *First Bullet.* As with MS-01 does the forensic analysis account for the differences in PAH transformation between different environments?

      Third Bullet. A simple comparison with the reference station concentrations indicates a lack of contribution of PAHs from potential up-gradient source areas.

   3. *Second Bullet.* While the offshore sampling effort would seem to answer it the first half of the question, that is "is Site 10 the source of lead contamination?", it would seem insufficient to answer the remaining question "if sampling indicates that contamination is not from Site 10, what *is* the source?". The description of "collect sediment samples offshore by Site 10" is too vague to evaluate in terms of potential effectiveness to answer both questions.

      Also, the additional scrutiny at MS-12 should involve some effort to evaluate the potential for sediment transport to MS-11.

   Response:

   1. Please see the Navy's responses to USEPA Comment Nos. 1.1 and 2.1.

   2. Please see the Navy's responses to USEPA Comment No. 1.2.

   3. The Navy agrees that the collected data may not be able to answer the second part of the question. However, it may be difficult, if even possible to determine the source of the elevated lead levels in the sediment especially if they are from historic inputs that are no longer present. Some of this will be presented in the DQOs for MS-12.

RESPONSE TO MEDEP COMMENTS DATED NOVEMBER 10, 2004
TECHNICAL MEMORANDUM: RECOMMENDED ADDITIONAL SCRUTINY AT MONITORING STATIONS M01, M11, and M12
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

1. **Comment:** M1, 2

   "Evaluate source signature of PAHs..."

   Please clarify if this refers to determining whether the PAHs or pyrogenic or petrogenic.

   Response: The source signature will determine more than whether the PAHs are pyrogenic or petrogenic. Specifically for MS-1, the PAH forensics will attempt to determine whether the signature of the PAHs in the sediment is similar to the signature of the PAHs in the ash at Site 34, or whether it is similar to other sources such as urban runoff, diesel fuel, etc.

2. **Comment:** M1, 3

   "Evaluate on-shore DDT data to determine if there is a link to the DDT levels in the offshore area."

   What sort of evaluation will this entail?

   "Evaluate the concentrations of pesticides in the on-shore and off-shore area."

   Weren't these areas already analyzed for pesticides?

   Response: The evaluation will be qualitative to try to determine if the concentrations of pesticides detected in the sediment are from activities related to Site 34 or to typical spraying activities across the shipyard. The Navy acknowledges that it may be difficult to reach a definitive conclusion regarding the source of the DDT in the sediment at MS-01 and ultimately professional judgment will be used to determine the likelihood regarding whether Site 34 is the source.

3. **Comment:** M11

   The Navy should also investigate if there is a source of lead from upstream of MS11, such as Site 10 and/or MS12.

   Response: Please see Navy's response to USEPA Comment No. 2.1 dated November 18, 2004.

4. **Comment:** M11, 1

   "Review data for onshore soils at Sites 6 and 29."

What specifically will the data be reviewed for in relation to MS11?

Response: The chemical data for the surface soil samples collected along the OU2 shoreline will be reviewed for MS-11.

5. **Comment:** M12, 2

"Evaluate source signature of PAHs in floor in Building 178 and compare to signatures observed in sediment at MS-12."

A positive correlation would be useful information. However, a negative correlation does not mean that Building 178 is not the source of PAHs in M12 sediments.

Response: A negative correlation would likely indicate that Building 178 is not a current source of PAHs to the sediment at MS-12. Also, the evaluation may conclude that the signature of PAHs in the sediment is similar to non-point sources making it more likely the Building 178 is not the source of PAHs at this station.

6. **Comment:** Deliverables

The MEDEP looks forward to receiving the work plan and DQOs in order to review the specifics of the additional scrutiny.

Response: Comment noted.

RESPONSES TO MEDEP COMMENTS DATED JULY 14, 2004
TECHNICAL MEMORANDUM, COMPARISON OF ANALYTICAL METHODS FOR THE INTERIM OFFSHORE MONITORING PROGRAM FOR OPERABLE UNIT 4
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

1. **Comment:** The Maine Department of Environmental Protection has reviewed the document referenced above. The Navy's proposal is acceptable but we do have one comment.

   The Navy states they will consider using EPA analytical methods for sediment samples that will not be included in the trend plots, i.e. extent samples. This is acceptable however the results of these samples in general should not be used to compare to the results of other samples that have been have been analyzed using the NOAA method.

   Response: It is the Navy's understanding that the comment is referring only to sediment samples that are analyzed using USEPA analytical methods. As indicated in the memorandum, although the chemical concentrations were similar using the NOAA and USEPA methods, the NOAA methods yielded greater concentrations for some metals which is why the Navy recommended using the NOAA methods for metals in sediment for samples included in the trend analysis. However, the differences were not great enough to preclude qualitatively comparing the results of other samples analyzed using USEPA methods to samples analyzed using the NOAA method, provided the ratio of the results using the two methods are discussed.

APPENDIX C

STANDARD OPERATING PROCEDURES AND FIELD FORMS

TETRA TECH NUS, INC.	STANDARD OPERATING PROCEDURES	Number HS-1.0	Page 1 of 15
		Effective Date 12/03	Revision 2
		Applicability Tetra Tech NUS, Inc.	
		Prepared Health & Safety	
Subject UTILITY LOCATING AND EXCAVATION CLEARANCE		Approved D. Senovich	

TABLE OF CONTENTS

SECTION **PAGE**

1.0 PURPOSE 2

2.0 SCOPE 2

3.0 GLOSSARY 2

4.0 RESPONSIBILITIES 3

5.0 PROCEDURES 3

5.1 BURIED UTILITIES 3
5.2 OVERHEAD POWER LINES 5

6.0 UNDERGROUND LOCATING TECHNIQUES 5

6.1 GEOPHYSICAL METHODS 5
6.2 PASSIVE DETECTION SURVEYS 6
6.3 INTRUSIVE DETECTION SURVEYS 6

7.0 INTRUSIVE ACTIVITIES SUMMARY 7

8.0 REFERENCES 8

ATTACHMENTS

1 Listing of Underground Utility Clearance Resources 9
2 Frost Line Penetration Depths by Geographic Location 11
3 Utility Clearance Form 12
4 OSHA Letter of Interpretation 13

1.0 PURPOSE

Utilities such as electric service lines, natural or propane gas lines, water and sewage lines, telecommunications, and steam lines are very often in the immediate vicinity of work locations. Contact with underground or overhead utilities can have serious consequences including employee injury/fatality, property and equipment damage, substantial financial impacts, and loss of utility service to users.

The purpose of this procedure is to provide minimum requirements and technical guidelines regarding the appropriate procedures to be followed when performing subsurface and overhead utility locating services. It is the policy of Tetra Tech NUS, Inc. (TtNUS) to provide a safe and healthful work environment for the protection of our employees. The purpose of this Standard Operating Procedure (SOP) is to aid in achieving the objectives of this policy, to present the acceptable procedures pertaining to utility locating and excavation clearance activities, and to present requirements and restrictions relevant to these types of activities. This SOP must be reviewed by any employee potentially involved with underground or overhead utility locating and avoidance activities.

2.0 SCOPE

This procedure applies to all TtNUS field activities where there may be potential contact with underground or overhead utilities. This procedure provides a description of the principles of operation, instrumentation, applicability, and implementability of typical methods used to determine the presence and avoidance of contact with utility services. This procedure is intended to assist with work planning and scheduling, resource planning, field implementation, and subcontractor procurement. Utility locating and excavation clearance requires site-specific information prior to the initiation of any such activities on a specific project. This SOP is not intended to provide a detailed description of methodology and instrument operation. Specialized expertise during both planning and execution of several of the methods presented may also be required.

3.0 GLOSSARY

Electromagnetic Induction (EMI) Survey - A geophysical exploration method whereby electromagnetic fields are induced in the ground and the resultant secondary electromagnetic fields are detected as a measure of ground conductivity.

Magnetometer – A device used for precise and sensitive measurements of magnetic fields.

Magnetic Survey – A geophysical survey method that depends on detection of magnetic anomalies caused by the presence of buried ferromagnetic objects.

Metal Detection – A geophysical survey method that is based on electromagnetic coupling caused by underground conductive objects.

Vertical Gradiometer – A magnetometer equipped with two sensors that are vertically separated by a fixed distance. It is best suited to map near surface features and is less susceptible to deep geologic features.

Ground Penetrating Radar – Ground Penetrating Radar (GPR) involves specialized radar equipment whereby a signal is sent into the ground via a transmitter. Some portion of the signal will be reflected from the subsurface material, which is then recorded with a receiver and electronically converted into a graphic picture.

4.0 RESPONSIBILITIES

Project Manager (PM)/Task Order Manager (TOM) - Responsible for ensuring that all field activities are conducted in accordance with this procedure.

Site Manager (SM)/Field Operations Leader (FOL) - Responsible for the onsite verification that all field activities are performed in compliance with approved SOPs or as otherwise directed by the approved project plan(s).

Site Health & Safety Officer (SHSO) – Responsible to provide technical assistance and verify full compliance with this SOP. The SHSO is also responsible for reporting any deficiencies to the Corporate Health and Safety Manager (HSM) and to the PM/TOM.

Health & Safety Manager (HSM) – Responsible for preparing, implementing, and modifying corporate health and safety policy and this SOP.

Site Personnel – Responsible for performing their work activities in accordance with this SOP and the TtNUS Health and Safety Policy.

5.0 PROCEDURES

This procedure addresses the requirements and technical procedures that must be performed to minimize the potential for contact with underground and overhead utility services. These procedures are addressed individually from a buried and overhead standpoint.

5.1 Buried Utilities

Buried utilities present a heightened concern because their location is not typically obvious by visual observation, and it is common that their presence and/or location is unknown or incorrectly known on client properties. This procedure must be followed prior to beginning any subsurface probing or excavation that might potentially be in the vicinity of underground utility services. In addition, the Utility Clearance Form (Attachment 3) must be completed for every location or cluster of locations where intrusive activities will occur.

Where the positive identification and de-energizing of underground utilities cannot be obtained and confirmed using the following steps, the PM/TOM is responsible for arranging for the procurement of a qualified, experienced, utility locating subcontractor who will accomplish the utility location and demarcation duties specified herein.

1. A comprehensive review must be made of any available property maps, blue lines, or as-builts prior to site activities. Interviews with local personnel familiar with the area should be performed to provide additional information concerning the location of potential underground utilities. Information regarding utility locations shall be added to project maps upon completion of this exercise.

2. A visual site inspection must be performed to compare the site plan information to actual field conditions. Any findings must be documented and the site plan/maps revised. The area(s) of proposed excavation or other subsurface activities must be marked at the site in white paint or pin flags to identify those locations of the proposed intrusive activities. The site inspection should focus on locating surface indications of potential underground utilities. Items of interest include the presence of nearby area lights, telephone service, drainage grates, fire hydrants, electrical service vaults/panels, asphalt/concrete scares and patches, and topographical depressions. Note the location of any emergency shut off switches. Any additional information regarding utility

locations shall be added to project maps upon completion of this exercise and returned to the PM/TOM.

3. If the planned work is to be conducted on private property (e.g., military installations, manufacturing facilities, etc.) the FOL must identify and contact appropriate facility personnel (e.g., public works or facility engineering) before any intrusive work begins to inquire about (and comply with) property owner requirements. It is important to note that private property owners may require several days to several weeks advance notice prior to locating utilities.

4. If the work location is on public property, the state agency that performs utility clearances must be notified (see Attachment 1). State "one-call" services must be notified prior to commencing fieldwork per their requirements. Most one-call services require, by law, 48- to 72-hour advance notice prior to beginning any excavation. Such services typically assign a "ticket" number to the particular site. This ticket number must be recorded for future reference and is valid for a specific period of time, but may be extended by contacting the service again. The utility service will notify utility representatives who then mark their respective lines within the specified time frame. It should be noted that most military installations own their own utilities but may lease service and maintenance from area providers. Given this situation, "one call" systems may still be required to provide location services on military installations.

5. Utilities must be identified and their locations plainly marked using pin flags, spray paint, or other accepted means. The location of all utilities must be noted on a field sketch for future inclusion on project maps. Utility locations are to be identified using the following industry-standard color code scheme, unless the property owner or utility locator service uses a different color code:

white	excavation/subsurface investigation location
red	electrical
yellow	gas, oil, steam
orange	telephone, communications
blue	water, irrigation, slurry
green	sewer, drain

6. Where utility locations are not confirmed with a high degree of confidence through drawings, schematics, location services, etc., the work area must be thoroughly investigated prior to beginning the excavation. In these situations, utilities must be identified using safe and effective methods such as passive and intrusive surveys, or the use of non-conductive hand tools. Also, in situations where such hand tools are used, they should always be used in conjunction with suitable detection equipment, such as the items described in Section 6.0 of this SOP. Each method has advantages and disadvantages including complexity, applicability, and price. It also should be noted that in some states, initial excavation is required by hand to a specified depth.

7. At each location where trenching or excavating will occur using a backhoe or other heavy equipment, and where utility identifications and locations cannot be confirmed prior to groundbreaking, the soil must be probed using a device such as a tile probe which is made of non-conductive material such as fiberglass. If these efforts are not successful in clearing the excavation area of suspect utilities, hand shoveling must be performed for the perimeter of the intended excavation.

8. All utilities uncovered or undermined during excavation must be structurally supported to prevent potential damage. Unless necessary as an emergency corrective measure, TtNUS shall not make any repairs or modifications to existing utility lines without prior permission of the utility owner, property owner, and Corporate HSM. All repairs require that the line be locked-out/tagged-out prior to work.

5.2 Overhead Power Lines

If it is necessary to work within the minimum clearance distance of an overhead power line, the overhead line must be de-energized and grounded, or re-routed by the utility company or a registered electrician. If protective measures such as guarding, isolating, or insulating are provided, these precautions must be adequate to prevent employees from contacting such lines directly with any part of their body or indirectly though conductive materials, tools, or equipment.

The following table provides the required minimum clearances for working in proximity to overhead power lines.

Nominal Voltage	Minimum Clearance
0 -50 kV	10 feet, or one mast length; whichever is greater
50+ kV	10 feet plus 4 inches for every 10 kV over 50 kV or 1.5 mast lengths; whichever is greater

6.0 UNDERGROUND LOCATING TECHNIQUES

A variety of supplemental utility locating approaches are available and can be applied when additional assurance is needed. The selection of the appropriate method(s) to employ is site-specific and should be tailored to the anticipated conditions, site and project constraints, and personnel capabilities.

6.1 Geophysical Methods

Geophysical methods include electromagnetic induction, magnetics, and ground penetrating radar. Additional details concerning the design and implementation of electromagnetic induction, magnetics, and ground penetrating radar surveys can be found in one or more of the TtNUS SOPs included in the References (Section 8.0).

Electromagnetic Induction

Electromagnetic Induction (EMI) line locators operate either by locating a background signal or by locating a signal introduced into the utility line using a transmitter. A utility line acts like a radio antenna, producing electrons, which can be picked up with a radiofrequency receiver. Electrical current carrying conductors have a 60HZ signal associated with them. This signal occurs in all power lines regardless of voltage. Utilities in close proximity to power lines or used as grounds may also have a 60HZ signal, which can be picked up with an EM receiver. A typical example of this type of geophysical equipment is an EM-61.

EMI locators specifically designed for utility locating use a special signal that is either indirectly induced onto a utility line by placing the transmitter above the line or directly induced using an induction clamp. The clamp induces a signal on the specific utility and is the preferred method of tracing since there is little chance of the resulting signals being interfered with. A good example of this type of equipment is the Schonstedt® MAC-51B locator. The MAC-51B performs inductively traced surveys, simple magnetic locating, and traced nonmetallic surveys.

When access can be gained inside a conduit to be traced, a flexible insulated trace wire can be used. This is very useful for non-metallic conduits but is limited by the availability of gaining access inside the pipe.

Magnetics

Magnetic locators operate by detecting the relative amounts of buried ferrous metal. They are incapable of locating or identifying nonferrous utility lines but can be very useful for locating underground storage tanks (UST's), steel utility lines, and buried electrical lines. A typical example of this type of equipment is the Schonstedt® GA-52Cx locator. The GA-52Cx is capable of locating 4-inch steel pipe up to 8 feet deep.

Non-ferrous lines are often located by using a typical plumbing tool (snake) fed through the line. A signal is then introduced to the snake that is then traced.

Ground Penetrating Radar

Ground Penetrating Radar (GPR) involves specialized radar equipment whereby a signal is sent into the ground via a transmitter. Some portion of the signal will be reflected from the subsurface material, which is then recorded with a receiver and electronically converted into a graphic picture. In general, an object which is harder than the surrounding soil will reflect a stronger signal. Utilities, tunnels, UST's, and footings will reflect a stronger signal than the surrounding soil. Although this surface detection method may determine the location of a utility, this method does not specifically identify utilities (i.e., water vs. gas, electrical vs. telephone); hence, verification may be necessary using other methods. This method is somewhat limited when used in areas with clay soil types or with a high water table.

6.2 Passive Detection Surveys

Acoustic Surveys

Acoustic location methods are generally most applicable to waterlines or gas lines. A highly sensitive Acoustic Receiver listens for background sounds of water flowing (at joints, leaks, etc.) or to sounds introduced into the water main using a transducer. Acoustics may also be applicable to determine the location of plastic gas lines.

Thermal Imaging

Thermal (i.e., infrared) imaging is a passive method for detecting the heat emitted by an object. Electronics in the infrared camera convert subtle heat differentials into a visual image on the viewfinder or a monitor. The operator does not look for an exact temperature; rather they look for heat anomalies (either elevated or suppressed temperatures) characteristic of a potential utility line.

The thermal fingerprint of underground utilities results from differences in temperature between the atmosphere and the fluid present in a pipe or the heat generated by electrical resistance. In addition, infrared scanners may be capable of detecting differences in the compaction, temperature and moisture content of underground utility trenches. High-performance thermal imagery can detect temperature differences to hundredths of a degree.

6.3 Intrusive Detection Surveys

Vacuum Excavation

Vacuum excavation is used to physically expose utility services. The process involves removing the surface material over approximately a 1' x 1' area at the site location. The air-vacuum process proceeds with the simultaneous action of compressed air-jets to loosen soil and vacuum extraction of the resulting

debris. This process ensures the integrity of the utility line during the excavation process, as no hammers, blades, or heavy mechanical equipment comes into contact with the utility line, eliminating the risk of damage to utilities. The process continues until the utility is uncovered. Vacuum excavation can be used at the proposed site location to excavate below the "utility window" which is usually 8 feet.

Hand Excavation

When the identification and location of underground utilities cannot be positively confirmed through document reviews and/or other methods, borings and excavations may be cleared via the use of non-conductive hand tools. This should always be done in conjunction with the use of detection equipment. This would be required for all locations where there is a potential to impact buried utilities. The minimum hand-excavation depth that must be reached is to be determined considering the geographical location of the work site. This approach recognizes that the placement of buried utilities is influenced by frost line depths that vary by geographical region. Attachment 2 presents frost line depths for the regions of the contiguous United States. At a minimum, hand excavation depths must be at least to the frost line depth (see Attachment 2) plus two (2) feet, but never less than 4 feet below ground surface (bgs). For hand excavation, the hole created must be reamed large enough to be at least the diameter of the drill rig auger or bit prior to drilling. For soil gas surveys, the survey probe shall be placed as close as possible to the cleared hand excavation. It is important to note that a post-hole digger must not be used in this type of hand excavation activity.

Tile Probe Surveys

For some soil types, site conditions, and excavation requirements, non-conductive tile probes may be used. A tile probe is a "T"-handled rod of varying lengths that can be pushed into the soil to determine if any obstructions exist at that location. Tile probes constructed of fiberglass or other nonconductive material are readily-available from numerous vendors. Tile probes must be performed to the same depth requirements as previously specified. As with other types of hand excavating activities, the use of a non-conductive tile probe, should always be in conjunction with suitable utility locating detection equipment.

7.0 INTRUSIVE ACTIVITIES SUMMARY

The following list summarizes the activities that must be performed prior to beginning subsurface activities:

1. Map and mark all subsurface locations and excavation boundaries using white paint or markers specified by the client or property owner.

2. Notify the property owner and/or client that the locations are marked. At this point, drawings of locations or excavation boundaries shall be provided to the property owner and/or client so they may initiate (if applicable) utility clearance.

   Note: Drawings with confirmed locations should be provided to the property owner and/or client as soon as possible to reduce potential time delays.

3. Notify "One Call" service. If possible, arrange for an appointment to show the One Call representative the surface locations or excavation boundaries in person. This will provide a better location designation to the utilities they represent. You should have additional drawings should you need to provide plot plans to the One Call service.

4. Implement supplemental utility detection techniques as necessary and appropriate to conform utility locations or the absence thereof.

5. Complete Attachment 3, Utility Clearance Form. This form should be completed for each excavation location. In situations where multiple subsurface locations exist within the close proximity of one another, one form may be used for multiple locations provided those locations are noted on the Utility Clearance Form. Upon completion, the Utility Clearance Form and revised/annotated utility location map becomes part of the project file.

8.0 REFERENCES

OSHA Letter of Interpretation, Mr. Joseph Caldwell, Attachment 4
OSHA 29 CFR 1926(b)(2)
OSHA 29 CFR 1926(b)(3)
TtNUS Utility Locating and Clearance Policy
TtNUS SOP GH-3.1; Resistivity and Electromagnetic Induction
TtNUS SOP GH-3.2; Magnetic and Metal Detection Surveys
TtNUS SOP GH-3.4; Ground-penetrating Radar Surveys

ATTACHMENT 1
LISTING OF UNDERGROUND UTILITY CLEARANCE RESOURCES

American Public Works Association
2345 Grand Boulevard, Suite 500, Kansas City, MO 64108-2625
Phone (816) 472-6100 • Fax (816) 472-1610
Web www.apwa.net • E-mail apwa@apwa.net

ONE-CALL SYSTEMS INTERNATIONAL CONDENSED DIRECTORY

Alabama
Alabama One-Call
1-800-292-8525

Alaska
Locate Call Center of Alaska, Inc.
1-800-478-3121

Arizona
Arizona Blue Stake
1-800-782-5348

Arkansas
Arkansas One Call System, Inc.
1-800-482-8998

California
Underground Service Alert North
1-800-227-2600
Underground Service Alert of Southern California
1-800-227-2600

Colorado
Utility Notification Center of Colorado
1-800-922-1987

Connecticut
Call Before You Dig
1-800-922-4455

Delaware
Miss Utility of Delmarva
1-800-282-8555

Florida
Sunshine State One-Call of Florida, Inc.
1-800-432-4770

Georgia
Underground Protection Center, Inc.
1-800-282-7411

Hawaii
Underground Service Alert North
1-800-227-2600

Idaho
Dig Line Inc.
1-800-342-1585
Kootenai County One-Call
1-800-428-4950
Shoshone - Benewah One-Call
1-800-398-3285

Illinois
JULIE, Inc.
1-800-892-0123
Digger (Chicago Utility Alert Network)
312-744-7000

Indiana
Indiana Underground Plant Protection Service
1-800-382-5544

Iowa
Iowa One-Call
1-800-292-8989

Kansas
Kansas One-Call System, Inc.
1-800-344-7233

Kentucky
Kentucky Underground Protection Inc.
1-800-752-6007

Louisiana
Louisiana One Call System, Inc.
1-800-272-3020

Maine
Dig Safe System, Inc.
1-888-344-7233

Maryland
Miss Utility
1-800-257-7777
Miss Utility of Delmarva
1-800-282-8555

Massachusetts
Dig Safe System, Inc.
1-888-344-7233

Michigan
Miss Dig System, Inc.
1-800-482-7171

Minnesota
Gopher State One Call
1-800-252-1168

Mississippi
Mississippi One-Call System, Inc
1-800-227-6477

Missouri
Missouri One-Call System, Inc.
1-800-344-7483

Montana
Utilities Underground Protection Center
1-800-424-5555
Montana One Call Center
1-800-551-8344

Nebraska
Diggers Hotline of Nebraska
1-800-331-5666

Nevada
Underground Service Alert North
1-800-227-2600

New Hampshire
Dig Safe System, Inc.
1-888-344-7233

New Jersey
New Jersey One Call
1-800-272-1000

New Mexico
New Mexico One Call System, Inc.
1-800-321-2537
Las Cruces- Dona Ana Blue Stakes
1-888-526-0400

New York
Dig Safely New York
1-800-962-7962
New York City- Long Island One Call Center
1-800-272-4480

North Carolina
The North Carolina One-Call Center, Inc.
1-800-632-4949

North Dakota
North Dakota One-Call
1-800-795-0555

Ohio
Ohio Utilities Protection Service
1-800-362-2764
Oil & Gas Producers Underground Protect'n Svc
1-800-925-0988

Oklahoma
Call Okie
1-800-522-6543

Oregon
Oregon Utility Notification Center/One Call Concepts
1-800-332-2344

Pennsylvania
Pennsylvania One Call System, Inc.
1-800-242-1776

Rhode Island
Dig Safe System, Inc.
1-888-344-7233

South Carolina
Palmetto Utility Protection Service Inc.
1-888-721-7877

South Dakota
South Dakota One Call
1-800-781-7474

Tennessee
Tennessee One-Call System, Inc.
1-800-351-1111

ATTACHMENT 1 (Continued)

Texas
Texas One Call System
1-800-245-4545
Texas Excavation Safety System, Inc.
1-800-344-8377
Lone Star Notification Center
1-800-669-8344

Utah
Blue Stakes of Utah
1-800-662-4111

Vermont
Dig Safe System, Inc.
1-888-344-7233

Virginia
Miss Utility of Virginia
1-800-552-7001
Miss Utility (Northern Virginia)
1-800-257-7777

Washington
Utilities Underground Location Center
1-800-424-5555
Northwest Utility Notification Center
1-800-553-4344
Inland Empire Utility Coordinating Council
509-456-8000

West Virginia
Miss Utility of West Virginia, Inc.
1-800-245-4848

Wisconsin
Diggers Hotline, Inc.
1-800-242-8511

Wyoming
Wyoming One-Call System, Inc.
1-800-348-1030
Call Before You Dig of Wyoming
1-800-849-2476

District of Columbia
Miss Utility
1-800-257-7777

Alberta
Alberta One-Call Corporation
1-800-242-3447

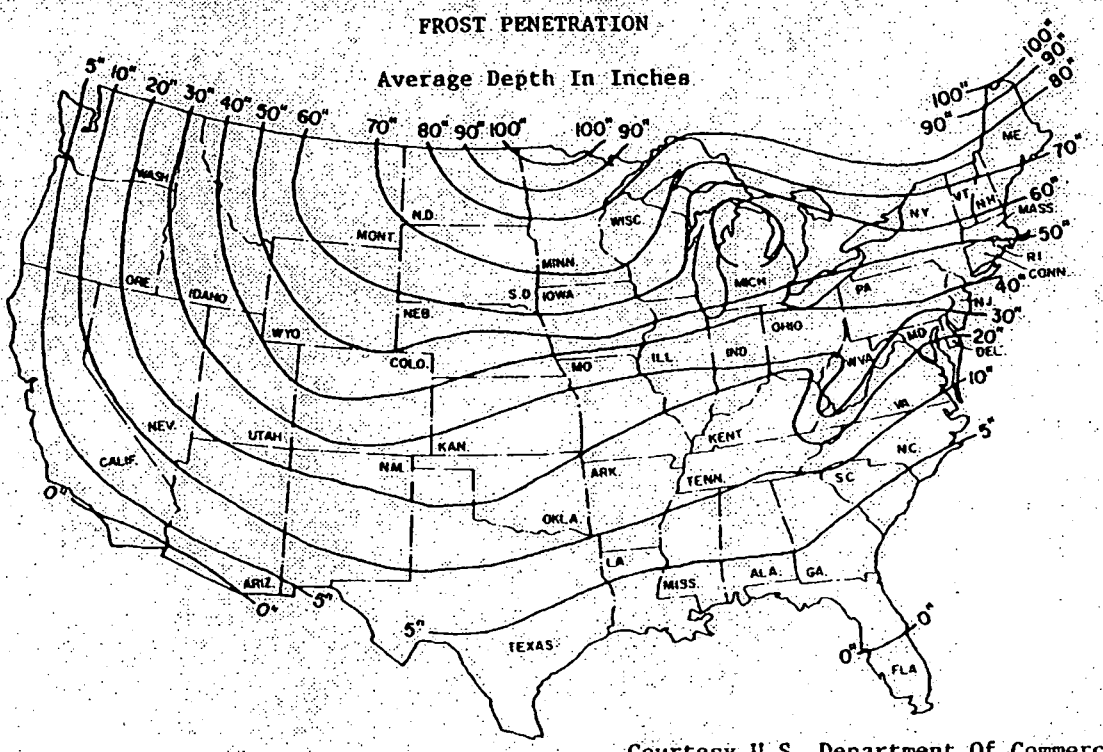
British Columbia
BC One Call
1-800-474-6886

Ontario
Ontario One-Call System
1-800-400-2255

Quebec
Info-Excavation
1-800-663-9228

ATTACHMENT 2

FROST LINE PENETRATION DEPTHS BY GEOGRAPHIC LOCATION



Courtesy U.S. Department Of Commerce

ATTACHMENT 3
UTILITY CLEARANCE FORM

Client: _____ Project Name: _____

Project No.: _____ Completed By: _____

Location Name: _____ Work Date: _____

Excavation Method/Overhead Equipment: _____

1. Underground Utilities — Circle One

a) Review of existing maps? yes no N/A

b) Interview local personnel? yes no N/A

c) Site visit and inspection? yes no N/A

d) Excavation areas marked in the field? yes no N/A

e) Utilities located in the field? yes no N/A

f) Located utilities marked/added to site maps? yes no N/A

g) Client contact notified yes no N/A
Name _____ Telephone: _____ Date: _____

g) State One-Call agency called? yes no N/A
Caller: _____
Ticket Number: _____ Date: _____

h) Geophysical survey performed? yes no N/A
Survey performed by: _____
Method: _____ Date: _____

i) Hand excavation performed (with concurrent use of utility detection device)? yes no N/A
Completed by: _____
Total depth: _____ feet Date: _____

j) Trench/excavation probed? yes no N/A
Probing completed by: _____
Depth/frequency: _____ Date: _____

2. Overhead Utilities — Present Absent

a) Determination of nominal voltage yes no N/A
b) Marked on site maps yes no N/A
c) Necessary to lockout/insulate/re-route yes no N/A
d) Document procedures used to lockout/insulate/re-route yes no N/A
e) Minimum acceptable clearance (SOP Section 5.2): _____

3. Notes:

_____

_____

_____

Approval:

_____ _____
Site Manager/Field Operations Leader Date

c: PM/Project File
Program File

ATTACHMENT 4
OSHA LETTER OF INTERPRETATION

Mr. Joseph Caldwell
Consultant
Governmental Liaison
Pipeline Safety Regulations
211 Wilson Boulevard
Suite 700
Arlington, Virginia 22201

Re: Use of hydro-vacuum or non-conductive hand tools to locate underground utilities.

Dear Mr. Caldwell:

In a letter dated July 7, 2003, we responded to your inquiry of September 18, 2002, regarding the use of hydro-vacuum equipment to locate underground utilities by excavation. After our letter to you was posted on the OSHA website, we received numerous inquiries that make it apparent that aspects of our July 7 letter are being misunderstood. In addition, a number of industry stakeholders, including the National Utility Contractors Association (NUCA), have provided new information regarding equipment that is available for this work.

To clarify these issues, we are withdrawing our July 7 letter and issuing this replacement response to your inquiry.

Question: Section 1926.651 contains several requirements that relate to the safety of employees engaged in excavation work. Specifically, paragraphs (b)(2) and (b)(3) relate in part to the safety of the means used to locate underground utility installations that, if damaged during an uncovering operation, could pose serious hazards to employees.

Under these provisions, what constitutes an acceptable method of uncovering underground utility lines, and further, would the use of hydro-vacuum excavation be acceptable under the standard?

Answer

Background

Two sections of 29 CFR 1926 Subpart P (Excavations), 1926.651(Specific excavation requirements), govern methods for uncovering underground utility installations. Specifically, paragraph (b)(2) states:

> When utility companies or owners cannot respond to a request to locate underground utility installations within 24 hours * * * or cannot establish the exact location of these installations, the employer may proceed, provided the employer does so with caution, and provided detection equipment or other acceptable means to locate utility installations are used. (emphasis added).

Paragraph (b)(3) provides:

ATTACHMENT 4 (Continued)

> When excavation operations approach the estimated location of underground installations, the exact location of the installations shall be determined by safe and acceptable means. (emphasis added).

Therefore, "acceptable means" must be used where the location of the underground utilities have not been identified by the utility companies and detection equipment is not used.

Subpart P does not contain a definition of either "other acceptable means" or "safe and acceptable means." The preambles to both the proposed rule and the final rule discussed the rationale behind the wording at issue. For example, the preamble to the proposed rule, 52 Fed. Reg. 12301 (April 15, 1987), noted that a 1972 version of this standard contained language that specified "careful probing or hand digging" as the means to uncover utilities. The preamble then noted that an amendment to the 1972 standard later deleted that language "to allow other, *equally effective means* of locating such installations." The preamble continued that in the 1987 proposed rule, OSHA again proposed using language in section (b)(3) that would provide another example of an acceptable method of uncovering utilities that could be used *where the utilities have not been marked and detection equipment is not being used* – "probing with hand-held tools." This method was rejected in the final version of 29 CFR 1926. As OSHA explained in the preamble to the final rule, 54 Fed. Reg. 45916 (October 31, 1989):

> OSHA received two comments * * * and input from ACCSH [OSHA's Advisory Committee on Construction Safety and Health] * * * on this provision. All commenters recommended dropping 'such as probing with hand-held tools' from the proposed provision, because this could create a hazard to employees by damaging the installation or its insulation.

In other words, the commenters objected to the use of hand tools being used unless detection equipment was used in conjunction with them. OSHA then concluded its discussion relative to this provision by agreeing with the commentators and ultimately not including any examples of "acceptable means" in the final provision.

Non-conductive hand tools are permitted

This raises the question of whether the standard permits the use of hand tools alone -- without also using detection equipment. NUCA and other industry stakeholders have recently informed us that non-conductive hand tools that are appropriate to be used to locate underground utilities are now commonly available.

Such tools, such as a "shooter" (which has a non-conductive handle and a snub nose) and non-conductive or insulated probes were not discussed in the rulemaking. Since they were not considered at that time, they were not part of the class of equipment that was thought to be unsafe for this purpose. Therefore, we conclude that the use of these types of hand tools, when used with appropriate caution, is an "acceptable means" for locating underground utilities.

ATTACHMENT 4 (Continued)

Hydro-vacuum excavation

It is our understanding that some hydro-vacuum excavation equipment can be adjusted to use a minimum amount of water and suction pressure. When appropriately adjusted so that the equipment will not damage underground utilities (especially utilities that are particularly vulnerable to damage, such as electrical lines), use of such equipment would be considered a "acceptable means" of locating underground utilities. However, if the equipment cannot be sufficiently adjusted, then this method would not be acceptable under the standard.

Other technologies

We are not suggesting that these are the only devices that would be "acceptable means" under the standard. Industry stakeholders have informed us that there are other types of special excavation equipment designed for safely locating utilities as well.

We apologize for any confusion our July 7 letter may have caused. If you have further concerns or questions, please feel free to contact us again by fax at: U.S. Department of Labor, OSHA, Directorate of Construction, Office of Construction Standards and Compliance Assistance, fax # 202-693-1689. You can also contact us by mail at the above office, Room N3468, 200 Constitution Avenue, N.W., Washington, D.C. 20210, although there will be a delay in our receiving correspondence by mail.

Sincerely,

Russell B. Swanson, Director
Directorate of Construction

NOTE: OSHA requirements are set by statute, standards and regulations. Our interpretation letters explain these requirements and how they apply to particular circumstances, but they cannot create additional employer obligations. This letter constitutes OSHA=s interpretation of the requirements discussed. Note that our enforcement guidance may be affected by changes to OSHA rules. Also, from time to time we update our guidance in response to new information. To keep apprised of such developments, you can consult OSHA's website at http://www.osha.gov.

TETRA TECH NUS, INC.	STANDARD OPERATING PROCEDURES	Number SA-1.2	Page 1 of 12
		Effective Date 09/03	Revision 5
		Applicability Tetra Tech NUS, Inc.	
		Prepared Earth Sciences Department	
Subject SURFACE WATER AND SEDIMENT SAMPLING		Approved D. Senovich	

TABLE OF CONTENTS

SECTION **PAGE**

1.0 PURPOSE 2

2.0 SCOPE 2

3.0 GLOSSARY 2

4.0 RESPONSIBILITIES 2

5.0 PROCEDURES 2

5.1 INTRODUCTION 2
5.2 DEFINING THE SAMPLING PROGRAM 3
5.2.1 Sampling Program Objectives 3
5.2.2 Location of Sampling Stations 3
5.2.3 Frequency of Sampling 4
5.3 SURFACE WATER SAMPLE COLLECTION 4
5.3.1 Streams, Rivers, Outfalls and Drainage Features (Ditches, Culverts) 4
5.3.2 Lakes, Ponds and Reservoirs 5
5.3.3 Estuaries 5
5.3.4 Surface Water Sampling Equipment 6
5.3.5 Surface Water Sampling Techniques 7
5.4 ONSITE WATER QUALITY TESTING 8
5.5 SEDIMENT SAMPLING 8
5.5.1 General 8
5.5.2 Sampling Equipment and Techniques 9

6.0 REFERENCES 10

ATTACHMENTS

A SURFACE WATER SAMPLE LOG SHEET 11
B SOIL & SEDIMENT SAMPLE LOG SHEET 12

1.0 PURPOSE

This procedure describes methods and equipment commonly used for collecting environmental samples of surface water and aquatic sediment for either onsite examination and chemical testing, or for subsequent laboratory analysis.

2.0 SCOPE

The information presented in this guideline is generally applicable to all environmental sampling of surface waters (Section 5.3) and aquatic sediments (Section 5.5), except where the analyte(s) may interact with the sampling equipment. The collection of concentrated sludges or hazardous waste samples from disposal or process lagoons often requires methods, precautions and equipment different from those described herein.

3.0 GLOSSARY

Environmental Sample - a sample containing (or suspected to contain) low-level concentrations of contaminants, which does not require special handling or transport considerations as detailed in SOP SA-6.1.

Hazardous Waste Sample - a sample containing (or suspected to contain) higher concentrations of contaminants thus requiring special handling and/or transport considerations per SOP SA-6.1.

4.0 RESPONSIBILITIES

Project Manager - The Project Manager has the overall responsibility for seeing that all surface water and sediment sampling activities are properly conducted by appropriately trained personnel.

Field Operations Leader - The Field Operations Leader (FOL) is responsible for the supervision of onsite water quality analyses, ensuring proper sample collection, handling, and the completion and accuracy of all field documentation, and making sure that custody of all samples obtained is maintained according to proper procedures.

5.0 PROCEDURES

5.1 Introduction

Collecting a representative sample from surface water or sediments is difficult because of water movement, stratification, or patchiness. To collect representative samples, one must standardize sampling bias related to site selection, sampling frequency, sample collection, sampling devices, and sample handling, preservation, and identification.

Representativeness is a qualitative description of the degree to which an individual sample accurately reflects population characteristics or parameter variations at a sampling point. It is therefore an important characteristic not only of assessment and quantification of environmental threats posed by the site, but also for providing information for engineering design and construction. Proper sample location selection and proper sample collection methods are important to ensure that a truly representative sample has been taken. Regardless of quality control applied during laboratory analyses and subsequent scrutiny of analytical data packages, reported data are no better than the confidence that can be placed in the representativeness of the samples.

5.2 Defining the Sampling Program

Many factors must be considered in developing a sampling program for surface water or sediments including study objectives, accessibility, site topography, physical characteristics of the water body (such as flow and mixing), point and diffuse sources of contamination, and personnel and equipment available to conduct the study. For waterborne constituents, dispersion depends on the vertical and lateral mixing within the body of water. For sediments, dispersion depends on bottom current or flow characteristics, sediment characteristics (density, size) and geochemical properties (which affect adsorption/desorption). The hydrogeologist developing the sampling plan must therefore know not only the mixing characteristics of streams and lakes, but also must understand the role of fluvial-sediment transport, deposition, and chemical sorption.

5.2.1 Sampling Program Objectives

The objective of surface water sampling is to determine the surface water quality entering, leaving or remaining within the site. The scope of the sampling program must consider the sources and potential pathways for transport of contamination to or within a surface water body. Sources may include point sources (leaky tanks, outfalls, etc.) or nonpoint sources (e.g., spills). The major pathways for surface water contamination (not including airborne deposition) are overland runoff, leachate influx to the waterbody, direct waste disposal (solid or liquid) into the water body; and groundwater flow influx from upgradient. The relative importance of these pathways, and therefore the design of the sampling program, is controlled by the physiographic and hydrologic features of the site, the drainage basin(s) which encompass the site, and the history of site activities.

Physiographic and hydrologic features to be considered include slopes and runoff direction, areas of temporary flooding or pooling, tidal effects, artificial surface runoff controls such as berms or drainage ditches (and when they were constructed relative to site operation), and locations of springs, seeps, marshes, etc. In addition, the obvious considerations such as the location of man-made discharge points to the nearest stream (intermittent or flowing), pond, lake, estuary, etc., shall be considered.

A more subtle consideration in designing the sampling program is the potential for dispersion of dissolved or sediment-associated contaminants away from the source. The dispersion could lead to a more homogeneous distribution of contamination at low or possibly non-detectable concentrations. Such dispersion does not, however, always readily occur. For example, obtaining a representative sample of contamination from a main stream immediately below an outfall or a tributary is difficult because the inflow frequently follows a stream bank with little lateral mixing for some distance. Sampling alternatives to overcome this situation are: (1) move the site far enough downstream to allow for adequate mixing, or (2) collect integrated samples in a cross section. Also, nonhomogeneous distribution is a particular problem with regard to sediment-associated contaminants, which may accumulate in low-energy environments (coves, river bends, deep spots, or even behind boulders) near or distant from the source while higher-energy areas (main stream channels) near the source may show no contaminant accumulation.

The distribution of particulates within a sample itself is an important consideration. Many organic compounds are only slightly water soluble and tend to adsorb onto particulate matter. Nitrogen, phosphorus, and the heavy metals may also be transported by particulates. Samples must be collected with a representative amount of suspended material; transfer from the sampling device shall include transferring a proportionate amount of the suspended material.

5.2.2 Location of Sampling Stations

Accessibility is the primary factor affecting sampling costs. The desirability and utility of a sample for analysis and consideration of site conditions must be balanced against the costs of collection as controlled

by accessibility. Bridges or piers are the first choice for locating a sampling station on a stream, because bridges provide ready access and also permit the sampling technician to sample any point across the stream. A boat or pontoon (with an associated increase in cost) may be needed to sample locations on lakes and reservoirs, as well as those on larger rivers. Frequently, however, a boat will take longer to cross a water body and will hinder manipulation of the sampling equipment. Wading for samples is not recommended unless it is known that contaminant levels are low so that skin contact will not produce adverse health effects. This provides a built in margin of safety in the event that wading boots or other protective equipment should fail to function properly. If it is necessary to wade into the water body to obtain a sample, the sampler shall be careful to minimize disturbance of bottom sediments and must enter the water body downstream of the sampling location. If necessary, the sampling technician shall wait for the sediments to settle before taking a sample.

Sampling in marshes or tidal areas may require the use of an all-terrain vehicle (ATV). The same precautions mentioned above with regard to sediment disturbance apply.

Under ideal and uniform contaminant dispersion conditions in a flowing stream, the same concentrations of each would occur at all points along the cross section. This situation is most likely downstream of areas of high turbulence. Careful site selection is needed in order to ensure, as nearly as possible, that samples are taken where uniform flow or deposition and good mixing conditions exist.

The availability of streamflow and sediment discharge records can be an important consideration in choosing sampling sites in streams. Streamflow data in association with contaminant concentration data are essential for estimating the total contaminant loads carried by the stream. If a gaging station is not conveniently located on a selected stream, the project hydrogeologist shall explore the possibility of obtaining streamflow data by direct or indirect methods.

5.2.3 Frequency of Sampling

The sampling frequency and the objectives of the sampling event will be defined by the project plan documents. For single-event site or area characterization sampling, both bottom material and overlying water samples shall be collected at the specified sampling stations. If valid data are available on the distribution of the contaminant between the solid and aqueous phases, it may be appropriate to sample only one phase, although this is not often recommended. If samples are collected primarily for monitoring purposes (i.e., consisting of repetitive, continuing measurements to define variations and trends at a given location), water samples shall be collected at a pre-established and constant interval as specified in the project plans (often monthly or quarterly, and during droughts and floods). Samples of bottom material shall be collected from fresh deposits at least yearly, and preferably seasonally, during both spring and fall.

The variability in available water-quality data shall be evaluated before determining the number and collection frequency of samples required to maintain an effective monitoring program.

5.3 Surface Water Sample Collection

5.3.1 Streams, Rivers, Outfalls and Drainage Features (Ditches, Culverts)

Methods for sampling streams, rivers, outfalls, and drainage features at a single point vary from the simplest of hand-sampling procedures to the more sophisticated multi-point sampling techniques known as the equal-width-increment (EWI) method or the equal-discharge-increment (EDI) methods (see below).

Samples from different depths or cross-sectional locations in the watercourse taken during the same sampling episode, shall be composited. However, samples collected along the length of the watercourse or at different times may reflect differing inputs or dilutions and therefore shall not be composited.

Generally, the number and type of samples to be taken depend on the river's width, depth, discharge and on the suspended sediment the stream or river transports. The greater the number of individual points that are sampled, the more likely that the composite sample will truly represent the overall characteristics of the water.

In small streams less than about 20 feet wide, a sampling site can generally be found where the water is well mixed. In such cases, a single grab sample taken at mid-depth in the center of the channel is adequate to represent the entire cross section.

For larger streams, at least one vertical composite shall be taken with one sample each from just below the surface, at mid-depth, and just above the bottom. The measurement of DO, pH, temperature, conductivity, etc., shall be made on each aliquot of the vertical composite and on the composite itself. For rivers, several vertical composites shall be collected, as directed in the project plan documents.

5.3.2 Lakes, Ponds and Reservoirs

Lakes, ponds, and reservoirs have a much greater tendency to stratify than rivers and streams. The relative lack of mixing requires that more samples be obtained.

The number of water sampling sites on a lake, pond, or impoundment will vary with the size and shape of the basin. In ponds and small lakes, a single vertical composite at the deepest point may be sufficient. Similarly, the measurement of DO, pH, temperature, etc., is to be conducted on each aliquot of the vertical composite and on the composite itself. In naturally-formed ponds, the deepest point may have to be determined empirically; in impoundments, the deepest point is usually near the dam.

In lakes and larger reservoirs, several vertical composites shall be composited to form a single sample. These verticals are often taken along a transect or grid. In some cases, it may be of interest to form separate composites of epilimnetic and hypolimnetic zones. In a stratified lake, the epilimnion is the thermocline which is exposed to the atmosphere. The hypolimnion is the lower, "confined" layer which is only mixed with the epilimnion and vented to the atmosphere during seasonal "overturn" (when density stratification disappears). These two zones may thus have very different concentrations of contaminants if input is only to one zone, if the contaminants are volatile (and therefore vented from the epilimnion but not the hypolimnion), or if the epilimnion only is involved in short-term flushing (i.e., inflow from or outflow to shallow streams). Normally, however, a composite consists of several verticals with samples collected at various depths.

In lakes with irregular shape and with bays and coves that are protected from the wind, separate composite samples may be needed to adequately represent water quality since it is likely that only poor mixing will occur. Similarly, additional samples are recommended where discharges, tributaries, land use characteristics, and other such factors are suspected of influencing water quality.

Many lake measurements are now made in-situ using sensors and automatic readout or recording devices. Single and multi-parameter instruments are available for measuring temperature, depth, pH, oxidation-reduction potential (ORP), specific conductance, dissolved oxygen, some cations and anions, and light penetration.

5.3.3 Estuaries

Estuarine areas are by definition, zones where inland freshwaters (both surface and ground) mix with oceanic saline waters. Estuaries are generally categorized into three types dependent upon freshwater inflow and mixing properties. Knowledge of the estuary type is necessary to determine sampling locations. Each type of estuarine area is described below:

- Mixed Estuary - characterized by the absence of a vertical halocline (gradual or no marked increase in salinity in the water column) and a gradual increase in salinity seaward. Typically this type of estuary is shallow and is found in major freshwater sheetflow areas. Being well mixed, the sampling locations are not critical in this type of estuary.

- Salt Wedge Estuary - characterized by a sharp vertical increase in salinity and stratified freshwater flow along the surface. In these estuaries, the vertical mixing forces cannot override the density differential between fresh and saline waters. In effect, a salt wedge tapering inland moves horizontally, back and forth, with the tidal phase. If contamination is being introduced into the estuary from upstream, water sampling from the salt wedge may miss it entirely.

- Oceanic Estuary - characterized by salinities approaching full-strength oceanic waters. Seasonally, freshwater inflow is small with the preponderance of the fresh-saline water mixing occurring near, or at, the shore line.

Sampling in estuarine areas is normally based upon the tidal phases, with samples collected on successive slack tides (i.e., when the tide turns). Estuarine sampling programs shall include vertical salinity measurements at 1- to 5-foot increments, coupled with vertical dissolved oxygen and temperature profiles.

5.3.4 Surface Water Sampling Equipment

The selection of sampling equipment depends on the site conditions and sample type to be acquired. The most frequently used samplers are:

- Open tube.
- Dip sampler.
- Weighted bottle.
- Hand pump.
- Kemmerer.
- Depth-Integrating Sampler.

The dip sampler and the weighted bottle sampler are used most often, and detailed discussions for these devices only (and the Kemmerer sampler) are addressed subsequently in this section.

The criteria for selecting a sampler include:

1. Disposability and/or easy decontamination.
2. Inexpensive cost (if the item is to be disposed).
3. Ease of operation.
4. Nonreactive/noncontaminating properties - Teflon-coated, glass, stainless-steel or PVC sample chambers are preferred (in that order).

As specified above, each sample (grab or each aliquot collected for compositing) shall be measured for but not limited to:

- Specific conductance.
- Temperature.
- pH.
- Dissolved oxygen (optional).

Sample measurements shall be conducted as soon as the sample is acquired. Measurement techniques described in SOP SA-1.1 shall be followed. All pertinent data and results shall be recorded in a field

notebook or on sample logsheets (see Attachment A). These analyses will provide information on water mixing/stratification and potential contamination.

Dip Sampling

Water is often sampled by filling a container either attached to a pole or held directly from just beneath the surface of the water (a dip or grab sample). Constituents measured in grab samples are only indicative of conditions near the surface of the water and may not be a true representation of the total concentration that is distributed throughout the water column and in the cross section. Therefore, whenever possible, it is recommended to augment dip samples with samples that represent both dissolved and suspended constituents and both vertical and horizontal distributions.

Weighted Bottle Sampling

A grab sample can also be taken using a weighted holder that allows a bottle to be lowered to any desired depth, opened for filling, closed, and returned to the surface. This allows discrete sampling with depth. Several of these samples can be combined to provide a vertical composite. Alternatively, an open bottle can be lowered to the bottom and raised to the surface at a uniform rate so that the bottle collects sample throughout the total depth and is just filled on reaching the surface. The resulting sample using either method will roughly approach what is known as a depth-integrated sample.

A closed weighted bottle sampler consists of a stopped glass or plastic bottle, a weight and/or holding device, and lines to open the stopper and lower or raise the bottle. The procedure for sampling with this device is:

- Gently lower the sampler to the desired depth so as not to remove the stopper prematurely (watch for bubbles).
- Pull out the stopper with a sharp jerk of the stopper line.
- Allow the bottle to fill completely, as evidenced by the absence of air bubbles.
- Raise the sampler and cap the bottle.
- Decontaminate the outside of the bottle. This bottle can be used as the sample container as long as the bottle is an approved container type.

Kemmerer

If samples are desired at a specific depth, and the parameters to be measured do not require a Teflon coated sampler, a standard Kemmerer sampler may be used. The Kemmerer sampler is a brass, stainless-steel or acrylic cylinder, with rubber stoppers that leave the ends open while being lowered in a vertical position (thus allowing free passage of water through the cylinder). A "messenger" is sent down the line when the sampler is at the designated depth, to cause the stoppers to close the cylinder, which is then raised. Water is removed through a valve to fill sample bottles.

5.3.5 Surface Water Sampling Techniques

Most samples taken during site investigations are grab samples. Typically, surface water sampling involves immersing the sample container in the body of water; however, the following suggestions are made to help ensure that the samples obtained are representative of site conditions:

- The most representative samples are obtained from mid-channel at a 0.6 foot stream depth in a well-mixed stream.

- Even though the containers used to obtain the samples are previously laboratory cleaned, it is suggested that the sample container be rinsed at least once with the water to be sampled before the sample is taken. This is not applicable when sample containers are provided "pre-preserved."

- For sampling moving water, it is suggested that the farthest downstream sample be obtained first, and that subsequent samples be taken as one works upstream. In general, work from zones suspected of low contamination to zones of high contamination.

- To sample a pond or other standing body of water, the surface area may be divided into grids. A series of samples taken from each grid node is combined into one sample, or several grid nodes are selected at random.

- Care should be taken to avoid excessive agitation of the water, as loss of volatile constituents could result.

- When obtaining samples in 40 mL septum vials for volatile organics analysis, it is important to exclude any air space in the top of the bottle and to be sure that the Teflon liner of the septum faces in after the vial is filled and capped. The vial can be turned upside down to check for air bubbles.

- Do not sample at the surface, unless sampling specifically for a known constituent which is immiscible and on top of the water. Instead, the sample container should be inverted, lowered to the approximate depth, and held at about a 45-degree angle with the mouth of the bottle facing upstream. When sample containers are provided "pre-preserved," use a dedicated, clean, un-preserved bottle for sampling and transfer to an appropriately-preserved container.

5.4 Onsite Water Quality Testing

Onsite water quality testing shall be conducted as described in SOP SA-1.1.

5.5 Sediment Sampling

5.5.1 General

Sediment samples are usually collected at the same verticals at which water samples were collected. If only one sediment sample is to be collected, the sampling location shall be approximately at the center of the water body.

Generally, the coarser grained sediments are deposited near the headwaters of the reservoir. Bed sediments near the center of a water body will be composed of fine-grained materials which may, because of their lower porosity and greater surface area available for adsorption, contain greater concentrations of contaminants. The shape, flow pattern, bathometry (i.e., depth distribution), and water circulation patterns must all be considered when selecting sediment sampling sites. In streams, areas likely to have sediment accumulation (e.g., bends, behind islands or boulders, quiet shallow areas or very deep, low-velocity areas) shall be sampled while areas likely to show net erosion (i.e., high-velocity, turbulent areas) and suspension of fine solid materials, shall be avoided.

Chemical constituents associated with bottom material may reflect an integration of chemical and biological processes. Bottom samples reflect the historical input to streams, lakes, and estuaries with respect to time, application of chemicals, and land use. Bottom sediments (especially fine-grained material) may act as a sink or reservoir for adsorbed heavy metals and organic contaminants (even if

water column concentrations are below detection limits). Therefore, it is important to minimize the loss of low-density "fines" during any sampling process.

All relevant information pertaining to sediment sampling shall be documented as applicably described in SOP SA-6.3 and Attachment B.

5.5.2 Sampling Equipment and Techniques

A bottom-material sample may consist of a single scoop or core, or may be a composite of several individual samples in the cross section. Sediment samples may be obtained using onshore or offshore techniques.

The following health and safety provisions apply when working on/over/near water.

Size of Work Team:

1) Never less than 2 persons [who are wearing USCG approved Personal Flotation Devices (PFDs)]

2) A minimum of 3 persons if *any* of the following conditions are anticipated or observed:

- Depth is greater than 3 feet
- Involves a waterway that is turbulent *or* swift
- The underwater walking surface (e.g., stream/river bed) is suspected or observed to involve conditions that increase the potential for a worker to fall into the water. Examples would include large/uneven rocks or boulders, dense mud or sediment that could entrap worker's feet, etc.)
- Waterway is tidal, and conditions such as those listed above could change

The third person in the above condition must be equipped and prepared to render emergency support [e.g., lifeline, tethered PFD (life saver), skiff, means to contact external emergency response support, etc.]

The following samplers may be used to collect bottom materials:

- Scoop sampler.
- Dredge samplers.

Each type of sampler is discussed subsequently.

Scoop Sampler

A scoop sampler consists of a pole to which a jar or scoop is attached. The pole may be made of bamboo, wood, PVC, or aluminum and be either telescoping or of fixed length. The scoop or jar at the end of the pole is usually attached using a clamp.

If the water body can be sampled from the shore or if it can be waded, the easiest and best way to collect a sediment sample is to use a scoop sampler. This reduces the potential for cross-contamination. This method is accomplished by reaching over or wading into the water body and, while facing upstream (into the current), scooping the sampler along the bottom in an upstream direction. It is very difficult not to disturb fine-grained materials of the sediment-water interface when using this method.

Dredges

Dredges are generally used to sample sediments which cannot easily be obtained using coring devices (i.e., coarse-grained or partially-cemented materials) or when large quantities of sample are required. Dredges generally consist of a clam shell arrangement of two buckets. The buckets may either close upon impact or be activated by use of a "messenger". Some dredges are heavy and may require use of a winch and crane assembly for sample retrieval. There are three major types of dredges: Peterson, Eckman and Ponar dredges.

The Peterson dredge is used when the bottom is rocky, in very deep water, or when the flow velocity is high. The Peterson dredge shall be lowered very slowly as it approaches bottom, because it can force out and miss lighter materials if allowed to drop freely.

The Eckman dredge has only limited usefulness. It performs well where bottom material is unusually soft, as when covered with organic sludge or light mud. It is unsuitable, however, for sandy, rocky, and hard bottoms and is too light for use in streams with high flow velocities.

The Ponar dredge is a Peterson dredge modified by the addition of side plates and a screen on the top of the sample compartment. The screen over the sample compartment permits water to pass through the sampler as it descends thus reducing the "shock wave". The Ponar dredge is easily operated by one person in the same fashion as the Peterson dredge. The Ponar dredge is one of the most effective samplers for general use on all types of substrates.

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ATTACHMENT A
SURFACE WATER SAMPLE LOG SHEET

Tetra Tech NUS, Inc. **SURFACE WATER SAMPLE LOG SHEET**

Page___ of ___

Project Site Name: _____
Project No.: _____

[] Stream
[] Spring
[] Pond
[] Lake
[] Other: _____
[] QA Sample Type: _____

Sample ID No.: _____
Sample Location: _____
Sampled By: _____
C.O.C. No.: _____

Type of Sample:
[] Low Concentration
[] High Concentration

SAMPLING DATA

	Color Visual	pH Standard	S.C. mS/cm	Temp. Degrees C	Turbidity NTU	DO mg/l	Salinity %	Other NA
Date:								
Time:								
Depth:								
Method:								

SAMPLE COLLECTION INFORMATION

Analysis	Preservative	Container Requirements	Collected

OBSERVATIONS/NOTES | **MAP**

Circle if Applicable:

MS/MSD	Duplicate ID No.:	Signature(s):

ATTACHMENT B
SOIL & SEDIMENT SAMPLE LOG SHEET

Tetra Tech NUS, Inc.

SOIL & SEDIMENT SAMPLE LOG SHEET

Page___ of ___

Project Site Name: _____
Project No.: _____

[] Surface Soil
[] Subsurface Soil
[] Sediment
[] Other: _____
[] QA Sample Type: _____

Sample ID No.: _____
Sample Location: _____
Sampled By: _____
C.O.C. No.: _____

Type of Sample:
[] Low Concentration
[] High Concentration

GRAB SAMPLE DATA:

Date:	Depth	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Time:			
Method:			
Monitor Reading (ppm):			

COMPOSITE SAMPLE DATA:

Date:	Time	Depth	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Method:				
Monitor Readings (Range in ppm):				

SAMPLE COLLECTION INFORMATION:

Analysis	Container Requirements	Collected	Other

OBSERVATIONS / NOTES:

MAP:

Circle if Applicable:

MS/MSD	Duplicate ID No.:

Signature(s):

TABLE OF CONTENTS

SECTION		PAGE
1.0	PURPOSE	2
2.0	SCOPE	2
3.0	GLOSSARY	2
4.0	RESPONSIBILITIES	3
5.0	PROCEDURES	3
5.1	OVERVIEW	3
5.2	SOIL SAMPLE COLLECTION	4
5.2.1	Procedure for Collecting Soil Samples for Volatile Organic Compounds	4
5.2.2	Procedure for Collecting Non-Volatile Soil Samples	6
5.2.3	Procedure for Collecting Undisturbed Soil Samples (ASTM D1587-83)	6
5.3	SURFACE SOIL SAMPLING	7
5.4	NEAR-SURFACE SOIL SAMPLING	7
5.5	SUBSURFACE SOIL SAMPLING WITH A HAND AUGER	8
5.6	SUBSURFACE SOIL SAMPLING WITH A SPLIT-BARREL SAMPLER (ASTM D1586-84)	9
5.7	SUBSURFACE SOL SAMPLING USING DIRECT PUSH TECHNOLOGY	10
5.8	EXCAVATION AND SAMPLING OF TEST PITS AND TRENCHES	10
5.8.1	Applicability	10
5.8.2	Test Pit and Trench Excavation	10
5.8.3	Sampling in Test Pits and Trenches	12
5.8.4	Backfilling of Trenches and Test Pits	15
5.9	RECORDS	15
6.0	REFERENCES	16

ATTACHMENTS

A	SOIL & SEDIMENT SAMPLE LOG SHEET	17
B	SPLIT-SPOON SAMPLER	18
C	TEST PIT LOG	19
D	REMOTE SAMPLE HOLDER FOR TEST PIT/TRENCH SAMPLING	20

1.0 PURPOSE

This procedure discusses the methods used to collect surface, near surface, and subsurface soil samples. Additionally, it describes the method for sampling of test pits and trenches to determine subsurface soil and rock conditions, and recover small-volume or bulk samples.

2.0 SCOPE

This procedure is applicable to the collection of surface, near surface and subsurface soils for laboratory testing, which are exposed through hand digging, hand augering, drilling, or machine excavating at hazardous substance sites.

3.0 GLOSSARY

Composite Sample - A composite sample exists as a combination of more than one sample at various locations and/or depths and times, which is homogenized and treated as one sample. This type of sample is usually collected when determination of an average waste concentration for a specific area is required. Composite samples are not to be collected for volatile organics analysis.

Grab Sample - One sample collected at one location and at one specific time.

Non-Volatile Sample - A non-volatile sample includes all other chemical parameters (e.g., semivolatiles, pesticides/PCBs, metals, etc.) and those engineering parameters that do not require undisturbed soil for their analysis.

Hand Auger - A sampling device used to extract soil from the ground in a relatively undisturbed form.

Thin-Walled Tube Sampler - A thin-walled metal tube (also called a Shelby tube) used to recover relatively undisturbed soil samples. These tubes are available in various sizes, ranging from 2 to 5 inches outside diameter (OD) and from 18 to 54 inches in length.

Split-Barrel Sampler - A steel tube, split in half lengthwise, with the halves held together by threaded collars at either end of the tube. Also called a split-spoon sampler, this device can be driven into resistant materials using a drive weight mounted in the drilling string. A standard split-barrel sampler is typically available in two common lengths, providing either 20-inch or 26-inch longitudinal clearance for obtaining 18-inch or 24-inch-long samples, respectively. These split-barrel samplers commonly range in size from 2-inch OD to 3-1/2 inch OD. The larger sizes are commonly used when a larger volume of sample material is required.

Test Pit and Trench - Open, shallow excavations, typically rectangular (if a test pit) or longitudinal (if a trench), excavated to determine the shallow subsurface conditions for engineering, geological, and soil chemistry exploration and/or sampling purposes. These pits are excavated manually or by machine (e.g., backhoe, clamshell, trencher excavator, or bulldozer).

Confined Space - As stipulated in 29 CFR 1910.146, a confined space means a space that: 1) is large enough and so configured that an employee can bodily enter and perform assigned work; 2) has limited or restricted means for entry or exit (for example tanks, vessels, silos, storage bins, hoppers, vaults, pits, and excavations); and 3) is not designed for continuous employee occupancy. TtNUS considers all confined space as permit-required confined spaces.

4.0 RESPONSIBILITIES

Project Manager - The Project Manager is responsible for determining sampling objectives, as well as, the field procedures used in the collection of soil samples. Additionally, in consultation with other project personnel (geologist, hydrogeologist, etc.), the Project Manager establishes the need for test pits or trenches, and determines their approximate locations and dimensions.

Site Safety Officer (SSO) - The SSO (or a qualified designee) is responsible for providing the technical support necessary to implement the project Health and Safety Plan. This will include (but not be limited to) performing air quality monitoring during sampling, boring and excavation activities, and to ensure that workers and offsite (downwind) individuals are not exposed to hazardous levels of airborne contaminants. The SSO/designee may also be required to advise the FOL on other safety-related matters regarding boring, excavation and sampling, such as mitigative measures to address potential hazards from unstable trench walls, puncturing of drums or other hazardous objects, etc.

Field Operations Leader (FOL) - The FOL is responsible for finalizing the location of surface, near surface, and subsurface (hand and machine borings, test pits/trenches) soil samples. He/she is ultimately responsible for the sampling and backfilling of boreholes, test pits and trenches, and for adherence to OSHA regulations during these operations.

Project Geologist/Sampler - The project geologist/sampler is responsible for the proper acquisition of soil samples and the completion of all required paperwork (i.e., sample log sheets, field notebook, boring logs, test pit logs, container labels, custody seals, and chain-of-custody forms).

Competent Person - A Competent Person, as defined in 29 CFR 1929.650 of Subpart P - Excavations, means one who is capable of identifying existing and predictable hazards in the surroundings, or working conditions which are unsanitary, hazardous, or dangerous to employees, and who has authorization to take prompt corrective measures to eliminate them.

5.0 PROCEDURES

5.1 Overview

Soil sampling is an important adjunct to groundwater monitoring. Sampling of the soil horizons above the groundwater table can detect contaminants before they have migrated into the water table, and can establish the amount of contamination sorbed on aquifer solids that have the potential of contributing to groundwater contamination.

Soil types can vary considerably on a hazardous waste site. These variations, along with vegetation, can affect the rate of contaminant migration through the soil. It is important, therefore, that a detailed record be maintained during the sampling operations, particularly noting the location, depth, and such characteristics as grain size, color, and odor. Subsurface conditions are often stable on a daily basis and may demonstrate only slight seasonal variation especially with respect to temperature, available oxygen and light penetration. Changes in any of these conditions can radically alter the rate of chemical reactions or the associated microbiological community, thus further altering specific site conditions. As a result, samples must be kept at their at-depth temperature or lower, protected from direct light, sealed tightly in approved glass containers, and be analyzed as soon as possible.

The physical properties of the soil, its grain size, cohesiveness, associated moisture, and such factors as depth to bedrock and water table, will limit the depth from which samples can be collected and the method required to collect them. Often this information on soil properties can be obtained from published soil surveys available through the U.S. Geological Surveys and other government or farm agencies. It is the

intent of this procedure to present the most commonly employed soil sampling methods used at hazardous waste sites.

~~5.2 Soil Sample Collection~~

5.2.1 Procedure for Collecting Soil Samples for Volatile Organic Compounds

The above described traditional sampling techniques, used for the collection of soil samples for volatile organic analysis, have recently been evaluated by the scientific community and determined to be ineffective in producing accurate results (biased low) due to the loss of volatile organics in the sampling stages and microbial degradation of aromatic volatiles. One of the newly adopted sampling procedures for collecting soil samples includes the field preservation of samples with methanol or sodium bisulfate to minimize volatilization and biodegradation. These preservation methods may be performed either in the field or laboratory, depending on the sampling methodology employed.

Soil samples to be preserved by the laboratory are currently being performed using method SW-846, 5035. Laboratories are currently performing low level analyses (sodium bisulfate preservation) and high level analyses (methanol preservation) depending on the end users needs.

It should be noted that a major disadvantage of the methanol preservation method is that the laboratory reporting limits will be higher than conventional testing. The reporting levels using the new method for most analytes are 0.5 µg/g for GC/MS and 0.05 µg/g for GC methods.

The alternative preservation method for collecting soil samples is with sodium bisulfate. This method is more complex to perform in the field and therefore is not preferred for field crews. It should also be noted that currently, not all laboratories have the capabilities to perform this analysis. The advantage to this method is that the reporting limits (0.001 µg/g for GC/PID or GC/ELCD, or 0.010 for GC/MS) are lower than those described above.

The following procedures outline the necessary steps for collecting soil samples to be preserved at the laboratory, and for collecting soil samples to be preserved in the field with methanol or sodium bisulfate.

5.2.1.1 Soil Samples to be Preserved at the Laboratory

Soil samples collected for volatile organics that are to be preserved at the laboratory will be obtained using a hermetically sealed sample vial such as an EnCore™ sampler. Each sample will be obtained using a reusable sampling handle provided with the EnCore™ sampler. The sample is collected by pushing the EnCore™ sampler directly into the soil, ensuring that the sampler is packed tight with soil, leaving zero headspace. Using this type of sampling device eliminates the need for field preservation and the shipping restrictions associated with preservatives. A complete set of instructions is included with each Encore™ sampler shipment by the manufacturer.

Once the sample is collected, it should be placed on ice immediately and shipped to the laboratory within 48 hours (following the chain-of-custody and documentation procedures outlined in SOP SA-6.1). Samples must be preserved by the laboratory within 48 hours of sample collection.

If the lower detection limits are necessary, an option would be to collect several EnCore™ samplers at a given sample location. Send all samplers to the laboratory and the laboratory can perform the required preservation and analyses.

5.2.1.2 Soil Samples to be Preserved in the Field

Soil samples preserved in the field may be prepared for analyses using both the low-level (sodium bisulfate preservation) method and medium-level (methanol preservation) method.

Methanol Preservation (Medium Level):

Soil samples to be preserved in the field with methanol will utilize 40-60 mL glass vials with septum lids. Each sample bottle will be filled with 25 mL of demonstrated analyte-free purge and trap grade methanol. Bottles may be prespiked with methanol in the laboratory or prepared in the field.

Soil will be collected with the use of a decontaminated (or disposable), small-diameter coring device such as a disposable tube/plunger-type syringe with the tip cut off. The outside diameter of the coring device must be smaller than the inside diameter of the sample bottle neck.

A small electronic balance or manual scale will be necessary for measuring the volume of soil to be added to the methanol preserved sample bottle. Calibration of the scale should be performed prior to use and intermittently throughout the day according to the manufacturers requirements.

The sample should be collected by pulling the plunger back and inserting the syringe into the soil to be sampled. The top several inches of soil should be removed before collecting the sample. Approximately 10 grams ±2g (8-12 grams) of soil should be collected. The sample should be weighed and adjusted until obtaining the required amount of sample. The sample weight should be recorded to the nearest 0.01 gram in the field logbook and/or sample log sheet. The soil should then be extruded into the methanol preserved sample bottle taking care not to contact the sample container with the syringe. The threads of the bottle and cap must be free of soil particles.

After capping the bottle, swirl the sample (do not shake) in the methanol and break up the soil such that all of the soil is covered with methanol. Place the sample on ice immediately and prepare for shipment to the laboratory as described in SOP SA-6.1.

Sodium Bisulfate Preservation (Low Level):

Samples to be preserved using the sodium bisulfate method are to be prepared as follows:

Add 1 gram of sodium bisulfate to 5 mL of laboratory grade deionized water in a 40-60 mL glass vial with septum lid. Bottles may be prespiked in the laboratory or prepared in the field. The soil sample should be collected in a manner as described above and added to the sample container. The sample should be weighed to the nearest 0.01 gram as described above and recorded in the field logbook or sample log sheet.

Care should be taken when adding the soil to the sodium bisulfate solution. A chemical reaction of soils containing carbonates (limestone) may cause the sample to effervesce or the vial to possibly explode.

When preparing samples using the sodium bisulfate preservation method, duplicate samples must be collected using the methanol preservation method on a one for one sample basis. The reason for this is because it is necessary for the laboratory to perform both the low level and medium level analyses. Place the sample on ice immediately and prepare for shipment to the laboratory as described in SOP SA-6.1.

If the lower detection limits are necessary, an option to field preserving with sodium bisulfate would be to collect 3 EnCore™ samplers at a given sample location. Send all samplers to the laboratory and the laboratory can perform the required preservation and analyses.

5.2.2 Procedure for Collecting Non-Volatile Soil Samples

Non-volatile soil samples may be collected as either grab or composite samples. The non-volatile soil sample is thoroughly mixed in a stainless steel or disposable, inert plastic tray, using a stainless steel trowel or other approved tool, then transferred into the appropriate sample container(s). Head space is permitted in a non-volatile soil sample container to allow for sample expansion.

5.2.3 Procedure for Collecting Undisturbed Soil Samples (ASTM D1587-83)

When it is necessary to acquire undisturbed samples of soil for purposes of engineering parameter analysis (e.g., permeability), a thin-walled, seamless tube sampler (Shelby tube) will be employed. The following method will be used:

1. Remove all surface debris (e.g., vegetation, roots, twigs, etc.) from the specific sampling location and drill and clean out the borehole to the sampling depth, being careful to minimize the chance for disturbance of the material to be sampled. In saturated material, withdraw the drill bit slowly to prevent loosening of the soil around the borehole and to maintain the water level in the hole at or above groundwater level.

2. The use of bottom discharge bits or jetting through an open-tube sampler to clean out the borehole shall not be allowed. Use of any side-discharge bits is permitted.

3. A stationary piston-type sampler may be required to limit sample disturbance and aid in retaining the sample. Either the hydraulically operated or control rod activated-type of stationary piston sampler may be used. Prior to inserting the tube sampler into the borehole, check to ensure that the sampler head contains a check valve. The check valve is necessary to keep water in the rods from pushing the sample out the tube sampler during sample withdrawal and to maintain a suction within the tube to help retain the sample.

4. To minimize chemical reaction between the sample and the sampling tube, brass tubes may be required, especially if the tube is stored for an extended time prior to testing. While steel tubes coated with shellac are less expensive than brass, they're more reactive, and shall only be used when the sample will be tested within a few days after sampling or if chemical reaction is not anticipated. With the sampling tube resting on the bottom of the hole and the water level in the boring at groundwater level or above, push the tube into the soil by a continuous and rapid motion, without impacting or twisting. In no case shall the tube be pushed farther than the length provided for the soil sample. Allow about 3 inches in the tube for cuttings and sludge.

5. Upon removal of the sampling tube from the hole, measure the length of sample in the tube and also the length penetrated. Remove disturbed material in the upper end of the tube and measure the length of sample again. After removing at least an inch of soil from the lower end and after inserting an impervious disk, seal both ends of the tube with at least a 1/2-inch thickness of wax applied in a way that will prevent the wax from entering the sample. Clean filler must be placed in voids at either end of the tube prior to sealing with wax. Place plastic caps on the ends of the sample tube, tape the caps in place, and dip the ends in wax.

6. Affix label(s) to the tube as required and record sample number, depth, penetration, and recovery length on the label. Mark the "up" direction on the side of the tube with indelible ink, and mark the end of the sample. Complete Chain-of-Custody (see SOP SA-6.3) and other required forms (including Attachment A of this SOP). Do not allow tubes to freeze, and store the samples vertically with the same orientation they had in the ground, (i.e., top of sample is up) in a cool place out of the sun at all times. Ship samples protected with suitable resilient packing material to reduce shock, vibration, and disturbance.

~~Thin-walled undisturbed tube samplers are restricted in their usage by the consistency of the soil to be sampled. Often, very loose and/or wet samples cannot be retrieved by the samplers, and soils with a consistency in excess of very stiff cannot be penetrated by the sampler. Devices such as Dennison or Pitcher core samplers can be used to obtain undisturbed samples of stiff soils. Using these devices normally increases sampling costs, and therefore their use shall be weighed against the need for acquiring an undisturbed sample.~~

5.3 Surface Soil Sampling

The simplest, most direct method of collecting surface soil samples (most commonly collected to a depth of 6 inches) for subsequent analysis is by use of a stainless steel trowel. Surface soils are considered 0-12 inches bgs.

In general, the following equipment is necessary for obtaining surface soil samples:

- Stainless steel or pre-cleaned disposable trowel.
- Real-time air monitoring instrument (e.g., PID, FID, etc.).
- Latex gloves.
- Required Personal Protective Equipment (PPE).
- Required paperwork (see SOP SA-6.3 and Attachment A of this SOP).
- Required decontamination equipment.
- Required sample container(s).
- Wooden stakes or pin flags.
- Sealable polyethylene bags (i.e., Ziploc® baggies).
- Heavy duty cooler.
- Ice.
- Chain-of-custody records and custody seals.

When acquiring surface soil samples, the following procedure shall be used:

1. Carefully remove vegetation, roots, twigs, litter, etc., to expose an adequate soil surface area to accommodate sample volume requirements.

2. Using a decontaminated stainless steel trowel, follow the procedure cited in Section 5.2.1 for collecting a volatile soil sample. Surface soil samples for volatile organic analysis should be collected from 6-12 inches bgs only.

3. Thoroughly mix (in-situ) a sufficient amount of soil to fill the remaining sample containers and transfer the sample into those containers utilizing the same stainless steel trowel employed above. Cap and securely tighten all sample containers.

4. Affix a sample label to each container. Be sure to fill out each label carefully and clearly, addressing all the categories described in SOP SA-6.3.

5. Proceed with the handling and processing of each sample container as described in SOP SA-6.2.

~~5.4 Near-Surface Soil Sampling~~

~~Collection of samples from near the surface (depth of 6-18 inches) can be accomplished with tools such as shovels and stainless steel or pre-cleaned disposable trowels.~~

The following equipment is necessary to collect near surface soil samples:

- Clean shovel.
- The equipment listed under Section 5.3 of this procedure.
- Hand auger.

To obtain near-surface soil samples, the following protocol shall be observed:

1. With a clean shovel, make a series of vertical cuts to the depth required in the soil to form a square approximately 1 foot by 1 foot.

2. Lever out the formed plug and scrape the bottom of the freshly dug hole with a decontaminated stainless steel or pre-cleaned disposable trowel to remove any loose soil.

3. Follow steps 2 through 5 listed under Section 5.3 of this procedure.

5.5 Subsurface Soil Sampling With a Hand Auger

A hand augering system generally consists of a variety of all stainless steel bucket bits (i.e., cylinders 6-1/2" long, and 2-3/4", 3-1/4", and 4" in diameter), a series of extension rods (available in 2', 3', 4' and 5' lengths), and a cross handle. A larger diameter bucket bit is commonly used to bore a hole to the desired sampling depth and then withdrawn. In turn, the larger diameter bit is replaced with a smaller diameter bit, lowered down the hole, and slowly turned into the soil at the completion depth (approximately 6 inches). The apparatus is then withdrawn and the soil sample collected.

The hand auger can be used in a wide variety of soil conditions. It can be used to sample soil both from the surface, or to depths in excess of 12 feet. However, the presence of rock layers and the collapse of the borehole normally contribute to its limiting factors.

To accomplish soil sampling using a hand augering system, the following equipment is required:

- Complete hand auger assembly (variety of bucket bit sizes).
- Stainless steel mixing bowls.
- The equipment listed under Section 5.3 of this procedure.

To obtain soil samples using a hand auger, the following procedure shall be followed:

1. Attach a properly decontaminated bucket bit to a clean extension rod and further attach the cross handle to the extension rod.

2. Clear the area to be sampled of any surface debris (vegetation, twigs, rocks, litter, etc.).

3. Begin augering (periodically removing accumulated soils from the bucket bit) and add additional rod extensions as necessary. Also, note (in a field notebook, boring log, and/or on standardized data sheets) any changes in the color, texture or odor of the soil.

4. After reaching the desired depth, slowly and carefully withdraw the apparatus from the borehole.

5. Remove the soiled bucket bit from the rod extension and replace it with another properly decontaminated bucket bit. The bucket bit used for sampling is commonly smaller in diameter than the bucket bit employed to initiate the borehole.

6. Carefully lower the apparatus down the borehole. Care must be taken to avoid scraping the borehole sides.

7. Slowly turn the apparatus until the bucket bit is advanced approximately 6 inches.

8. Discard the top of the core (approximately 1"), which represents any loose material collected by the bucket bit before penetrating the sample material.

9. Fill volatile sample container(s), using a properly decontaminated stainless steel trowel, with sample material directly from the bucket bit. Refer to Section 5.2.1 of this procedure.

10. Utilizing the above trowel, remove the remaining sample material from the bucket bit and place into a properly decontaminated stainless steel mixing bowl and thoroughly homogenize the sample material prior to filling the remaining sample containers. Refer to Section 5.2.2 of this procedure.

11. Follow steps 4 and 5 listed under Section 5.3 of this procedure.

5.6 Subsurface Soil Sampling With a Split-Barrel Sampler (ASTM D1586-84)

Split-barrel (split-spoon) samplers consist of a heavy carbon steel or stainless steel sampling tube that can be split into two equal halves to reveal the soil sample (see Attachment B). A drive head is attached to the upper end of the tube and serves as a point of attachment for the drill rod. A removable tapered nosepiece/drive shoe attaches to the lower end of the tube and facilitates cutting. A basket-like sample retainer can be fitted to the lower end of the split tube to hold loose, dry soil samples in the tube when the sampler is removed from the drill hole. This split-barrel sampler is made to be attached to a drill rod and forced into the ground by means of a 140-lb. or larger casing driver.

Split-barrel samplers are used to collect soil samples from a wide variety of soil types and from depths greater than those attainable with other soil sampling equipment.

The following equipment is used for obtaining split-barrel samples:

- Drilling equipment (provided by subcontractor).
- Split-barrel samplers (O.D. 2 inches, I.D. 1-3/8 inches, either 20 inches or 26 inches long); Larger O.D. samplers are available if a larger volume of sample is needed.
- Drive weight assembly, 140-lb. weight, driving head and guide permitting free fall of 30 inches.
- Stainless steel mixing bowls.
- Equipment listed under Section 5.3 of this procedure.

The following steps shall be followed to obtain split-barrel samples:

1. Remove the drive head and nosepiece, and open the sampler to reveal the soil sample. Immediately scan the sample core with a real-time air monitoring instrument (e.g., FID, PID, etc.). Carefully separate the soil core, with a decontaminated stainless steel knife or trowel, at about 6-inch intervals while scanning the center of the core for elevated readings. Also scan stained soil, soil lenses, and anomalies (if present), and record readings.

2. Collect the volatile sample from the center of the core where elevated readings occurred. If no elevated readings where encountered the sample material should still be collected from the core's

center (this area represents the least disturbed area with minimal atmospheric contact). Refer to Section 5.2.1 of this procedure.

3. Using the same trowel, remove remaining sample material from the split-barrel sampler (except for the small portion of disturbed soil usually found at the top of the core sample) and place the soil into a decontaminated stainless steel mixing bowl. Thoroughly homogenize the sample material prior to filling the remaining sample containers. Refer to Section 5.2.2 of this procedure.

4. Follow steps 4 and 5 listed under Section 5.3 of this procedure.

5.7 Subsurface Sol Sampling Using Direct Push Technology

Subsurface soil samples can be collected to depths of 40+ feet using direct push technology (DPT). DPT equipment, responsibilities, and procedures are described in SOP SA-2.5.

5.8 Excavation and Sampling of Test Pits and Trenches

5.8.1 Applicability

This subsection presents routine test pit or trench excavation techniques and specialized techniques that are applicable under certain conditions.

During the excavation of trenches or pits at hazardous waste sites, several health and safety concerns arise which control the method of excavation. No personnel shall enter any test pit or excavation over 4 feet deep except as a last resort, and then only under direct supervision of a Competent Person (as defined in 29 CFR 1929.650 of Subpart P - Excavations). Whenever possible, all required chemical and lithological samples should be collected using the excavator bucket or other remote sampling apparatus. If entrance is still required, all test pits or excavations must be stabilized by bracing the pit sides using specifically designed wooden or steel support structures. Personnel entering the excavation may be exposed to toxic or explosive gases and oxygen-deficient environments. Any entry may constitute a Confined Space and must be done in conformance with all applicable regulations. In these cases, substantial air monitoring is required before entry, and appropriate respiratory gear and protective clothing is mandatory. There must be at least two persons present at the immediate site before entry by one of the investigators. The reader shall refer to OSHA regulations 29 CFR 1926, 29 CFR 1910.120, 29 CFR 1910.134, and 29 CFR 1910.146.

Excavations are generally not practical where a depth of more than about 15 feet is desired, and they are usually limited to a few feet below the water table. In some cases, a pumping system may be required to control water levels within the pit, providing that pumped water can be adequately stored or disposed. If data on soils at depths greater than 15 feet are required, the data are usually obtained through test borings instead of test pits.

In addition, hazardous wastes may be brought to the surface by excavation equipment. This material, whether removed from the site or returned to the subsurface, must be properly handled according to any and all applicable federal, state, and local regulations.

5.8.2 Test Pit and Trench Excavation

These procedures describe the methods for excavating and logging test pits and trenches excavated to determine subsurface soil and rock conditions. Test pit operations shall be logged and documented (see Attachment C).

Test pits and trenches may be excavated by hand or by power equipment to permit detailed description of the nature and contamination of the in-situ materials. The size of the excavation will depend primarily on the following:

- The purpose and extent of the exploration.
- The space required for efficient excavation.
- The chemicals of concern.
- The economics and efficiency of available equipment.

Test pits normally have a cross section that is 4 to 10 feet square; test trenches are usually 3 to 6 feet wide and may be extended for any length required to reveal conditions along a specific line. The following table, which is based on equipment efficiencies, gives a rough guide for design consideration:

Equipment	Typical Widths, in Feet
Trenching machine	2
Backhoe	2-6
Track dozer	10
Track loader	10
Excavator	10
Scraper	20

The lateral limits of excavation of trenches and the position of test pits shall be carefully marked on area base maps. If precise positioning is required to indicate the location of highly hazardous waste materials, nearby utilities, or dangerous conditions, the limits of the excavation shall be surveyed. Also, if precise determination of the depth of buried materials is needed for design or environmental assessment purposes, the elevation of the ground surface at the test pit or trench location shall also be determined by survey. If the test pit/trench will not be surveyed immediately, it shall be backfilled and its position identified with stakes placed in the ground at the margin of the excavation for later surveying.

The construction of test pits and trenches shall be planned and designed in advance as much as possible. However, field conditions may necessitate revisions to the initial plans. The final depth and construction method shall be determined by the field geologist. The actual layout of each test pit, temporary staging area, and spoils pile will be predicated based on site conditions and wind direction at the time the test pit is made. Prior to excavation, the area can be surveyed by magnetometer or metal detector to identify the presence of underground utilities or drums.

As mentioned previously, no personnel shall enter any test pit or excavation except as a last resort, and then only under direct supervision of a Competent Person. If entrance is still required, Occupational Safety and Health Administration (OSHA) requirements must be met (e.g., walls must be braced with wooden or steel braces, ladders must be in the hole at all times, and a temporary guardrail must be placed along the surface of the hole before entry). It is emphasized that the project data needs should be structured such that required samples can be collected without requiring entrance into the excavation. For example, samples of leachate, groundwater, or sidewall soils can be taken with telescoping poles, etc.

Dewatering may be required to assure the stability of the side walls, to prevent the bottom of the pit from heaving, and to keep the excavation dry. This is an important consideration for excavations in cohesionless material below the groundwater table. Liquids removed as a result of dewatering operations must be handled as potentially contaminated materials. Procedures for the collection and disposal of such materials should be discussed in the site-specific project plans.

5.8.3 Sampling in Test Pits and Trenches

5.8.3.1 General

Test pits and trenches are usually logged as they are excavated. Records of each test pit/trench will be made as presented in Attachment C. These records include plan and profile sketches of the test pit/trench showing materials encountered, their depth and distribution in the pit/trench, and sample locations. These records also include safety and sample screening information.

Entry of test pits by personnel is extremely dangerous, shall be avoided unless absolutely necessary, and can occur only after all applicable Health and Safety and OSHA requirements have been met.

The final depth and type of samples obtained from each test pit will be determined at the time the test pit is excavated. Sufficient samples are usually obtained and analyzed to quantify contaminant distribution as a function of depth for each test pit. Additional samples of each waste phase and any fluids encountered in each test pit may also be collected.

In some cases, samples of soil may be extracted from the test pit for reasons other than waste sampling and chemical analysis, for instance, to obtain geotechnical information. Such information would include soil types, stratigraphy, strength, etc., and could therefore entail the collection of disturbed (grab or bulk) or relatively undisturbed (hand-carved or pushed/driven) samples, which can be tested for geotechnical properties. The purposes of such explorations are very similar to those of shallow exploratory or test borings, but often test pits offer a faster, more cost-effective method of sampling than installing borings.

5.8.3.2 Sampling Equipment

The following equipment is needed for obtaining samples for chemical or geotechnical analysis from test pits and trenches:

- Backhoe or other excavating machinery.
- Shovels, picks, hand augers, and stainless steel trowels/disposable trowels.
- Sample container - bucket with locking lid for large samples; appropriate bottleware for chemical or geotechnical analysis samples.
- Polyethylene bags for enclosing sample containers; buckets.
- Remote sampler consisting of 10-foot sections of steel conduit (1-inch-diameter), hose clamps and right angle adapter for conduit (see Attachment D).

5.8.3.3 Sampling Methods

The methods discussed in this section refer to test pit sampling from grade level. If test pit entry is required, see Section 5.8.3.4.

- Excavate trench or pit in several depth increments. After each increment, the operator will wait while the sampler inspects the test pit from grade level to decide if conditions are appropriate for sampling. (Monitoring of volatiles by the SSO will also be used to evaluate the need for sampling.) Practical depth increments range from 2 to 4 feet.

- The backhoe operator, who will have the best view of the test pit, will immediately cease digging if:

  - Any fluid phase or groundwater seepage is encountered in the test pit.
  - Any drums, other potential waste containers, obstructions or utility lines are encountered.
  - Distinct changes of material are encountered.

This action is necessary to permit proper sampling of the test pit and to prevent a breach of safety protocol. Depending upon the conditions encountered, it may be required to excavate more slowly and carefully with the backhoe.

For obtaining test pit samples from grade level, the following procedure shall be followed:

- Remove loose material to the greatest extent possible with backhoe.

- Secure walls of pit if necessary. (There is seldom any need to enter a pit or trench which would justify the expense of shoring the walls. All observations and samples should be taken from the ground surface.)

- Samples of the test pit material are to be obtained either directly from the backhoe bucket or from the material once it has been deposited on the ground. The sampler or Field Operations Leader directs the backhoe operator to remove material from the selected depth or location within the test pit/trench. The bucket is brought to the surface and moved away from the pit. The sampler and/or SSO then approaches the bucket and monitors its contents with a photoionization or flame ionization detector. The sample is collected from the center of the bucket or pile and placed in sample containers using a decontaminated stainless steel trowel or disposable spatula.

- If a composite sample is desired, several depths or locations within the pit/trench are selected and a bucket is filled from each area. It is preferable to send individual sample bottles filled from each bucket to the laboratory for compositing under the more controlled laboratory conditions. However, if compositing in the field is required, each sample container shall be filled from materials that have been transferred into a mixing bucket and homogenized. Note that homogenization/compositing is not applicable for samples to be subjected to volatile organic analysis.

- Using the remote sampler shown in Attachment D, samples can be taken at the desired depth from the side wall or bottom of the pit. The face of the pit/trench shall first be scraped (using a long-handled shovel or hoe) to remove the smeared zone that has contacted the backhoe bucket. The sample shall then be collected directly into the sample jar, by scraping with the jar edge, eliminating the need to utilize samplers and minimizing the likelihood of cross-contamination. The sample jar is then capped, removed from the assembly, and packaged for shipment.

- Complete documentation as described in SOP SA-6.3 and Attachment C of this SOP.

5.8.3.4 <u>In-Pit Sampling</u>

Under rare conditions, personnel may be required to enter the test pit/trench. This is necessary only when soil conditions preclude obtaining suitable samples from the backhoe bucket (e.g., excessive mixing of soils or wastes within the test pit/trench) or when samples from relatively small discrete zones within the test pit are required. This approach may also be necessary to sample any seepage occurring at discrete levels or zones in the test pit that are not accessible with remote samplers.

In general, personnel shall sample and log pits and trenches from the ground surface, except as provided for by the following criteria:

- There is no practical alternative means of obtaining such data.

- The Site Safety Officer and Competent Person determines that such action can be accomplished without breaching site safety protocol. This determination will be based on actual monitoring of the pit/trench after it is dug (including, at a minimum, measurements of volatile organics, explosive gases and available oxygen).

- A Company-designated Competent Person determines that the pit/trench is stable or is made stable (by grading the sidewalls or using shoring) prior to entrance of any personnel. OSHA requirements must be strictly observed.

If these conditions are satisfied, one person will enter the pit/trench. On potentially hazardous waste sites, this individual will be dressed in safety gear as required by the conditions in the pit. He/she will be affixed to a safety rope and continuously monitored while in the pit.

A second individual will be fully dressed in protective clothing including a self-contained breathing device and on standby during all pit entry operations. The individual entering the pit will remain therein for as brief a period as practical, commensurate with performance of his/her work. After removing the smeared zone, samples shall be obtained with a decontaminated trowel or spoon. As an added precaution, it is advisable to keep the backhoe bucket in the test pit when personnel are working below grade. Such personnel can either stand in or near the bucket while performing sample operations. In the event of a cave-in they can either be lifted clear in the bucket, or at least climb up on the backhoe arm to reach safety.

5.8.3.5 Geotechnical Sampling

In addition to the equipment described in Section 5.8.3.2, the following equipment is needed for geotechnical sampling:

- Soil sampling equipment, similar to that used in shallow drilled boring (i.e., open tube samplers), which can be pushed or driven into the floor of the test pit.

- Suitable driving (i.e., a sledge hammer) or pushing (i.e., the backhoe bucket) equipment which is used to advance the sampler into the soil.

- Knives, spatulas, and other suitable devices for trimming hand carved samples.

- Suitable containers (bags, jars, tubes, boxes, etc.), labels, wax, etc. for holding and safely transporting collected soil samples.

- Geotechnical equipment (pocket penetrometer, torvane, etc.) for field testing collected soil samples for classification and strength properties.

Disturbed grab or bulk geotechnical soil samples may be collected for most soils in the same manner as comparable soil samples for chemical analysis. These collected samples may be stored in jars or plastic-lined sacks (larger samples), which will preserve their moisture content. Smaller samples of this type are usually tested for their index properties to aid in soil identification and classification, while larger bulk samples are usually required to perform compaction tests.

Relatively undisturbed samples are usually extracted in cohesive soils using open tube samplers, and such samples are then tested in a geotechnical laboratory for their strength, permeability and/or compressibility. The techniques for extracting and preserving such samples are similar to those used in performing Shelby tube sampling in borings, except that the sampler is advanced by hand or backhoe,

rather than by a drill rig. Also, the sampler may be extracted from the test pit by excavation around the sampler when it is difficult to pull it out of the ground. If this excavation requires entry of the test pit, the requirements described in Section 5.8.3.4 of this procedure must be followed. The open tube sampler shall be pushed or driven vertically into the floor or steps excavated in the test pit at the desired sampling elevations. Extracting tube samples horizontally from the walls of the test pit is not appropriate, because the sample will not have the correct orientation.

A sledge hammer or the backhoe may be used to drive or push the sampler or tube into the ground. Place a piece of wood over the top of the sampler or sampling tube to prevent damage during driving/pushing of the sample. Pushing the sampler with a constant thrust is always preferable to driving it with repeated blows, thus minimizing disturbance to the sample. If the sample cannot be extracted by rotating it at least two revolutions (to shear off the sample at the bottom), hand-excavate to remove the soil from around the sides of the sampler. If hand-excavation requires entry of the test pit, the requirements in Section 5.8.3.4 of this procedure must be followed. Prepare, label, pack and transport the sample in the required manner, as described in SOP SA-6.3 and SA-6.1.

5.8.4 Backfilling of Trenches and Test Pits

All test pits and excavations must be either backfilled, covered, or otherwise protected at the end of each day. No excavations shall remain open during non-working hours unless adequately covered or otherwise protected.

Before backfilling, the onsite crew shall photograph all significant features exposed by the test pit and trench and shall include in the photograph a scale to show dimensions. Photographs of test pits shall be marked to include site number, test pit number, depth, description of feature, and date of photograph. In addition, a geologic description of each photograph shall be entered in the site logbook. All photographs shall be indexed and maintained as part of the project file for future reference.

After inspection, backfill material shall be returned to the pit under the direction of the FOL.

If a low permeability layer is penetrated (resulting in groundwater flow from an upper contaminated flow zone into a lower uncontaminated flow zone), backfill material must represent original conditions or be impermeable. Backfill could consist of a soil-bentonite mix prepared in a proportion specified by the FOL (representing a permeability equal to or less than original conditions). Backfill can be covered by "clean" soil and graded to the original land contour. Revegetation of the disturbed area may also be required.

5.9 Records

The appropriate sample log sheet (see Attachment A of this SOP) must be completed by the site geologist/sampler. All soil sampling locations should be documented by tying in the location of two or more nearby permanent landmarks (building, telephone pole, fence, etc.) or obtaining GPS coordinates; and shall be noted on the appropriate sample log sheet, site map, or field notebook. Surveying may also be necessary, depending on the project requirements.

~~Test pit logs (see Attachment C of this SOP) shall contain a sketch of pit conditions. In addition, at least one photograph with a scale for comparison shall be taken of each pit. Included in the photograph shall be a card showing the test pit number. Boreholes, test pits and trenches shall be logged by the field geologist in accordance with SOP GH-1.5.~~

Other data to be recorded in the field logbook include the following:

- Name and location of job.
- Date of boring and excavation.

- Approximate surface elevation.
- Total depth of boring and excavation.
- ~~Dimensions of pit~~.
- Method of sample acquisition.
- Type and size of samples.
- Soil and rock descriptions.
- Photographs.
- ~~Groundwater levels~~.
- ~~Organic gas or methane levels~~.
- Other pertinent information, such as waste material encountered.

6.0 REFERENCES

American Society for Testing and Materials, 1987. ASTM Standards D1587-83 and D1586-84. ASTM Annual Book of Standards. ASTM. Philadelphia, Pennsylvania. Volume 4.08.

NUS Corporation, 1986. Hazardous Material Handling Training Manual.

NUS Corporation and CH2M Hill, August, 1987. Compendium of Field Operation Methods. Prepared for the U.S. EPA.

OSHA, Excavation, Trenching and Shoring 29 CFR 1926.650-653.

OSHA, Confined Space Entry 29 CFR 1910.146.

ATTACHMENT A
SOIL & SEDIMENT SAMPLE LOG SHEET

Tetra Tech NUS, Inc.

SOIL & SEDIMENT SAMPLE LOG SHEET

Page ___ of ___

Project Site Name: _____
Project No.: _____

[] Surface Soil
[] Subsurface Soil
[] Sediment
[] Other: _____
[] QA Sample Type: _____

Sample ID No.: _____
Sample Location: _____
Sampled By: _____
C.O.C. No.: _____

Type of Sample:
[] Low Concentration
[] High Concentration

GRAB SAMPLE DATA

Date:	Depth	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Time:			
Method:			
Monitor Reading (ppm):			

COMPOSITE SAMPLE DATA

Date:	Time	Depth	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Method:				
Monitor Readings (Range in ppm):				

SAMPLE COLLECTION INFORMATION

Analysis	Container Requirements	Collected	Other

OBSERVATIONS / NOTES:

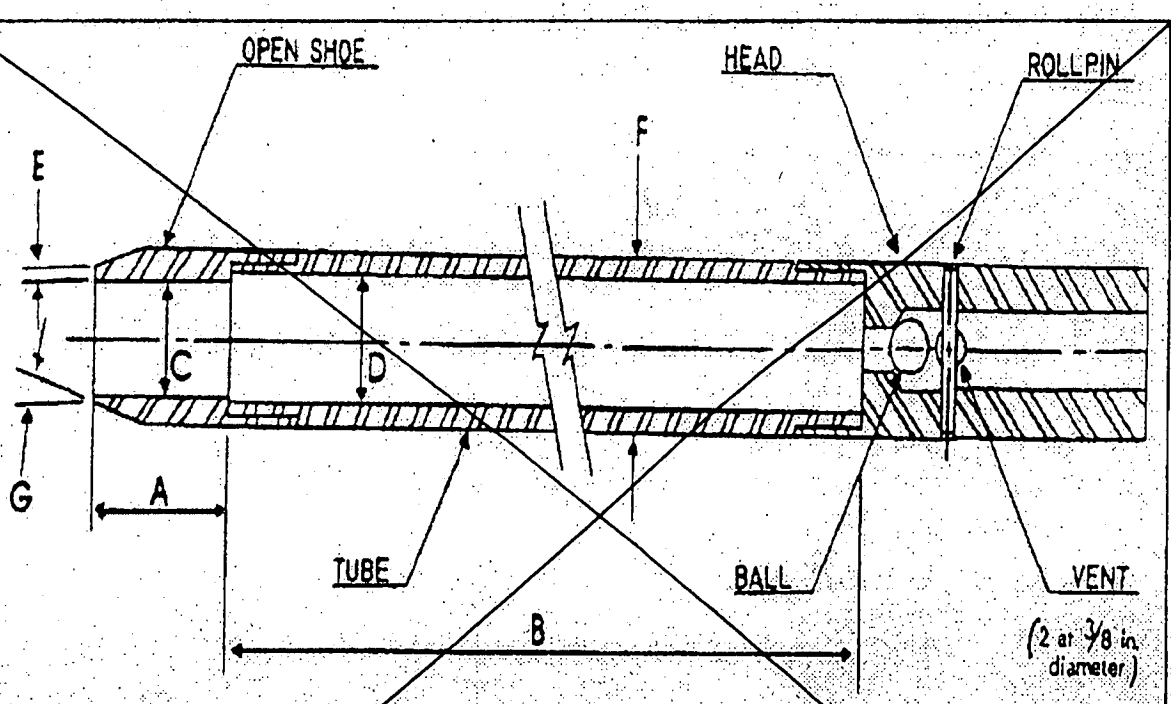
MAP:

Circle if Applicable:

MS/MSD	Duplicate ID No.:

Signature(s):

ATTACHMENT B
SPLIT-SPOON SAMPLER



A = 1.0 to 2.0 in. (25 to 50 mm)
B = 18.0 to 30.0 in. (0.457 to 0.762 m)
C = 1.375 ± 0.005 in. (34.93 ± 0.13 mm)
D = 1.50 ± 0.05 – 0.00 in. (38.1 ± 1.3 – 0.0 mm)
E = 0.10 ± 0.02 in. (2.54 ± 0.25 mm)
F = 2.00 ± 0.05 – 0.00 in. (50.8 ± 1.3 – 0.0 mm)
G = 16.0° to 23.0°

The 1½ in. (38 mm) inside diameter split barrel may be used with a 16-gage wall thickness split liner. The penetrating end of the drive shoe may be slightly rounded. Metal or plastic retainers may be used to retain soil samples.

ATTACHMENT C
TEST PIT LOG

Tetra Tech NUS, Inc.

TEST PIT LOG

Page ___ of ___

PROJECT NAME: _____ TEST PIT No.: _____
PROJECT NUMBER: _____ DATE: _____
LOCATION: _____ GEOLOGIST: _____

Depth (Ft.)	Lithology Change (Depth/Ft.)	MATERIAL DESCRIPTION Soil/Waste Characteristics (lithology, density, color, etc.)	USCS	Remarks	PID/FID READING Outer (ppm)	PID/FID READING Inner (ppm)

TEST PIT CROSS SECTION AND / OR PLAN VIEW

REMARKS: _____

PHOTO LOG: _____

ATTACHMENT D
REMOTE SAMPLE HOLDER FOR TEST PIT/TRENCH SAMPLING

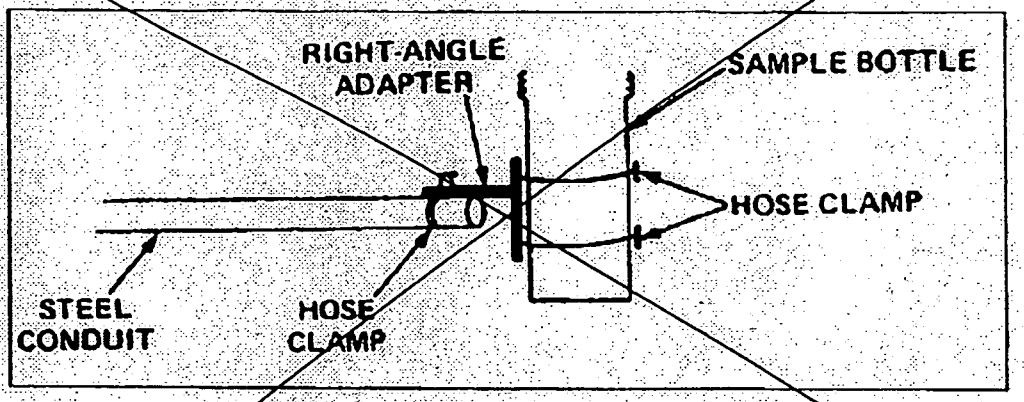


TABLE OF CONTENTS

SECTION		PAGE
1.0	PURPOSE	2
2.0	SCOPE	2
3.0	GLOSSARY	2
4.0	RESPONSIBILITIES	2
5.0	PROCEDURES	2
5.1	INTRODUCTION	2
5.2	SAMPLE IDENTIFICATION FIELD REQUIREMENTS	3
5.3	EXAMPLE SAMPLE FIELD DESIGNATIONS	4
5.4	EXAMPLES OF SAMPLE NOMENCLATURE	5
5.5	FIELD QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) SAMPLE NOMENCLATURE)	6
5.6	EXAMPLES OF FIELD QA/QC SAMPLE NOMENCLATURE	6
6.0	DEVIATIONS	6

1.0 PURPOSE

The purpose of this document is to specify a consistent sample nomenclature system that will facilitate subsequent data management in a cost-effective manner. The sample nomenclature system has been devised such that the following objectives can be attained:

- Sorting of data by matrix.
- Sorting of data by depth.
- Maintenance of consistency (field, laboratory, and data base sample numbers).
- Accommodation of all project-specific requirements.
- Accommodation of laboratory sample number length constraints (maximum of 20 characters).

2.0 SCOPE

The methods described in this procedure shall be used consistently for all projects requiring electronic data.

3.0 GLOSSARY

None.

4.0 RESPONSIBILITIES

Program Manager - It shall be the responsibility of the Program Manager (or designee) to inform contract-specific Project Managers of the existence and requirements of this Standard Operating Procedure.

Project Manager - It shall be the responsibility of the Project Manager to determine the applicability of this Standard Operating Procedure based on: (1) program-specific requirements, and (2) project size and objectives. It shall be the responsibility of the Project Manager (or designee) to ensure that the sample nomenclature is thoroughly specified in the relevant project planning document (e.g., sampling and analysis plan) and is consistent with this Standard Operating Procedure if relevant. It shall be the responsibility of the project manager to ensure that the Field Operations Leader is familiar with the sample nomenclature system.

Field Operations Leader - It shall be the responsibility of the Field Operations Leader to ensure that all field technicians or sampling personnel are thoroughly familiar with this Standard Operating Procedure and the project-specific sample nomenclature system. It shall be the responsibility of the Field Operations Leader to ensure that the sample nomenclature system is used during all project-specific sampling efforts.

5.0 PROCEDURES

5.1 Introduction

The sample identification (ID) system can consist of as few as 8 but not more than 20 distinct alpha-numeric characters. The sample ID will be provided to the laboratory on the sample labels and chain-of-custody forms. The basic sample ID provided to the lab has three segments and shall be as follows where "A" indicates "alpha," and "N" indicates "numeric":

A or N 3- or 4-Characters	AAA 2- or 3-Characters	A or N 3- to 6-Characters
Site Identifier	Sample Type	Sample Location

Additional segments may be added as needed. For example:

(1) Soil and Sediment Sample ID

A or N 3- or 4-Characters	AAA 2- or 3-Characters	A or N 3- to 6-Characters	NNNN 4-Characters
Site Identifier	Sample Type	Sample Location	Sample Depth

(2) Aqueous (groundwater or surface water) Sample ID

A or N 3- or 4-Characters	AAA 2- or 3-Characters	A or N 3- to 6-Characters	NN 2-Characters	-A
Site Identifier	Sample type	Sample Location	Round Number	Filtered Sample only

(3) Biota Sample ID

A or N 3- or 4-Characters	AAA 2- or 3-Characters	A or N 3- to 6-Characters	AA 2-Characters	NNN 3-Characters
Site Identifier	Sample Type	Sample Location	Species Identifier	Sample Group Number

5.2 Sample Identification Field Requirements

The various fields in the sample ID will include but are not limited to the following:

- Site Identifier
- Sample Type
- Sample Location
- Sample Depth
- Sampling Round Number
- Filtered
- Species Identifier
- Sample Group Number

The site identifier must be a three- or four-character field (numeric characters, alpha characters, or a mixture of alpha and numeric characters may be used). A site number is necessary since many facilities/sites have multiple individual sites, SWMUs, operable units, etc. Several examples are presented in Section 5.3 of this SOP.

The sample type must be a two- or three-character alpha field. Suggested codes are provided in Section 5.3 of this SOP.

The sample location must be at least a three-character field but may have up to six-characters (alpha, numeric, or a mixture). The six-characters may be useful in identifying a monitoring well to be sampled or describing a grid location.

The sample depth field is used to note the depth below ground surface (bgs) at which a soil or sediment sample is collected. The first two numbers of the four-number code specify the top interval, and the third and fourth specify the bottom interval in feet bgs of the sample. If the sample depth is equal to or greater than 100, then only the top interval would be represented and the sampling depth would be truncated to

three-characters. The depths will be noted in whole numbers only; further detail, if needed, will be recorded on the sample log sheet, boring log, logbook, etc.

A two-digit round number will be used to track the number of aqueous samples taken from a particular aqueous sample location. The first sample collected from a location will be assigned the round identifier 01, the second 02, etc. This applies to both existing and proposed monitoring wells and surface water locations.

Aqueous samples that are field filtered (dissolved analysis) will be identified with an "-F" in the last field segment. No entry in this segment signifies an unfiltered (total) sample.

The species identifier must be a two-character alpha field. Several suggested codes are provided in Section 5.3 of this SOP.

The three digit sample group number will be used to track the number of biota sample groups (a particular group size may be determined by sample technique, media type, the number of individual caught, weight issues, time, etc.) by species and location. The first sample group of a particular species collected from a given location will be assigned the sample group number 001 and the second sample group of the same species collected from the same location will be assigned the sample group number 002.

5.3 Example Sample Field Designations

Examples of each of the fields are as follows:

Site Identifier - Examples of site numbers/designations are as follows:

A01 - Area of Concern Number 1
125 - Solid Waste Management Unit Number 125
000 - Base or Facility Wide Sample (e.g., upgradient well)
BBG - Base Background

The examples cited are only suggestions. Each Project Manager (or designee) must designate appropriate (and consistent) site designations for their individual project.

Sample Type - Examples of sample types are as follows:

AH - Ash Sample
AS - Air Sample
BM - Building Material Sample
BSB - Biota Sample Full Body
BSF - Biota Sample Fillet
CP - Composite Sample
CS - Chip Sample
DS - Drum Sample
DU - Dust Sample
FP - Free Product
IDW - Investigation Derived Waste Sample
LT - Leachate Sample
MW - Monitoring Well Groundwater Sample
OF - Outfall Sample
RW - Residential Well Sample
SB - Soil Boring Sample
SD - Sediment Sample
SC - Scrape Sample

SG - Soil Gas Sample
SL - Sludge Sample
SP - Seep Sample
SS - Surface Soil Sample
ST - Storm Sewer Water Sample
SW - Surface Water Sample
TP - Test Pit Sample
TW - Temporary Well Sample
WC - Well Construction Material Sample
WP - Wipe Sample
WS - Waste/Solid Sample
WW - Wastewater Sample

Sample Location - Examples of the location field are as follows:

001 - Monitoring Well 1
N32E92 - Grid location 32 North and 92 East
D096 - Investigation derived waste drum number 96

Species Identifier - Examples of species identifier are as follows:

~~BC - Blue Crab~~
~~GB - Blue Gill~~
~~CO - Corn~~
~~SB - Soybean~~

5.4 Examples of Sample Nomenclature

The first round monitoring well groundwater sample collected from existing monitoring well 001 at SWMU 16 for a filtered sample would be designated as 016MW00101-F.

The second round monitoring well groundwater sample collected from existing monitoring well C20P2 at Site 23 for an unfiltered sample would be designated as 023MWC20P202.

The second surface water sample collected from point 01 at SWMU 130 for an unfiltered sample would be designated as 130SW00102.

A surface soil sample collected from grid location 32 North and 92 East at Site 32 at the 0- to 2-foot interval would be designated as 032SSN32E920002.

A subsurface soil sample from soil boring 03 at SWMU 32 at an interval of 4 to 5 feet bgs would be designated as 032SB0030405.

A sediment sample collected at SWMU 19 from 0 to 6 inches at location 14 would be designated as 019SD0140001. The sample data sheet would reflect the precise depth at which this sample was collected.

During biota sampling for full body analysis the first time a minnow trap was checked at grid location A25 of SWMU 1415 three small blue gills were captured, collected and designated with the sample ID of 1415BSBA25BG001. The second time blue gill were collected at the same location (grid location A25 at SWMU 1415) the sample ID designation given was 1415BSBA25BG002.

Note: No dash (-) or spacing is used between the segments with the exception of the filtered segment. The "F" used for a filtered aqueous sample is preceded by a dash "-F".

5.5 Field Quality Assurance/Quality Control (QA/QC) Sample Nomenclature)

Field QA/QC will be designated using a different coding system. The QC code will consist of a three- to four-segment alpha-numeric code that identifies the sample QC type, the date the sample was collected, and the number of this type of QC sample collected on that date.

AA	NNNNNN	NN	-F
QC Type	Date	Sequence Number (per day)	Filtered (aqueous only, if needed)

The QC types are identified as:

TB = Trip Blank
RB = Rinsate Blank (Equipment Blank)
FD = Field Duplicate
AB = Ambient Conditions Blank
WB = Source Water Blank

The sampling time recorded on the Chain-of-Custody Form, labels, and tags for duplicate samples will be 0000 so that the samples are "blind" to the laboratory. Notes detailing the sample number, time, date, and type will be recorded on the routine sample log sheets and will document the location of the duplicate sample (sample log sheets are not provided to the laboratory). Documentation for all other QC types (TB, RB, AB, and WB) will be recorded on the QC Sample Log sheet (see SOP on Field Documentation).

5.6 Examples of Field QA/QC Sample Nomenclature

The first duplicate of the day for a filtered ground water sample collected on June 3, 2000 would be designated as FD06030001-F.

The third duplicate of the day taken of a subsurface soil sample collected on November 17, 2003 would be designated as FD11170303.

The first trip blank associated with samples collected on October 12, 2000 would be designated as TB10120001.

The only rinsate blank collected on November 17, 2001 would be designated as RB11170101.

6.0 DEVIATIONS

Any deviation from this SOP must be addressed in detail in the site specific planning documents.

TABLE OF CONTENTS

SECTION **PAGE**

1.0 PURPOSE 2

2.0 SCOPE 2

3.0 GLOSSARY 2

4.0 RESPONSIBILITIES 2

5.0 PROCEDURES 2

5.1 SITE LOGBOOK 2
5.1.1 General 2
5.1.2 Photographs 3
5.2 FIELD NOTEBOOKS 3
5.3 FIELD FORMS 4
5.3.1 Sample Collection, Labeling, Shipment, Request for Analysis, and Field Test Results 4
5.3.2 Hydrogeological and Geotechnical Forms 5
5.3.3 Equipment Calibration and Maintenance Form 6
5.4 FIELD REPORTS 6
5.4.1 Daily Activities Report 6
5.4.2 Weekly Status Reports 7

6.0 LISTING OF TETRA TECH NUS FIELD FORMS FOUND ON THE TTNUS INTRANET SITE. HTTP://INTRANET.TTNUS.COM CLICK ON FIELD LOG SHEETS 7

ATTACHMENTS

A TYPICAL SITE LOGBOOK ENTRY 9
B SAMPLE LABEL 10
C CHAIN-OF-CUSTODY RECORD FORM 11
D CHAIN-OF-CUSTODY SEAL 12

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to identify and designate the field data record forms, logs and reports generally initiated and maintained for documenting Tetra Tech NUS field activities.

2.0 SCOPE

Documents presented within this procedure (or equivalents) shall be used for all Tetra Tech NUS field activities, as applicable. Other or additional documents may be required by specific client contracts or project planning documents.

3.0 GLOSSARY

None

4.0 RESPONSIBILITIES

Project Manager (PM) - The Project Manager is responsible for obtaining hardbound, controlled-distribution logbooks (from the appropriate source), as needed. In addition, the Project Manager is responsible for placing all field documentation used in site activities (i.e., records, field reports, sample data sheets, field notebooks, and the site logbook) in the project's central file upon the completion of field work.

Field Operations Leader (FOL) - The Field Operations Leader is responsible for ensuring that the site logbook, notebooks, and all appropriate and current forms and field reports illustrated in this guideline (and any additional forms required by the contract) are correctly used, accurately filled out, and completed in the required time-frame.

5.0 PROCEDURES

5.1 Site Logbook

5.1.1 General

The site logbook is a hard-bound, paginated, controlled-distribution record book in which all major onsite activities are documented. At a minimum, the following activities/events shall be recorded or referenced (daily) in the site logbook:

- All field personnel present
- Arrival/departure of site visitors
- Time and date of H&S training
- Arrival/departure of equipment
- Time and date of equipment calibration
- Start and/or completion of borehole, trench, monitoring well installation, etc.
- Daily onsite activities performed each day
- Sample pickup information
- Health and Safety issues (level of protection observed, etc.)
- Weather conditions

A site logbook shall be maintained for each project. The site logbook shall be initiated at the start of the first onsite activity (e.g., site visit or initial reconnaissance survey). Entries are to be made for every day

that onsite activities take place which involve Tetra Tech NUS or subcontractor personnel. Upon completion of the fieldwork, the site logbook must become part of the project's central file.

The following information must be recorded on the cover of each site logbook:

- Project name
- Tetra Tech NUS project number
- Sequential book number
- Start date
- End date

Information recorded daily in the site logbook need not be duplicated in other field notebooks (see Section 5.2), but must summarize the contents of these other notebooks and refer to specific page locations in these notebooks for detailed information (where applicable). An example of a typical site logbook entry is shown in Attachment A.

If measurements are made at any location, the measurements and equipment used must either be recorded in the site logbook or reference must be made to the field notebook in which the measurements are recorded (see Attachment A).

All logbook, notebook, and log sheet entries shall be made in indelible ink (black pen is preferred). No erasures are permitted. If an incorrect entry is made, the entry shall be crossed out with a single strike mark, and initialed and dated. At the completion of entries by any individual, the logbook pages used must be signed and dated. The site logbook must also be signed by the Field Operations Leader at the end of each day.

5.1.2 Photographs

When movies, slides, or photographs are taken of a site or any monitoring location, they must be numbered sequentially to correspond to logbook/notebook entries. The name of the photographer, date, time, site location, site description, and weather conditions must be entered in the logbook/notebook as the photographs are taken. A series entry may be used for rapid-sequence photographs. The photographer is not required to record the aperture settings and shutter speeds for photographs taken within the normal automatic exposure range. However, special lenses, films, filters, and other image-enhancement techniques must be noted in the logbook/notebook. If possible, such techniques shall be avoided, since they can adversely affect the accuracy of photographs. Chain-of-custody procedures depend upon the subject matter, type of camera (digital or film), and the processing it requires. Film used for aerial photography, confidential information, or criminal investigation require chain-of-custody procedures. Once processed, the slides of photographic prints shall be consecutively numbered and labeled according to the logbook/notebook descriptions. The site photographs and associated negatives and/or digitally saved images to compact disks must be docketed into the project's central file.

5.2 Field Notebooks

Key field team personnel may maintain a separate dedicated field notebook to document the pertinent field activities conducted directly under their supervision. For example, on large projects with multiple investigative sites and varying operating conditions, the Health and Safety Officer may elect to maintain a separate field notebook. Where several drill rigs are in operation simultaneously, each site geologist assigned to oversee a rig must maintain a field notebook.

5.3 Field Forms

All Tetra Tech NUS field forms (see list in Section 6.0 of this SOP) can be found on the company's intranet site (http://intranet.ttnus.com) under Field Log Sheets. Forms may be altered or revised for project-specific needs contingent upon client approval. Care must be taken to ensure that all essential information can be documented. Guidelines for completing these forms can be found in the related sampling SOP.

5.3.1 Sample Collection, Labeling, Shipment, Request for Analysis, and Field Test Results

5.3.1.1 Sample Log Sheet

Sample Log Sheets are used to record specified types of data while sampling. The data recorded on these sheets are useful in describing the sample as well as pointing out any problems, difficulties, or irregularities encountered during sampling. A log sheet must be completed for each sample obtained, including field quality control (QC) samples.

5.3.1.2 Sample Label

A typical sample label is illustrated in Attachment B. Adhesive labels must be completed and applied to every sample container. Sample labels can usually be obtained from the appropriate Program source electronically generated in-house, or are supplied from the laboratory subcontractor.

5.3.1.3 Chain-of-Custody Record Form

The Chain-of-Custody (COC) Record is a multi-part form that is initiated as samples are acquired and accompanies a sample (or group of samples) as they are transferred from person to person. This form must be used for any samples collected for chemical or geotechnical analysis whether the analyses are performed on site or off site. One carbonless copy of the completed COC form is retained by the field crew, one copy is sent to the Project Manager (or designee), while the original is sent to the laboratory. The original (top, signed copy) of the COC form shall be placed inside a large Ziploc-type bag and taped inside the lid of the shipping cooler. If multiple coolers are sent but are included on one COC form, the COC form should be sent with the cooler containing vials for VOC analysis or the cooler with the air bill attached. The air bill should then state how many coolers are included with that shipment. An example of a Chain-of-Custody Record form is provided as Attachment C. Once the samples are received at the laboratory, the sample cooler and contents are checked and any problems are noted on the enclosed COC form (any discrepancies between the sample labels and COC form and any other problems that are noted are resolved through communication between the laboratory point-of-contact and the Tetra Tech NUS Project Manager). The COC form is signed and copied. The laboratory will retain the copy while the original becomes part of the samples' corresponding analytical data package.

5.3.1.4 Chain-of-Custody Seal

Attachment D is an example of a custody seal. The Custody seal is an adhesive-backed label. It is part of a chain-of-custody process and is used to prevent tampering with samples after they have been collected in the field and sealed in coolers for transport to the laboratory. The COC seals are signed and dated by the sampler(s) and affixed across the lid and body of each cooler (front and back) containing environmental samples (see SOP SA-6.1). COC seals may be available from the laboratory; these seals may also be purchased from a supplier.

5.3.1.5 Geochemical Parameters Log Sheets

Field Analytical Log Sheets are used to record geochemical and/or natural attenuation field test results.

5.3.2 Hydrogeological and Geotechnical Forms

5.3.2.1 Groundwater Level Measurement Sheet

A Groundwater Level Measurement Sheet must be filled out for each round of water level measurements made at a site.

5.3.2.2 Data Sheet for Pumping Test

During the performance of a pumping test (or an in-situ hydraulic conductivity test), a large amount of data must be recorded, often within a short time period. The Pumping Test Data Sheet facilitates this task by standardizing the data collection format for the pumping well and observation wells, and allowing the time interval for collection to be laid out in advance.

5.3.2.3 Packer Test Report Form

A Packer Test Report Form must be completed for each well upon which a packer test is conducted.

5.3.2.4 Boring Log

During the progress of each boring, a log of the materials encountered, operation and driving of casing, and location of samples must be kept. The Summary Log of Boring, or Boring Log is used for this purpose and must be completed for each soil boring performed. In addition, if volatile organics are monitored on cores, samples, cuttings from the borehole, or breathing zone, (using a PID or FID), these readings must be entered on the boring log at the appropriate depth. The "Remarks" column can be used to subsequently enter the laboratory sample number, the concentration of key analytical results, or other pertinent information. This feature allows direct comparison of contaminant concentrations with soil characteristics.

5.3.2.5 Monitoring Well Construction Details Form

A Monitoring Well Construction Details Form must be completed for every monitoring well, piezometer, or temporary well point installed. This form contains specific information on length and type of well riser pipe and screen, backfill, filter pack, annular seal and grout characteristics, and surface seal characteristics. This information is important in evaluating the performance of the monitoring well, particularly in areas where water levels show temporal variation, or where there are multiple (immiscible) phases of contaminants. Depending on the type of monitoring well (in overburden or bedrock, stick-up or flush mount), different forms are used.

5.3.2.6 Test Pit Log

When a test pit or trench is constructed for investigative or sampling purposes, a Test Pit Log must be filled out by the responsible field geologist or sampling technician.

5.3.2.7 Miscellaneous Monitoring Well Forms

Monitoring Well Materials Certificate of Conformance should be used as the project directs to document all materials utilized during each monitoring well installation.

The Monitoring Well Development Record should be used as the project directs to document all well development activities.

5.3.2.8 Miscellaneous Field Forms - QA and Checklists

Container Sample and Inspection Sheet should be used as the project directs each time a container (drum, tank, etc.) is sampled and/or inspected.

QA Sample Log Sheet should be used at the project directs each time a QA sample is colleted, such as Rinsate Blank, Source Blank, etc.

Field Task Modification Request (FTMR) will be prepared for all deviations from the project planning documents. The FOL is responsible for initiating the FTMRs. Copies of all FTMRs will be maintained with the onsite planning documents and originals will be placed in the final evidence file.

The Field Project Daily Activities Check List and Field Project Pre-Mobilization Checklist should be used during both the planning and field effort to assure that all necessary tasks are planned for and completed. These two forms are not a requirement but a useful tool for most field work.

5.3.3 Equipment Calibration and Maintenance Form

The calibration or standardization of monitoring, measuring or test equipment is necessary to assure the proper operation and response of the equipment, to document the accuracy, precision or sensitivity of the measurement, and determine if correction should be applied to the readings. Some items of equipment require frequent calibration, others infrequent. Some are calibrated by the manufacturer, others by the user.

Each instrument requiring calibration has its own Equipment Calibration Log which documents that the manufacturer's instructions were followed for calibration of the equipment, including frequency and type of standard or calibration device. An Equipment Calibration Log must be maintained for each electronic measuring device used in the field; entries must be made for each day the equipment is used or in accordance with the manufacturer's recommendations.

5.4 Field Reports

The primary means of recording onsite activities is the site logbook. Other field notebooks may also be maintained. These logbooks and notebooks (and supporting forms) contain detailed information required for data interpretation or documentation, but are not easily useful for tracking and reporting of progress. Furthermore, the field logbook/notebooks remain onsite for extended periods of time and are thus not accessible for timely review by project management.

5.4.1 Daily Activities Report

To provide timely oversight of onsite contractors, Daily Activities Reports are completed and submitted as described below.

5.4.1.1 Description

The Daily Activities Report (DAR) documents the activities and progress for each day's field work. This report must be filled out on a daily basis whenever there are drilling, test pitting, well construction, or other related activities occurring which involve subcontractor personnel. These sheets summarize the work performed and form the basis of payment to subcontractors. The DAR form can be found on the TtNUS intranet site.

5.4.1.2 Responsibilities

It is the responsibility of the rig geologist to complete the DAR and obtain the driller's signature acknowledging that the times and quantities of material entered are correct.

5.4.1.3 Submittal and Approval

At the end of the shift, the rig geologist must submit the Daily Activities Report to the Field Operations Leader (FOL) for review and filing. The Daily Activities Report is not a formal report and thus requires no further approval. The DAR reports are retained by the FOL for use in preparing the site logbook and in preparing weekly status reports for submission to the Project Manager.

5.4.2 Weekly Status Reports

To facilitate timely review by project management, photocopies of logbook/notebook entries may be made for internal use.

It should be noted that in addition to summaries described herein, other summary reports may also be contractually required.

All Tetra Tech NUS field forms can be found on the company's intranet site at http://intranet.ttnus.com under Field Log Sheets.

6.0 LISTING OF TETRA TECH NUS FIELD FORMS FOUND ON THE TTNUS INTRANET SITE. HTTP://INTRANET.TTNUS.COM CLICK ON FIELD LOG SHEETS

Groundwater Sample Log Sheet
Surface Water Sample Log Sheet
Soil/Sediment Sample Log Sheet
Container Sample and Inspection Sheet
Geochemical Parameters (Natural Attenuation)
Groundwater Level Measurement Sheet
Pumping Test Data Sheet
Packer Test Report Form
Boring Log
Monitoring Well Construction Bedrock Flush Mount
Monitoring Well Construction Bedrock Open Hole
Monitoring Well Construction Bedrock Stick Up
Monitoring Well Construction Confining Layer
Monitoring Well Construction Overburden Flush Mount
Monitoring Well Construction Overburden Stick Up
Test Pit Log
Monitoring Well Materials Certificate of Conformance
Monitoring Well Development Record

Daily Activities Record
Field Task Modification Request
Hydraulic Conductivity Test Data Sheet
Low Flow Purge Data Sheet
QA Sample Log Sheet
Equipment Calibration Log
Field Project Daily Activities Checklist
Field Project Pre-Mobilization Checklist

ATTACHMENT A
TYPICAL SITE LOGBOOK ENTRY

START TIME: _____ DATE: _____

SITE LEADER: _____
PERSONNEL:

TtNUS	DRILLER	SITE VISITORS
_____	_____	_____
_____	_____	_____
_____	_____	_____

WEATHER: Clear, 68°F, 2-5 mph wind from SE

ACTIVITIES:

1. Steam jenney and fire hoses were set up.
2. Drilling activities at well ____ resumes. Rig geologist was _____. See Geologist's Notebook, No. 1, page 29-30, for details of drilling activity. Sample No. 123-21-S4 collected; see sample logbook, page 42. Drilling activities completed at 11:50 and a 4-inch stainless steel well installed. See Geologist's Notebook, No. 1, page 31, and well construction details for well _____.
3. Drilling rig No. 2 steam-cleaned at decontamination pit. Then set up at location of well _____.
4. Well _____ drilled. Rig geologist was _____. See Geologist's Notebook, No. 2, page ____ for details of drilling activities. Sample numbers 123-22-S1, 123-22-S2, and 123-22-S3 collected; see sample logbook, pages 43, 44, and 45.
5. Well _____ was developed. Seven 55-gallon drums were filled in the flushing stage. The well was then pumped using the pitcher pump for 1 hour. At the end of the hour, water pumped from well was "sand free."
6. EPA remedial project manger arrives on site at 14:25 hours.
7. Large dump truck arrives at 14:45 and is steam-cleaned. Backhoe and dump truck set up over test pit _____.
8. Test pit _____ dug with cuttings placed in dump truck. Rig geologist was _____. See Geologist's Notebook, No. 1, page 32, for details of test pit activities. Test pit subsequently filled. No samples taken for chemical analysis. Due to shallow groundwater table, filling in of test pit ___ resulted in a very soft and wet area. A mound was developed and the area roped off.
9. Express carrier picked up samples (see Sample Logbook, pages 42 through 45) at 17:50 hours. Site activities terminated at 18:22 hours. All personnel off site, gate locked.

_____

Field Operations Leader

ATTACHMENT B

Tetra Tech NUS, Inc. 661 Andersen Drive Pittsburgh, 15220 (412)921-7090	Project: Site: Location:	
Sample No:		Matrix:
Date:	Time:	Preserve:
Analysis:		
Sampled by:	Laboratory:	

ATTACHMENT C

TETRA TECH NUS, INC. CHAIN OF CUSTODY | NUMBER 3413 | PAGE ___ OF ___

PROJECT NO:	FACILITY:	PROJECT MANAGER	PHONE NUMBER	LABORATORY NAME AND CONTACT:
SAMPLERS (SIGNATURE)		FIELD OPERATIONS LEADER	PHONE NUMBER	ADDRESS
		CARRIER/WAYBILL NUMBER		CITY, STATE

STANDARD TAT ☐
RUSH TAT ☐
☐ 24 hr. ☐ 48 hr. ☐ 72 hr. ☐ 7 day ☐ 14 day

CONTAINER TYPE PLASTIC (P) or GLASS (G)
PRESERVATIVE USED
TYPE OF ANALYSIS

DATE YEAR	TIME	SAMPLE ID	LOCATION ID	TOP DEPTH (FT)	BOTTOM DEPTH (FT)	MATRIX (GW, SO, SW, SD, QC, ETC.)	COLLECTION METHOD GRAP (G) COMP (C)	No. OF CONTAINERS									COMMENTS

	DATE	TIME		DATE	TIME
1. RELINQUISHED BY			1. RECEIVED BY		
2. RELINQUISHED BY			2. RECEIVED BY		
3. RELINQUISHED BY			3. RECEIVED BY		

COMMENTS

DISTRIBUTION: WHITE (ACCOMPANIES SAMPLE) YELLOW (FIELD COPY) PINK (FILE COPY)

4/02R
FORM NO. TtNUS-001

ATTACHMENT D

CHAIN-OF-CUSTODY SEAL

CUSTODY SEAL	**CUSTODY SEAL**
Date	**Date**
Signature	**Signature**

TABLE OF CONTENTS

SECTION **PAGE**

1.0 PURPOSE **2**

2.0 SCOPE **2**

3.0 GLOSSARY **2**

4.0 RESPONSIBILITIES **3**

5.0 PROCEDURES **3**

5.1 SAMPLE CONTAINERS 3
5.2 SAMPLE PRESERVATION 3
5.2.1 Overview 4
5.2.2 Preparation and Addition of Reagents 4
5.3 FIELD FILTRATION 5
5.4 SAMPLE PACKAGING AND SHIPPING 6
5.4.1 Environmental Samples 6

6.0 REFERENCES **7**

ATTACHMENTS

A GENERAL SAMPLE CONTAINER AND PRESERVATION REQUIREMENTS 8
B ADDITIONAL REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES 9

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide information on sample preservation, packaging, and shipping procedures to be used in handling environmental samples submitted for chemical constituent, biological, or geotechnical analysis. Sample chain-of-custody procedures and other aspects of field documentation are addressed in SOP SA-6.3. Sample identification is addressed in SOP CT-04.

2.0 SCOPE

This procedure describes the appropriate containers to be used for samples depending on the analyses to be performed, and the steps necessary to preserve the samples when shipped off site for chemical analysis.

3.0 GLOSSARY

Hazardous Material - A substance or material which has been determined by the Secretary of Transportation to be capable of posing an unreasonable risk to health, safety, and property when transported in commerce, and which has been so designated. Under 49 CFR, the term includes hazardous substances, hazardous wastes, marine pollutants, and elevated temperature materials, as well as materials designated as hazardous under the provisions of §172.101 and §172.102 and materials that meet the defining criteria for hazard classes and divisions in Part 173. With slight modifications, IATA has adopted DOT "hazardous materials" as IATA "Dangerous Goods."

Hazardous Waste - Any substance listed in 40 CFR, Subpart D (y261.30 et seq.), or otherwise characterized as ignitable, corrosive, reactive, or toxic (as defined by Toxicity Characteristic Leaching Procedure, TCLP, analysis) as specified under 40 CFR, Subpart C (y261.20 et seq.), that would be subject to manifest requirements specified in 40 CFR 262. Such substances are defined and regulated by EPA.

Marking - A descriptive name, identification number, instructions, cautions, weight, specification or UN marks, or combination thereof required on outer packaging of hazardous materials.

n.o.i - Not otherwise indicated (may be used interchangeably with n.o.s.).

n.o.s. - Not otherwise specified.

Packaging - A receptacle and any other components or materials necessary for compliance with the minimum packaging requirements of 49 CFR 174, including containers (other than freight containers or overpacks), portable tanks, cargo tanks, tank cars, and multi-unit tank-car tanks to perform a containment function in conformance with the minimum packaging requirements of 49 CFR 173.24(a) & (b).

Placard - Color-coded, pictorial sign which depicts the hazard class symbol and name and which is placed on the side of a vehicle transporting certain hazardous materials.

Common Preservatives:

- Hydrochloric Acid - HCl
- Sulfuric Acid - H_2SO_4
- Nitric Acid - HNO_3
- Sodium Hydroxide - NaOH

Other Preservatives

- Zinc Acetate
- Sodium Thiosulfate - $Na_2S_2O_3$

Normality (N) - Concentration of a solution expressed as equivalent per liter, an equivalent being the amount of a substance containing 1 gram-atom of replaceable hydrogen or its equivalent.

Reportable Quantity (RQ) - For the purposes of this SOP, means the quantity specified in column 3 of the Appendix to DOT 49 CFR §172.101 for any material identified in column 1 of the appendix. A spill greater than the amount specified must be reported to the National Response Center.

Sample - A sample is physical evidence collected from a facility or the environment, which is representative of conditions at the location and time of collection.

4.0 RESPONSIBILITIES

Field Operations Leader - Directly responsible for the bottling, preservation, labeling, packaging, shipping, and custody of samples up to and including release to the shipper.

Field Samplers - Responsible for initiating the Chain-of-Custody Record (per SOP SA-6.3), implementing the packaging and shipping requirements, and maintaining custody of samples until they are relinquished to another custodian or to the shipper.

5.0 PROCEDURES

Sample identification, labeling, documentation, and chain-of-custody are addressed by SOP SA-6.3.

5.1 Sample Containers

Different types of chemicals react differently with sample containers made of various materials. For example, trace metals adsorb more strongly to glass than to plastic, whereas many organic chemicals may dissolve various types of plastic containers. Attachments A and B show proper containers (as well as other information) per 40 CFR 136. In general, the sample container shall allow approximately 5-10 percent air space ("ullage") to allow for expansion/vaporization if the sample warms during transport. However, for collection of volatile organic compounds, head space shall be omitted. The analytical laboratory will generally provide certified-clean containers for samples to be analyzed for chemical constituents. Shelby tubes or other sample containers are generally provided by the driller for samples requiring geotechnical analysis. Sufficient lead time shall be allowed for a delivery of sample container orders. Therefore, it is critical to use the correct container to maintain the integrity of the sample prior to analysis.

Once opened, the container must be used at once for storage of a particular sample. Unused but opened containers are to be considered contaminated and must be discarded. Because of the potential for introduction of contamination, they cannot be reclosed and saved for later use. Likewise, any unused containers which appear contaminated upon receipt, or which are found to have loose caps or a missing Teflon liner (if required for the container), shall be discarded.

5.2 Sample Preservation

Many water and soil samples are unstable and therefore require preservation to prevent changes in either the concentration or the physical condition of the constituent(s) requiring analysis. Although complete and irreversible preservation of samples is not possible, preservation does retard the chemical and biological

changes that inevitably take place after the sample is collected. Preservation techniques are usually limited to pH control, chemical addition(s), and refrigeration/ freezing (certain biological samples only).

5.2.1 Overview

The preservation techniques to be used for various analytes are listed in Attachments A and B. Reagents required for sample preservation will either be added to the sample containers by the laboratory prior to their shipment to the field or be added in the field (in a clean environment). Only high purity reagents shall be used for preservation. In general, aqueous samples of low-concentration organics (or soil samples of low- or medium-concentration organics) are cooled to 4°C. Medium-concentration aqueous samples, high-hazard organic samples, and some gas samples are typically not preserved. Low-concentration aqueous samples for metals are acidified with HNO_3, whereas medium-concentration and high-hazard aqueous metal samples are not preserved. Low- or medium-concentration soil samples for metals are cooled to 4°C, whereas high-hazard samples are not cooled.

The following subsections describe the procedures for preparing and adding chemical preservatives. Attachments A and B indicate the specific analytes which require these preservatives.

The FOL is responsible for ensuring that an accurate Chemical Inventory is created and maintained for all hazardous chemicals brought to the work site (see Section 5 of the TtNUS Health and Safety Guidance Manual). Furthermore, the FOL must ensure that a corresponding Material Safety Data Sheet (MSDS) is collected for every substance entered on the site Chemical Inventory, and that all persons using/handling/ disposing of these substances review the appropriate MSDS for substances they will work with. The Chemical Inventory and the MSDSs must be maintained at each work site in a location and manner where they are readily-accessible to all personnel.

5.2.2 Preparation and Addition of Reagents

Addition of the following acids or bases may be specified for sample preservation; these reagents shall be analytical reagent (AR) grade or purer and shall be diluted to the required concentration with deionized water before field sampling commences. To avoid uncontrolled reactions, be sure to Add Acid to water (not vice versa). A dilutions guide is provided below.

Acid/Base	Dilution	Concentration	Estimated Amount Required for Preservation
Hydrochloric Acid (HCl)	1 part concentrated HCl: 1 part double-distilled, deionized water	6N	5-10 mL
Sulfuric Acid (H_2SO_4)	1 part concentrated H_2SO_4: 1 part double-distilled, deionized water	18N	2 - 5 mL
Nitric Acid (HNO_3)	Undiluted concentrated HNO_3	16N	2 - 5 mL
Sodium Hydroxide (NaOH)	400 grams solid NaOH dissolved in 870 mL double-distilled, deionized water; yields 1 liter of solution	10N	2 mL

The amounts required for preservation shown in the above table assumes proper preparation of the preservative and addition of the preservative to one liter of aqueous sample. This assumes that the sample is initially at pH 7, is poorly buffered, and does not contain particulate matter; as these conditions vary, more preservative may be required. Consequently, the final sample pH must be checked using narrow-range pH paper, as described in the generalized procedure detailed below:

- Pour off 5-10 mL of sample into a dedicated, clean container. Use some of this sample to check the initial sample pH using wide range (0-14) pH paper. Never dip the pH paper into the sample; always apply a drop of sample to the pH paper using a clean stirring rod or pipette.

- Add about one-half of the estimated preservative required to the original sample bottle. Cap and invert gently several times to mix. Check pH (as described above) using medium range pH paper (pH 0-6 or pH 7.5-14, as applicable).

- Cap sample bottle and seal securely.

Additional considerations are discussed below:

- To test if ascorbic acid must be used to remove oxidizing agents present in the sample before it can be properly preserved, place a drop of sample on KI-starch paper. A blue color indicates the need for ascorbic acid addition.

  If required, add a few crystals of ascorbic acid to the sample and retest with the KI-starch paper. Repeat until a drop of sample produces no color on the KI-starch paper. Then add an additional 0.6 grams of ascorbic acid per each liter of sample volume.

  Continue with proper base preservation of the sample as described above.

- Samples for sulfide analysis must be treated by the addition of 4 drops (0.2 mL) of 2N zinc acetate solution per 100 ml of sample.

  The 2N zinc acetate solution is made by dissolving 220 grams of zinc acetate in 870 mL of double-distilled, deionized water to make 1 liter of solution.

  The sample pH is then raised to 9 using the NaOH preservative.

- Sodium thiosulfate must be added to remove residual chlorine from a sample. To test the sample for residual chlorine use a field test kit specially made for this purpose.

  If residual chlorine is present, add 0.08 grams of sodium thiosulfate per liter of sample to remove the residual chlorine.

  Continue with proper acidification of the sample as described above.

For biological samples, 10% buffered formalin or isopropanol may also be required for preservation. Questions regarding preservation requirements should be resolved through communication with the laboratory before sampling begins.

5.3 Field Filtration

At times, field-filtration may be required to provide for the analysis of dissolved chemical constituents. Field-filtration must be performed prior to the preservation of samples as described above. General procedures for field filtration are described below:

- The sample shall be filtered through a non-metallic, 0.45-micron membrane filter, immediately after collection. The filtration system shall consist of dedicated filter canister, dedicated tubing, and a peristaltic pump with pressure or vacuum pumping squeeze action (since the sample is filtered by mechanical peristalsis, the sample travels only through the tubing).

- To perform filtration, thread the tubing through the peristaltic pump head. Attach the filter canister to the discharge end of the silicon tubing (note flow direction arrow); attach the aqueous sample container to the intake end of the silicon tubing. Turn the peristaltic pump on and perform filtration. Run approximately 100 ml of sample through the filter and discard prior to sample collection.

- Continue by preserving the filtrate (contained in the filter canister), as applicable and generally described above.

5.4 Sample Packaging and Shipping

Only employees who have successfully completed the TtNUS "Shipping Hazardous Materials" training course are authorized to package and ship hazardous substances. These trained individuals are responsible for performing shipping duties in accordance with this training.

Samples collected for shipment from a site shall be classified as either environmental or hazardous material samples. Samples from drums containing materials other than Investigative Derived Waste (IDW) and samples obtained from waste piles or bulk storage tanks are generally shipped as hazardous materials. A distinction must be made between the two types of samples in order to:

- Determine appropriate procedures for transportation of samples (if there is any doubt, a sample shall be considered hazardous and shipped accordingly.)

- Protect the health and safety of transport and laboratory personnel receiving the samples (special precautions are used by the shipper and at laboratories when hazardous materials are received.)

Detailed procedures for packaging environmental samples are outlined in the remainder of this section.

5.4.1 Environmental Samples

Environmental samples are packaged as follows:

- Place properly identified sample container, with lid securely fastened, in a plastic bag (e.g. Ziploc baggie), and seal the bag.

- Place sample in a cooler constructed of sturdy material which has been lined with a large, plastic bag (e.g. "garbage" bag). Drain plugs on coolers must be taped shut.

- Pack with enough cushioning materials such as bubble wrap (shoulders of bottles must be iced if required) to minimize the possibility of the container breaking.

- If cooling is required (see Attachments A and B), place ice around sample container shoulders, and on top of packing material (minimum of 8 pounds of ice for a medium-size cooler).

- Seal (i.e., tape or tie top in knot) large liner bag.

- The original (top, signed copy) of the COC form shall be placed inside a large Ziploc-type bag and taped inside the lid of the shipping cooler. If multiple coolers are sent but are included on one COC form, the COC form should be sent with the cooler containing the vials for VOC analysis. The COC form should then state how many coolers are included with that shipment.

- Close and seal outside of cooler as described in SOP SA-6.3. Signed custody seals must be used.

Coolers must be marked as containing "Environmental Samples." The appropriate side of the container must be marked "This End Up" and arrows placed appropriately. No DOT marking or labeling is required; there are no DOT restrictions on mode of transportation.

6.0 REFERENCES

American Public Health Association, 1981. Standard Methods for the Examination of Water and Wastewater, 15th Edition. APHA, Washington, D.C.

International Air Transport Association (latest issue). Dangerous Goods Regulations, Montreal, Quebec, Canada.

U.S. Department of Transportation (latest issue). Hazardous Materials Regulations, 49 CFR 171-177.

U.S. EPA, 1984. "Guidelines Establishing Test Procedures for the Analysis of Pollutants under Clean Water Act." Federal Register, Volume 49 (209), October 26, 1984, p. 43234.

U.S. EPA, 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020, U.S. EPA-EMSL, Cincinnati, Ohio.

ATTACHMENT A

GENERAL SAMPLE CONTAINER AND PRESERVATION REQUIREMENTS

Sample Type and Concentration		Container[1]	Sample Size	Preservation[2]	Holding Time[2]
WATER					
Organics (GC&GC/MS)	VOC Low	Borosilicate glass	2 x 40 ml	Cool to 4°C HCl to ≤ 2	14 days[9]
	Extractables (Low SVOCs and pesticide/PCBs)	Amber glass	2x2 L or 4x1 L	Cool to 4°C	7 days to extraction; 40 days after extraction
	Extractables (Medium SVOCs and pesticide/PCBs)	Amber glass	2x2 L or 4x1 L	None	7 days to extraction; 40 days after extraction
Inorganics	Metals Low	High-density polyethylene	1 L	HNO_3 to pH ≤2	6 months (Hg-28 days)
	Medium	Wide-mouth glass	16 oz.	None	6 months
	Cyanide Low	High-density polyethylene	1 L	NaOH to pH>12	14 days
	Cyanide Medium	Wide-mouth glass	16 oz.	None	14 days
Organic/ Inorganic	High Hazard	Wide-mouth glass	8 oz.	None	14 days
SOIL					
Organics (GC&GC/MS)	VOC	EnCore Sampler	(3) 5 g Samplers	Cool to 4°C	48 hours to lab preservation
	Extractables (Low SVOCs and pesticides/PCBs)	Wide-mouth glass	8 oz.	Cool to 4°C	14 days to extraction; 40 days after extraction
	Extractables (Medium SVOCs and pesticides/PCBs)	Wide-mouth glass	8 oz.	Cool to 4°C	14 days to extraction; 40 days after extraction
Inorganics	Low/Medium	Wide-mouth glass	8 oz.	Cool to 4°C	6 months (Hg - 28 days) Cyanide (14 days)
Organic/Inorganic	High Hazard	Wide-mouth glass	8 oz.	None	NA
Dioxin/Furan	All	Wide-mouth glass	4 oz.	None	35 days until extraction; 40 days after extraction
TCLP	All	Wide-mouth glass	8 oz.	None	7 days until preparation, analysis as per fraction
AIR					
Volatile Organics	Low/Medium	Charcoal tube - 7 cm long, 6 mm OD, 4 mm ID	100 L air	Cool to 4°C	5 days recommended

1 All glass containers should have Teflon cap liners or septa.
2 See Attachment E. Preservation and maximum holding time allowances per 40 CFR 136.

ATTACHMENT B

ADDITIONAL REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter Number/Name	Container[1]	Preservation[2][3]	Maximum Holding Time[4]
INORGANIC TESTS:			
Acidity	P, G	Cool, 4°C	14 days
Alkalinity	P, G	Cool, 4°C	14 days
Ammonia - Nitrogen	P, G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Biochemical Oxygen Demand (BOD)	P, G	Cool, 4°C	48 hours
Bromide	P, G	None required	28 days
Chemical Oxygen Demand (COD)	P, G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Chloride	P, G	None required	28 days
Chlorine, Total Residual	P, G	None required	Analyze immediately
Color	P, G	Cool, 4°C	48 hours
Cyanide, Total and Amenable to Chlorination	P, G	Cool, 4°C; NaOH to pH 12; 0.6 g ascorbic acid[5]	14 days[6]
Fluoride	P	None required	28 days
Hardness	P, G	HNO_3 to pH 2; H_2SO_4 to pH 2	6 months
Total Kjeldahl and Organic Nitrogen	P, G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Nitrate - Nitrogen	P, G	None required	48 hours
Nitrate-Nitrite - Nitrogen	P, G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Nitrite - Nitrogen	P, G	Cool, 4°C	48 hours
Oil & Grease	G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Total Organic Carbon (TOC)	P, G	Cool, 4°C; HCl or H_2SO_4 to pH 2	28 days
Orthophosphate	P, G	Filter immediately; Cool, 4°C	48 hours
Oxygen, Dissolved-Probe	G Bottle & top	None required	Analyze immediately
Oxygen, Dissolved-Winkler	G Bottle & top	Fix on site and store in dark	8 hours
Phenols	G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Phosphorus, Total	P, G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Residue, Total	P, G	Cool, 4°C	7 days
Residue, Filterable (TDS)	P, G	Cool, 4°C	7 days
Residue, Nonfilterable (TSS)	P, G	Cool, 4°C	7 days
Residue, Settleable	P, G	Cool, 4°C	48 hours
Residue, Volatile (Ash Content)	P, G	Cool, 4°C	7 days
Silica	P	Cool, 4°C	28 days
Specific Conductance	P, G	Cool, 4°C	28 days
Sulfate	P, G	Cool, 4°C	28 days

ATTACHMENT B
ADDITIONAL REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES
PAGE TWO

Parameter Number/Name	Container[1]	Preservation[2][3]	Maximum Holding Time[4]
INORGANIC TESTS (Cont'd):			
Sulfide	P, G	Cool, 4°C, add zinc acetate plus sodium hydroxide to pH 9	7 days
Sulfite	P, G	None required	Analyze immediately
Turbidity	P, G	Cool, 4°C	48 hours
METALS:[7]			
Chromium VI (Hexachrome)	P, G	Cool, 4°C	24 hours
Mercury (Hg)	P, G	HNO_3 to pH 2	28 days
Metals, except Chromium VI and Mercury	P, G	HNO_3 to pH 2	6 months
ORGANIC TESTS:[8]			
Purgeable Halocarbons	G, Teflon-lined septum	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]	14 days
Purgeable Aromatic Hydrocarbons	G, Teflon-lined septum	Cool, 4°C; 0.008% $Na_2S_2O_3$[5] HCl to pH 2[9]	14 days
Acrolein and Acrylonitrile	G, Teflon-lined septum	Cool, 4°C; 0.008% $Na_2S_2O_3$[5] adjust pH to 4-5[10]	14 days
Phenols[11]	G, Teflon-lined cap	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction
Benzidines[11],[12]	G, Teflon-lined cap	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]	7 days until extraction[13]
Phthalate esters[11]	G, Teflon-lined cap	Cool, 4°C	7 days until extraction; 40 days after extraction
Nitrosamines[11],[14]	G, Teflon-lined cap	Cool, 4°C; store in dark; 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction
PCBs[11]	G, Teflon-lined cap	Cool, 4°C	7 days until extraction; 40 days after extraction
Nitroaromatics & Isophorone[11]	G, Teflon-lined cap	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]; store in dark	7 days until extraction; 40 days after extraction
Polynuclear Aromatic Hydrocarbons (PAHs)[11],[14]	G, Teflon-lined cap	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]; store in dark	7 days until extraction; 40 days after extraction
Haloethers[11]	G, Teflon-lined cap	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction
Dioxin/Furan (TCDD/TCDF)[11]	G, Teflon-lined cap	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction

ATTACHMENT B
ADDITIONAL REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES
PAGE THREE

(1) Polyethylene (P): generally 500 ml or Glass (G): generally 1L.
(2) Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.
(3) When any sample is to be shipped by common carrier or sent through the United States Mail, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172).
(4) Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer periods, and has received a variance from the Regional Administrator.
(5) Should only be used in the presence of residual chlorine.
(6) Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested with lead acetate paper before pH adjustments are made to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.
(7) Samples should be filtered immediately on site before adding preservative for dissolved metals.
(8) Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.
(9) Sample receiving no pH adjustment must be analyzed within 7 days of sampling.
(10) The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.
(11) When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6-9; samples preserved in this manner may be held for 7 days before extraction and for 40 days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (re: the requirement for thiosulfate reduction of residual chlorine) and footnotes 12, 13 (re: the analysis of benzidine).
(12) If 1,2-diphenylthydrazine is likely to be present, adjust the pH of the sample to 4.0 ± 0.2 to prevent rearrangement to benzidine.
(13) Extracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosphere.
(14) For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$ and adjust pH to 7-10 with NaOH within 24 hours of sampling.
(15) The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $Na_2S_2O_3$.

TABLE OF CONTENTS

SECTION **PAGE**

1.0 PURPOSE **2**

2.0 SCOPE **2**

3.0 GLOSSARY **2**

4.0 RESPONSIBILITIES **3**

5.0 PROCEDURES **3**

5.1 DECONTAMINATION DESIGN/CONSTRUCTIONS CONSIDERATIONS 3
5.1.1 Temporary Decontamination Pads 3
5.1.2 Decontamination Activities at Drill Rigs/DPT Units 4
5.1.3 Decontamination Activities at Remote Sample Locations 5
5.2 EQUIPMENT DECONTAMINATION PROCEDURES 5
5.2.1 Monitoring Well Sampling Equipment 5
5.2.2 Down-Hole Drilling Equipment 6
5.2.3 Soil/Sediment Sampling Equipment 6
5.3 CONTACT WASTE/MATERIALS 7
5.3.1 Decontamination Solutions 7
5.4 DECONTAMINATION EVALUATION 7

1.0 PURPOSE

Decontamination is the process of removing and/or neutralizing site contaminants that have contacted and/or accumulated on equipment. The objective/purpose of this SOP is intended to protect site personnel, general public, and the sample integrity through the prevention of cross contamination onto unaffected persons or areas. It is further intended through this procedure to provide guidelines regarding the appropriate procedures to be followed when decontaminating drilling equipment, monitoring well materials, chemical sampling equipment and field analytical equipment.

2.0 SCOPE

This procedure applies to all equipment including drilling equipment, heavy equipment, monitoring well materials, as well as chemical sampling and field analytical equipment decontamination that may be used to provide access/acquire environmental samples. Where technologically and economically feasible, single use sealed disposable equipment will be employed to minimize the potential for cross contamination. This procedure also provides general reference information on the control of contaminated materials.

3.0 GLOSSARY

Acid - For decontamination of equipment when sampling for trace levels of inorganics, a 10% solution of nitric acid in deionized water should be used. Due to the leaching ability of nitric acid, it should not be used on stainless steel.

Alconox/Liquinox - A brand of phosphate-free laboratory-grade detergent.

Decontamination Solution - Is a solution selected/identified within the Health and Safety Plan or Project-Specific Quality Assurance Plan. The solution is selected and employed as directed by the project chemist/health and safety professional.

Deionized Water (DI) - Deionized water is tap water that has been treated by passing through a standard deionizing resin column. This water may also pass through additional filtering media to attain various levels of analyte-free status. The DI water should meet CAP and NCCLS specifications for reagent grade, Type I water.

Potable Water - Tap water used from any municipal water treatment system. Use of an untreated potable water supply is not an acceptable substitute for tap water.

Pressure Washing - Employs high pressure pumps and nozzle configuration to create a high pressure spray of potable water. High pressure spray is employed to remove solids.

Solvent - The solvent of choice is pesticide-grade Isopropanol. Use of other solvents (methanol, acetone, pesticide-grade hexane, or petroleum ether) may be required for particular projects or for a particular purpose (e.g. for the removal of concentrated waste) and must be justified in the project planning documents. As an example, it may be necessary to use hexane when analyzing for trace levels of pesticides, PCBs, or fuels. In addition, because many of these solvents are not miscible in water, the equipment should be air dried prior to use. Solvents should not be used on PVC equipment or well construction materials.

Steam Pressure Washing - This method employs a high pressure spray of heated potable water. This method through the application of heat provides for the removal of various organic/inorganic compounds.

4.0 RESPONSIBILITIES

Project Manager - Responsible for ensuring that all field activities are conducted in accordance with approved project plan(s) requirements.

Field Operations Leader (FOL) - Responsible for the onsite verification that all field activities are performed in compliance with approved Standards Operating Procedures or as otherwise dictated by the approved project plan(s).

Site Health and Safety Officer (SHSO) - The SHSO exercises shared responsibility with the FOL concerning decontamination effectiveness. All equipment arriving on-site (as part of the equipment inspection), leaving the site, moving between locations are required to go through a decontamination evaluation. This is accomplished through visual examination and/or instrument screening to determine the effectiveness of the decontamination process. Failure to meet these objectives are sufficient to restrict equipment from entering the site/exiting the site/ or moving to a new location on the site until the objectives are successfully completed.

5.0 PROCEDURES

The process of decontamination is accomplished through the removal of contaminants, neutralization of contaminants, or the isolation of contaminants. In order to accomplish this activity a level of preparation is required. This includes site preparation, equipment selection, and evaluation of the process. Site contaminant types, concentrations, media types, are primary drivers in the selection of the types of decontamination as well as where it will be conducted. For purposes of this SOP discussion will be provided concerning general environmental investigation procedures.

The decontamination processes are typically employed at:

- Temporary Decontamination Pads/Facilities
- Sample Locations
- Centralized Decontamination Pad/Facilities
- Combination of some or all of the above

The following discussion represents recommended site preparation in support of the decontamination process.

5.1 Decontamination Design/Constructions Considerations

5.1.1 Temporary Decontamination Pads

Temporary decontamination pads are constructed at satellite locations in support of temporary work sites. These structures are generally constructed to support the decontamination of heavy equipment such as drill rigs and earth moving equipment but can be employed for smaller articles.

The purpose of the decontamination pad is to contain wash waters and potentially contaminated soils generated during decontamination procedures. Therefore, construction of these pads should take into account the following considerations

- Site Location – The site selected should be within a reasonable distance from the work site but should avoid:

  - Pedestrian/Vehicle thoroughfares
  - Areas where control/custody cannot be maintained
  - Areas where a potential releases may be compounded through access to storm water transport systems, streams or other potentially sensitive areas.
  - Areas potentially contaminated.

- Pad – The pad should be constructed to provide the following characteristics

  - Size – The size of the pad should be sufficient to accept the equipment to be decontaminated as well as permitting free movement around the equipment by the personnel conducting the decontamination.

  - Slope – An adequate slope will be constructed to permit the collection of the water and potentially contaminated soils within a trough or sump constructed at one end. The collection point for wash waters should be of adequate distance that the decontamination workers do not have to walk through the wash waters while completing their tasks.

  - Sidewalls – The sidewalls should be a minimum of 6-inches in height to provide adequate containment for wash waters and soils. If splash represents a potential problem, splash guards should be constructed to control overspray. Sidewalls maybe constructed of wood, inflatables, sand bags, etc. to permit containment.

  - Liner – Depending on the types of equipment and the decontamination method the liner should be of sufficient thickness to provide a puncture resistant barrier between the decontamination operation and the unprotected environment. Care should be taken to examine the surface area prior to placing the liner to remove sharp articles (sticks, stones, debris) that could puncture the liner. Liners are intended to form an impermeable barrier. The thickness may vary from a minimum recommended thickness of 10 mil to 30 mil. Achieving the desired thickness maybe achieved through layering lighter constructed materials. It should be noted that various materials (rubber, polyethylene sheeting) become slippery when wet. To minimize this potential hazard associated with a sloped liner a light coating of sand maybe applied to provide traction as necessary.

  - Wash/drying Racks – Auger flights, drill/drive rods require racks positioned off of the ground to permit these articles to be washed, drained, and dried while secured from falling during this process. A minimum ground clearance of 2-feet is recommended.

  - Maintenance – The work area should be periodically cleared of standing water, soils, and debris. This action will aid in eliminating slip, trip, and fall hazards. In addition, these articles will reduce potential backsplash and cross contamination. Hoses should be gathered when not in use to eliminate potential tripping hazards.

5.1.2 Decontamination Activities at Drill Rigs/DPT Units

During subsurface sampling activities including drilling and direct push activities decontamination of drive rods, Macro Core Samplers, split spoons, etc. are typically conducted at an area adjacent to the operation. Decontamination is generally accomplished using a soap/water wash and rinse utilizing buckets and brushes. This area requires sufficient preparation to accomplish the decontamination objectives.

Buckets shall be placed within mortar tubs or similar secondary containment tubs to prevent splash and spills from reaching unprotected media. Drying racks will be employed as directed for temporary pads to permit parts to dry and be evaluated prior to use/re-use.

5.1.3 Decontamination Activities at Remote Sample Locations

When sampling at remote locations sampling devices such as trowels, pumps/tubing should be evacuated of potentially contaminated media to the extent possible. This equipment should be wrapped in plastic for transport to the temporary/centralized decontamination location for final cleaning and disposition.

5.2 Equipment Decontamination Procedures

The following represents procedures to be employed for the decontamination of equipment that may have contacted and/or accumulated contamination through site investigation activities.

5.2.1 Monitoring Well Sampling Equipment

5.2.1.1 Groundwater sampling pumps – This includes pumps inserted into the monitoring well such as Bladder pumps, Whale pumps, Redi-Flo, reusable bailers, etc.

1) Evacuate to the extent possible, any purge water within the pump.

2) Scrub using soap and water and/or steam clean the outside of the pump and tubing, where applicable.

3) Insert the pump and tubing into a clean container of soapy water. Pump a sufficient amount of soapy water through the pump to flush any residual purge water. Once flushed, circulate soapy water through the pump to ensure the internal components are thoroughly flushed.

4) Remove the pump and tubing from the container, rinse external components using tap water. Insert the pump and tubing into a clean container of tap water. Pump a sufficient amount of tap water through the pump to evacuate all of the soapy water (until clear).

5) Rinse equipment with pesticide grade isopropanol

6) Repeat item #4 using deionized water through the hose to flush out the tap water and solvent residue as applicable.

7) Drain residual deionized water to the extent possible, allow components to air dry.

8) Wrap pump in aluminum foil or a clear clean plastic bag for storage.

5.2.1.2 Electronic Water Level Indicators/Sounders/Tapes

During water level measurements, rinsing with the extracted tape and probe with deionized water and wiping the surface of the extracted tape is acceptable. However, periodic full decontamination should be conducted as indicated below.

- The solvent should be employed when samples contain oil, grease, PAHs, PCBs, and other hard to remove materials. If these are not of primary concern, the solvent step may be omitted. In addition, do not rinse PE, PVC, and associated tubing with solvents.

1) Wash with soap and water
2) Rinse with tap water
3) Rinse with deionized water

Note: In situations where oil, grease, free product, other hard to remove materials are encountered probes and exposed tapes should be washed in hot soapy water.

5.2.1.3 Miscellaneous Equipment

Miscellaneous equipment including analytical equipment (water quality testing equipment) should be cleaned per manufacturer's instructions. This generally includes wiping down the sensor housing and rinsing with tap and deionized water.

Coolers/Shipping Containers employed to ship samples are received from the lab in a variety of conditions from marginal to extremely poor. Coolers should be evaluated prior to use for

- Structural integrity – Coolers missing handles or having breaks within the outer housing should be removed and not used. Notify the laboratory that the risk of shipping samples will not be attempted and request a replacement unit.

- Cleanliness – As per protocol only volatile organic samples are accompanied by a trip blank. If a cooler's cleanliness is in question (visibly dirty/stained) or associated with noticeable odors it should be decontaminated prior to use.

  1) Wash with soap and water
  2) Rinse with tap water
  3) Dry

If these measures fail to clean the cooler to an acceptable level, remove the unit from use as a shipping container and notify the laboratory to provide a replacement unit.

5.2.2 Down-Hole Drilling Equipment

This includes any portion of the drill rig that is over the borehole including auger flights, drill stems, rods, and associated tooling that would extend over the borehole. This procedure is to be employed prior to initiating the drilling/sampling activity, then between locations.

1) Remove all soils to the extent possible using shovels, scrapers, etc. to remove loose soils.
2) Through a combination of scrubbing using soap and water and/or steam cleaning remove visible dirt/soils.
3) Rinse with tap water.
4) Rinse equipment with pesticide grade isopropanol
5) To the extent possible allow components to air dry.
6) Wrap or cover equipment in clear plastic until it is time to be used.

5.2.3 Soil/Sediment Sampling Equipment

This consists of soil sampling equipment including but not limited to hand augers, stainless steel trowels/spoons, bowls, dredges, scoops, split spoons, Macro Core samplers, etc.

1) Remove all soils to the extent possible.

2) Through a combination of scrubbing using soap and water and/or steam cleaning remove visible dirt/soils.

3) Rinse with tap water.

4) Rinse equipment with pesticide grade isopropanol

5) Rinse with deionized water

6) To the extent possible allow components to air dry.

7) If the device is to be used immediately, screen with a PID/FID to insure all solvents (if they were used) and trace contaminants have been adequately removed.

8) Once these devices have been dried wrap in aluminum foil for storage until it is time to be used.

5.3 Contact Waste/Materials

During the course of field investigations disposable/single use equipment becomes contaminated. These items include tubing, trowels, PPE (gloves, overboots, splash suits, etc.) broken sample containers.

With the exception of the broken glass, single use articles should be cleaned (washed and rinsed) of visible materials and disposed of as normal refuse. The exception to this rule is that extremely soiled materials that cannot be cleaned should be containerized for disposal in accordance with applicable federal state and local regulations.

5.3.1 Decontamination Solutions

All waste decontamination solutions and rinses must be assumed to contain the hazardous chemicals associated with the site unless there are analytical or other data to the contrary. The waste solution volumes could vary from a few gallons to several hundred gallons in cases where large equipment required cleaning.

Containerized waste rinse solutions are best stored in 55-gallon drums (or equivalent containers) that can be sealed until ultimate disposal at an approved facility. These containers must be appropriately labeled.

5.4 Decontamination Evaluation

Determining the effectiveness of the decontamination process will be accomplished in the following manner

- Visual Evaluation – A visual evaluation will be conducted to insure the removal of particulate matter. This will be done to insure that the washing/rinsing process is working as intended.

- Instrument Screening – A PID and/or an FID should be used to evaluate the presence of the contaminants or solvents used in the cleaning process. The air intake of the instrument should be passed over the article to be evaluated. A positive detection requires a repeat the decontamination process. It should be noted that the instrument scan is only viable if the contaminants are detectable within the instruments capabilities.

- Rinsate Blanks – It is recommended that Rinsate samples be collected to

  - Evaluate the decontamination procedure representing different equipment applications (pumps versus drilling equipment) and different decontamination applications.

  - Single use disposable equipment – The number of samples should represent different types of equipment as well as different Lot Numbers of single use articles.

The collection and the frequency of collection of rinsate samples are as follows:

- Per decontamination method
- Per disposable article/Batch number of disposable articles

It is recommended that an initial rinsate sample be collected early in the project to ensure that the decontamination process is functioning properly and in an effort to avoid using a contaminated batch of single use articles. It is recommended that a follow up sample be collected during the execution of the project to insure those conditions do not change. Lastly, rinsate samples collection may be driven by types of and/or contaminant levels. Hard to remove contaminants, oils/greases, some PAHs/PCBs, etc. may also support the collection of additional rinsates due to the obvious challenges to the decontamination process. This is a field consideration to be determined by the FOL.

STANDARD OPERATING PROCEDURES

Round 8 and Additional Scrutiny Sampling
Portsmouth Naval Shipyard, Kittery, Maine

Standard operating procedures (SOP) are based on Rounds 1 through 7 of the Interim Offshore Monitoring Program and the Additional Scrutiny Quality Assurance Project Plan.

1.0 STATION LOCATION

This section described the procedures for locating each station location. Coordinates for each station location will be provided by Tetra Tech NUS (TtNUS) prior to sampling dates.

1.1 EQUIPMENT LIST

- 24 ft Privateer boat with hydraulic winch and davit, fathometer, radio and required safety equipment including local charts
- Boat GPS - Differential GPS Leica MX 420 with 421B Smart Antenna mounted over davit, accurate to within 1 meter
- Hand held GPS - Differential GPS Leica MX 420 placed in a backpack with a short (1 meter) antenna, accurate to within 1 meter.
- Field log book and data sheet, aerial photographs of station location and station coordinates
- Cellular phone

1.2 METHODS

- Approach subtidal stations by boat using provided coordinates. Anchor the boat. Record station coordinates (note that because the boat may move slightly during sampling the stations coordinates may be several feet away from the actual sample location.
- Approach intertidal stations by boat or by foot using provided coordinates. Record sample coordinates. Permanent markers are available at some of the intertidal stations. If a permanent marker is available, record the distance from the marker to where the sample is collected.

2.0 SEDIMENT SAMPLING

2.1 EQUIPMENT LIST

- Boat GPS - Differential GPS Leica MX 420 with 421B Smart Antenna mounted over davit, accurate to within 1 meter
- 24 ft Privateer boat with 2 anchors hydraulic winch and davit, fathometer, radio and required safety equipment including local charts
- Hand held GPS - Differential GPS Leica MX 420 placed in a backpack with a short (1 meter) antenna, accurate to within1 meter.
- Seabird Microcat CTD - water quality profiler
- Van Veen and Ponar grab samplers (larger samples are stainless steel with Kyner coated, smaller samplers are stainless steel) with weights (increase penetration) and extensions (reduce penetration). A 0.1 m^2 and .04 m^2 are available. Both open from the top
- Stainless steel bowl
- Stainless steel scoops (Teflon scoops may be used in place of stainless steel scoops
- Sample jar (supplied by laboratory) and pre-printed sample labels
- Cooler, ice and temperature blank
- Deionized water, Alconox, isopropanol alcohol, 10% Nitric Acid
- Squirt bottles
- Nitrile gloves
- Acid resistant gloves
- Waste container
- Chain-of-custody forms, field log sheets, field data sheets, and log book
- Ziploc bags
- Disposable latex gloves and trash bags
- Scrub brushes and buckets
- Field log book and data sheet, aerial photographs of station location and station coordinates
- Container to collect decontamination fluids
- Cellular phone

2.2 METHODS

2.2.1 Subtidal Sample Collection

- Collect water quality data (temperature, dissolved oxygen, salinity) using Seabird Microcat CTD at the surface, mid depth and bottom at each Round 8 sampling location. Record dGPS location and time when instrument deployed.
- Deploy cleaned grab sampler. Sampler size will be dependent on bottom type. Estimate the depth of the sample. Accept only complete samples – those that

penetrate the sediment 15 cm, where the surface is undisturbed and the sampler has completely closed.

- Add weights if the sampler does not penetrate to the required depth. Add extensions to reduce the penetration if sediment exits the top of the sampler indicating that the sampler penetrated too deep into the sediment.
- Record type of sampler used, added weights or horizontal extensions used to attain successful sample and estimate of sampler penetration into the sediment
- Carefully decant surface water through top of sampler.
- Record estimate of redox discontinuity (as determine by sediment color change from brown to black) and presence of any biota in the sampler.
- Using stainless steel scoop, remove sediment to 10 cm from the top of the sampler and place in stainless steel bowl.
- Samples collected as part Round 8 will be a composite of **three** successful grab samples; move the boat slightly between grabs. Samples collected as part of Additional Scrutiny will be from **one** grab sample.
- Homogenize samples in the bowl and sub sample into labeled jars for analysis.
- Seal jars in Ziploc bags and store in cooler on wet ice.
- Surrender samples to the TtNUS field personal at the end of each sampling day.

2.2.2 Intertidal Sample Collection

- If station is approached by boat, collect sample as described above (2.2.1 Subtidal Sample Collection).
- If station is approached by foot, collect sediment sample to a depth of 10 cm using a stainless steel scoop and place in stainless steel bowl.
- Homogenize samples in the bowl and sub sample into labeled jars for analysis.
- Seal jars in Ziploc bags and store in cooler on wet ice.
- Surrender samples to the TtNUS field personal at the end of each sampling day.

2.2.3 Decontamination

- Decontaminate grab sampler, mixing bowl and scoop between samples as follows:
    - Rinse with seawater to remove visible sediment
    - Rinse with potable water
    - Wash with scrub brush and Alconox
    - Rinse with potable water
    - Rinse with 10% nitric acid
    - Rinse with deionized water
    - Rinse with isopropol alcohol
    - Rinse with distilledwater
    - Air dry
- Collect all decontamination fluids for proper disposal.

2.3 STATION DOCUMENTATION

- For each station a field data sheet will be completed which includes the following information:
  - Date and time sample was collected
  - Benthic features – mud flat, sandy area, seeps, etc,
  - Biota present and/or biota indicators
    - Seagrasses, mussels, etc.
    - Record size of eelgrass bed (if present)
    - Burrows
  - Debris present – metal scraps, garbage
  - Collection Methods
    - Method of locating the sample station
    - Distance to permanent marker
    - Equipment used (i.e., grab sampler, stainless steel scoop, weights or wings added)
    - Difficulty collecting sample
  - Sediment description – color, texture, smell, redox depth
  - Presence and direction of seeps
  - Indicate if duplicate samples were collected
- Sample jar labeling
  - Label jars with sample date and time (the sample number and analysis will be pre-printed on the label).
- Record sampling activities, field conditions, and weather condition in a field log book.

TETRA TECH NUS
FIELD TASK MODIFICATION REQUEST FORM

Project/Installation Name _____ CTO & Project Number _____ Task Mod. Number _____

Modification To (e.g. Work Plan) _____ Site/Sample Location _____ Date _____

Activity Description: _____

Reason for Change: _____

Recommended Disposition: _____

Field Operations Leader (Signature) _____ Date _____

Approved Disposition:

Project/Task Order Manager (Signature) _____ Date _____

Distribution:

Program/Project File –
Project/Task Order Manager –
Field Operations Leader –

Other: _____

Tetra Tech NUS, Inc.

SOIL & SEDIMENT SAMPLE LOG SHEET

Page___ of ___

Project Site Name: _____
Project No.: _____

[] Surface Soil
[] Subsurface Soil
[] Sediment
[] Other: _____
[] QA Sample Type: _____

Sample ID No.: _____
Sample Location: _____
Sampled By: _____
C.O.C. No.: _____

Type of Sample:
[] Low Concentration
[] High Concentration

GRAB SAMPLE DATA:

	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Date:			
Time:			
Method:			
Monitor Reading (ppm):			

COMPOSITE SAMPLE DATA:

	Time	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Date:				
Method:				
Monitor Readings (Range in ppm):				

SAMPLE COLLECTION INFORMATION:

Analysis	Container Requirements	Collected	Other

OBSERVATIONS / NOTES:

MAP:

Circle if Applicable:

MS/MSD	Duplicate ID No.:

Signature(s):

Tetra Tech NUS, Inc.

QA SAMPLE LOG SHEET

Page___ of ___

Project Site Name: _____ Sample ID Number: _____
Project Number: _____ Sampled By: _____
Sample Location: _____ C.O.C. Number: _____
QA Sample Type:

[] Trip Blank [] Rinsate Blank
[] Source Water Blank [] Other Blank _____

SAMPLING DATA:

Date: _____
Time: _____
Method: _____

WATER SOURCE:

[] Laboratory Prepared [] Tap
[] Purchased [] Fire Hydrant
[] Other _____

PURCHASED WATER INFORMATION (If Applicable as Source or Rinsate Water):

Product Name: _____
Supplier: _____
Manufacturer: _____
Order Number: _____
Lot Number: _____
Expiration Date: _____

RINSATE INFORMATION (If Applicable):

Media Type: _____
Equipment Used: _____
Equipment Type:

[] Dedicated
[] Reusable

SAMPLE COLLECTION INFORMATION:

Analysis	Preservative	Container Requirements	Collected
Volatiles	Cool 4°C & HCl		YES / NO
Semivolatiles	Cool 4°C		YES / NO
Pesticide / PCB	Cool 4°C		YES / NO
Metals	Cool 4°C & HNO_3		YES / NO
Cyanide	Cool 4°C & NaOH		YES / NO

OBSERVATIONS / NOTES:

Signature(s):

ANALYTICAL LABORATORY STANDARD OPERATING PROCEDURES (SOPs) FOR ROUND 8 OF THE INTERIM OFFSHORE MONITORING PROGRAM AND THE ADDITIONAL SCRUTINY INVESTIGATION FOR OPERABLE UNIT 4
PORTSMOUTH NAVAL SHIPYARD
KITTERY, MAINE

Round 8 and Additional Scrutiny SOPs

1. Organochlorine Pesticides by Gas Chromatography SW-846 8081A & EPA TO-4A
2. Determination of Extractable PAH Compounds by Gas Chromatography/Mass Spectrometry Selective Ion Monitoring (GC/MS-SIM)

Round 8 SOPs

3. Analysis of Polychlorinated Biphenyl Congeners Based on SW-846 Method 8082
4. Analysis of Polychlorinated Dioxins/Furans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Based on Methods 8290, 1613B, 23, 0023A, and TO-9A
5. Acid Digestion for Total Metals in Sediments, Soils, Coal, and Flyash (Summary of Standard Operating Procedures)
6. Determination of Trace Elements by Inductively Coupled Plasma – Mass Spectrometry using a Perkin-Elmer ELAN DRC II (Summary of Standard Operating Procedures)
7. Determination of Total Organic Carbon in Soils and Sediment
8. Particle-Size Analysis of Soils, ASTM D422-63

Additional Scrutiny SOPs

9. Determination of Trace Elements by ICP-MS
10. Determination of Mercury in Solid or Semisolid Waste Semi-Automated Cold Vapor Technique
11. Shaker Table Extraction
12. Analysis of Parent and Alkylated Polynuclear Aromatic Hydrocarbons, Selected Heterocyclic Compounds, Steranes, Diterpanes and Triterpanes by GC/MS-SIM
13. Total Petroleum Hydrocarbons, Gas Chromatography, and Flame Ionization Technique Method 8100 (Modified)
14. Total Organic Carbon in Soil, Sediment, and Water

June 2005

SEVERN TRENT STL

STANDARD OPERATING PROCEDURE
ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY
SW-846 8081A & EPA TO- 4A

Applicable Matrices: Non-Potable Water, Solid & Chemical Materials, Tissue and Air

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APPROVAL SIGNATURES

Laboratory Director: Michael F. Wheeler, Ph.D. Date: 12/20/04

QA Manager: Kirstin L. McCracken Date: 12-20-04

Department Manager: Jennifer L. Clements Date: 12/20/04

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure used to determine the concentration of various organochlorine pesticides that were extracted from non-potable water, solid and chemical materials including TCLP leachates, tissue and air matrices using dual column GC/ECD. This SOP is applicable to the analytical procedure. The procedures for the extraction and extract cleanup methods referenced in this SOP are described in the following laboratory SOPs:

LM-OP-3510	Separatory Funnel Extraction
LM-OP-3540	Soxhlet Extraction
LM-OP-3550	Ultrasonic Extraction
LM-OP-Cleanup	Extract Cleanup Procedures
LM-OP-GPC	Gel Permeation Chromatography

1.2 The compound list and associated reporting limit(s) are given in Table 1, Section 17.0 along with the in-house control limits used to evaluate accuracy (%R) and precision (%RPD).

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample is extracted using an appropriate matrix-specific extraction technique. After extraction, the extract may be subject to cleanup depending on the nature of matrix interference and the target analytes. After cleanup, the extract is analyzed by injecting a 2 uL aliquot into a dual capillary column, gas chromatograph equipped with electron capture detectors (GC/ECD).

2.2 This procedure is based on SW-846 Method 8081A, Organochlorine Pesticides by Gas Chromatography and Compendium Method TO-4A, Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air using High Volume Polyurethane Foam (PUF) Sampling followed by GC/MD (GC/Multi-detector).

3.0 DEFINITIONS

3.1 A list of terms and definitions is given in Appendix C.

4.0 INTERFERENCES

4.1 Interference can be caused by contaminated solvents, reagents or equipment. To reduce the occurrence of this type of interference, glassware must be cleaned thoroughly prior to use following the procedure given in laboratory SOP LM-OP-Glass and only reagent-grade solvents and reagents may be used.

4.2 Non-target compounds co-extracted from the sample matrix can also cause interference, the extent of which will vary considerably depending on the nature of the samples.

4.3 Phthalate esters introduced during sample preparation can pose a problem in the determination of pesticides. Common flexible plastics contain varying amounts of

phthalate esters, and these can be easily extracted or leached during extraction. To minimize this interference, avoid contact with any plastic materials.

4.4 Elemental sulfur is often found in sediment samples and its presence will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Samples are screened prior to analysis and those samples that contain high levels of sulfur are subject to cleanup using activated copper before analysis (SW-846 3660B).

4.5 Waxes, lipids, other high molecular weight materials and co-eluting organophosphorous pesticides may be removed with extract cleanup by gel permeation chromatography (GPC). Co-eluting chlorophenols can be eliminated by cleanup with silica gel (SW-846 3630), or Florisil (SW-846 3620).

4.6 The presence of PCBs may interfere with the analysis of organochlorine pesticides and the interference is most severe for multicomponent analytes such as Chlordane and Toxaphene.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2 Specific Concerns or Requirements

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.3 Primary Materials Used

Table 2, Section 17.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. **Note: The table does not include all materials used in the procedure. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used can be found in section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 EQUIPMENT AND SUPPLIES

6.1 Gas chromatograph equipped with an electron capture detector (GC/ECD) and autosampler capable of a 2 uL injection.

Hewlett Packard 6890 or equivalent.

6.2 GC Columns

- RTX-CLPesticides (30m x 0.32 mmID x 0.25um), Restek or equivalent
- RTX-CLPesticidesII, (30m x 0.32 mmID x 0.25um), Restek or equivalent

6.3 Autosampler Vials, National Scientific or equivalent

6.4 Volumetric Syringes, Class "A" (10uL, 25uL, 50uL, 100uL, 250uL and 500uL), Hamilton or equivalent.

6.5 Data system capable of handling a minimum of 200 chromatographic peaks per detector.

- Data Acquisition: Multichrom Version 2.0 or equivalent.
- Data Processing and Report Generation: Target Version 3.5 or equivalent.

7.0 REAGENTS AND STANDARDS

7.1. Reagents

Hexane (JT Baker Ultra-Resi analyzed) or equivalent.

Acetone (JT Baker Ultra-Resi analyzed) or equivalent.

Methanol (JT Baker Ultra-Resi analyzed) or equivalent.

7.2 Standards

Stock standard solutions are purchased premade from commercial vendors. Intermediate and working standards solutions are prepared in the laboratory by diluting a known volume of stock standard in an appropriate solvent and diluting to a specified volume. "Recipes" for the preparation of intermediate and working standard solutions are provided in Appendix A.

8.0 SAMPLE HANDLING AND PRESERVATION

8.1 Sample extracts must be stored at 4°C ± (2°) until the time of analysis.

8.2 The analytical holding time is 40 days from date of sample extraction.

8.3 Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days and then disposed of in accordance with applicable regulations.

9.0 QUALITY CONTROL

The following section provides a brief description of the QC check samples analyzed with this method. The minimum frequency requirements, acceptance criteria and recommended corrective action for all QC samples are summarized in Section 17.0, Table 3.

9.1. A method blank (MB) and laboratory control sample (LCS) are prepared with each extraction batch. Matrix spikes (MS/MSD) are prepared with each extraction batch or every 20 project samples if sufficient sample volume is available. Sample duplicates (SD) and/or client-specific MS/MSD are performed per client request.

9.2 After instrument calibration (ICAL) the performance of the instrument is checked with second source calibration verification standard (ICV) and continuing calibration verification standards (CCV). A breakdown check (Endrin / DDT) is performed prior to each calibration and prior to each CCV.

9.3 Surrogate spike is added to all field and QC sample prior to extraction to assess the ability of the method to successfully recover specific non-target analytes from the actual matrix.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument Operating Conditions

Install a five meter deactivated guard column to the injection port and connect the guard column to the separate analytical columns attached to dual ECD detectors using a glass "Y".

The recommended instrument operating conditions are as follows:

Initial Temperature:	120°C for 1 minute
Temperature Program:	16°C per minute to 210°C to 6°C per minute to 245°C to 12.5°C per minute to 300°C. Hold for 4 minutes.
Detector Temperature	300°C
Injector Temperature:	225°C
Injection volume:	2µL
Carrier Gas:	Hydrogen (supplied by hydrogen generators)

Optimize the flow rate of the carrier gas by injecting an un-retained substance onto the column at an isothermal oven state and adjusting the flow to obtain the recommended dead volume time.

The GC conditions listed above may be changed provided the elution orders are documented and compound separations are maintained but once the operating conditions are established, use the same conditions for both calibration and analysis of field samples.

10.2 Initial Calibration

Perform initial calibration prior to any sample analysis (initial method set-up), whenever a new column is installed, when significant instrument maintenance has been performed, and when the CCV standard does not meet acceptance criteria. Significant instrument maintenance includes installing new columns, changing the lengths of the analytical columns and baking or installing detectors.

Refer to Section 11.1 for instruction in setting up the autosampler sequence.

Analyze a column prime standard before initial calibration and if the instrument has been idle for longer than 8 hours.

Analyze an instrument blank comprised of hexane and the surrogates prior to injection of the calibration standards. No peaks should be detected at the retention time for any target analyte. If contamination is found, investigate the source and correct prior to analysis of the calibration standards.

Analyze a breakdown check standard that contains Endrin and DDT to verify the inertness of the injection port prior to calibration. The individual breakdown values should not exceed 15% and the combined breakdown of Endrin and DDT must be <30%. The equation for the calculation of breakdown is in provided in Appendix B. If the breakdown criteria are not met, correct the problem and reanalyze. Reanalyze the breakdown check standard prior to each CCV.

Prepare the calibration standards using the "recipes" in Appendix A. Unless otherwise specified for a specific project, the individual pesticides are calibrated using a minimum of five calibration points. The analysis of the multi-component pesticides employs a single-point calibration at the low-point of the calibration range. The multi-component calibration standard is used for pattern recognition for each column. If the multi-component analytes are detected in a sample, re-analyze the sample after a five-point calibration curve has been established.

Inject 2 uL of each calibration standard. Review the data and determine if the calibration is acceptable. The %RSD for each analyte must be ≤ 20% and the acceptance criteria must be met on both columns. If the criteria are not met, correct the problem and repeat the calibration. The equations for calculation of calibration factor, response factor, and relative standard deviation are provided in Appendix B.

10.2.1 Retention Time Windows

The retention time for each target analyte is derived from the mid-point standard analyzed in the initial calibration. Set the RT window for each target analyte to ± 0.05 minutes from the retention times established from the mid-point of the calibration range.

10.2.2 Second Source Calibration Verification (ICV)

After each calibration, verify the accuracy of the initial calibration by analyzing the ICV standard. Prepare the ICV following the recipe given in Appendix A. The percent recovery of the ICV must be +/-15% from the expected value. If criteria are not met, correct the problem and reanalyze the ICV. If the reanalysis fails, remake the calibration standards and recalibrate.

10.2.3 Calibration Verification (CCV)

Analyze a continuing calibration verification (CCV) standard each day prior to sample analysis, after every ten samples and at the end of each analytical batch to ensure the instrument is reliable and has not changed significantly from the current initial calibration curve. The CCV should include all target analytes and the concentration of the CCV standard should be varied within the calibration range. When a multi-component analyte is detected in field samples, analyze a multi-component CCV varying the concentration within the analytical batch.

Inject 2 uL of each calibration standard, acquire the data and determine if the calibration relationship is still valid.

The percent difference of the instrument response between the initial calibration and the CCV must not exceed ±15% for each analyte. Refer to Appendix B for equations to calculate percent difference.

Compare the retention time windows of each analyte in the CCV with those established during initial calibration. Each analyte should be within ± 0.05 minutes from the retention time established in the mid-point of the calibration curve.

The acceptance criteria must be met on both columns. If the criteria are not met, correct the problem then reanalyze the CCV and all samples since the last successful calibration verification. Sample data associated with a CCV that did not meet criteria may be reported if the acceptance criteria for the CCV are exceeded high and there are no detects in the associated samples. Otherwise, corrective action should be performed. If corrective action fails, repeat initial calibration.

11.0 PROCEDURE

11.1 Analysis

Transfer approximately 100 uL of each QC standard and sample extract to an autosampler vial and place the vials in the auto-sampler.

An example analysis sequence that includes initial calibration is given below:

Column Prime

Instrument Blank
Breakdown Check Standard (BCS)
Instrument Calibration

- INDA_B-1
- INDA_B-2
- INDA_B-3
- INDA_B-4
- INDA_B-5
- Technical Chlordane (50 ppb)
- Toxaphene (500 ppb)

Second Source Standard (ICV)
10 samples including QC samples and field samples
BCS
CCV
10 samples including QC samples and field samples
BCS
CCV

Enter the sample ID's into the data acquisition program in the same order that the samples were placed in the auto-sampler. Start the analytical sequence and acquire the data.

The data system tentatively identifies target analytes by comparing the retention time of the peaks to the retention times of the mid-point standard from the initial calibration using a set retention time window of ± 0.05 minutes from the mid-point of the calibration curve. Detects are confirmed if the peak is within the retention time window on both columns. If the data system does not properly integrate a peak, perform manual integration. All manual integration must be performed and documented in accordance with laboratory SOP LP-LB-0006 *Manual Integration.*

Quantitation of target analytes is performed by the data system using the equations given in Appendix B. Unless otherwise specified, the lower result between the two columns is reported. The relative percent difference of the results between the two columns should be less than 25% (CLP criteria). If the RPD exceeds this, the results should be flagged in the data report to alert the data user of the discrepancy.

The multicomponent analytes (Toxaphene and Chlordane) are identified by pattern recognition and are quantitiated on the basis of 3-5 major peaks. Calculate a calibration factor for the 3-5 major peaks using height or area and use the average quantitation of the 3-5 major peaks for reporting.

After the analytical sequence is complete, calculate and evaluate results (See Section 12.0 and Section 13.0). Dilute and reanalyze samples whose results exceed the calibration range. The diluted analysis should result in a determination within the calibration curve, preferably in the top half.

11.2 Data Reporting

Adjust sample results to reflect dilutions performed and unless otherwise specified, report the results for soils, sediments, sludge and other solid matrices on a dry weight basis.

Report the data to the reporting limit (RL) adjusted for sample matrix, percent moisture, and sample dilution/concentration. The reporting limit is the threshold value below which results are reported as non-detected. Report sample results whose concentration for a target analyte is less than the RL as RL "U".

Some projects may require MDL↔RL reporting. When this is the case, report the values between the MDL and the RL as estimated indicating that in this region (MDL↔RL) the analyte can be qualitatively detected by not accurately quantified. Flag all results reported between the MDL and RL with a "J" data qualifier.

Some projects may require RLs that are less than the laboratory's routine RL. Sample results may be reported to the project RL if the project RL is greater than the quantitation limit (QL). In this context, the QL is defined as the concentration of the low calibration standard. If the project RL is less than the QL, all values less than the QL must be reported as estimated and qualified with a "J".

The laboratory's RL for each target analyte is provided in Table 1.

Further guidance on the application and use of method detection limits (MDLs), reporting limits (RLs) and quantitation limits (QL) for the reporting analytical data is provided in laboratory SOP LP-LB-009 *Determination of Method Detection Limits.*

12.0 CALCULATIONS

12.1 See Appendix B.

13.0 DATA ASSESSMENT, CORRECTIVE ACTION & REPORTING

13.1. Data Review and Corrective Action

Review the samples, standards and QC samples against the acceptance criteria given in Table 3*. If the results do not fall within the established limits, perform the recommended corrective action. If corrective action is not taken or is unsuccessful, document the situation with a nonconformance report and qualify the data using an appropriate data qualifier (See Appendix C for data qualifier definitions). For additional guidance regarding the laboratory's protocol and required elements for each level of data review (primary, secondary, and tertiary) refer to laboratory SOP LP-LB-003 *Data Review. *Control limits may be project specified; in the absence of project requirements, use in-house control limits for data evaluation.*

14.0 METHOD PERFORMANCE

14.1. A demonstration of analyst capability (IDOC) is required prior to use of this SOP and any time there is a significant change in instrument type, personnel or test method. IDOC

procedures are further described in laboratory SOP LP-QA-011, *Employee Training.*

14.2. A Method Detection Limit (MDL) Study is performed at initial method set-up and subsequently once per 12 month period. The procedure and acceptance criteria for MDL studies are given in laboratory SOP LP-LB-009 *Method Detection Limits.*

14.3. The laboratory statistically derived control limits used to evaluate accuracy, precision and surrogate recoveries are provided in Table 1. The control limits for accuracy are based on compiled data and are set at 3 standard deviations around the mean using the procedures described in laboratory SOP LP-QA-012 *Control Limits.* Unless otherwise specified, the laboratory's in-house limits are used to evaluate laboratory control samples, matrix spikes, sample duplicates and surrogates.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 Waste Streams Produced by the Method

The following waste streams are produced when this procedure is performed:

- Vials containing sample extracts

Waste streams produced in the laboratory are accumulated in satellite containers located in the work area. The satellite containers are labeled "Hazardous Waste" along with the type of waste category generated. Authorized personnel routinely transfer the contents of the satellite containers to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations. The procedures for waste management are further given in laboratory SOP LP-LB-001 *Hazardous Waste.*

16.0 REFERENCES

16.1 SW-846 Method 8081A, Organochlorine Pesticides by Gas Chromatography, Test Methods for the Chemical Analysis of Water and Wastes, Revision 1, December 1996.

16.2 Compendium Method TO-4A, Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air using High Volume Polyerethane Foam (PUF) Sampling followed by GC/MD, EPA Center for Environmental Research Information, January 1999.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

17.1 Table 1: *Target Compound List, Reporting Limit and Control Limits*
17.2 Table 2: *Primary Materials Used*
17.3 Table 3: *QC Summary and Recommended Corrective Action*

17.4 Appendix A: *Standard Preparation Tables*
17.5 Appendix B: *Equations*
17.6 Appendix C: *Terms and Definitions*

Table 1: Target Compound List, Reporting Limits and Control Limits

Analyte	Reporting Limit			Accuracy Limit[2] (%R)			Precision[2] (%RPD)	
	Water ug/L	Solid ug/Kg	Air ug/Media	Water	Solid[1]	Air	Water	Solid / Air[1]
alpha-BHC	0.05	1.7	0.05	70-130	50-130	65-125	≤ 50	≤ 50
beta-BHC	0.05	1.7	0.05	75-135	50-140	65-125	≤ 50	≤ 50
delta-BHC	0.05	1.7	0.05	70-130	40-140	65-125	≤ 50	≤ 50
gamma-BHC (Lindane)	0.05	1.7	0.05	70-130	50-130	65-125	≤ 35	≤ 50
Heptachlor	0.05	1.7	0.05	60-170	40-135	65-125	≤ 50	≤ 50
Aldrin	0.05	1.7	0.05	60-120	50-120	65-125	≤ 50	≤ 50
Heptachlor Epoxide	0.05	1.7	0.05	75-135	50-135	65-125	≤ 50	≤ 50
Endosulfan I	0.05	1.7	0.05	65-125	40-130	65-125	≤ 40	≤ 50
Dieldrin	0.10	3.3	0.10	75-135	50-140	65-125	≤ 40	≤ 50
4,4-DDE	0.10	3.3	0.10	70-130	50-140	65-125	≤ 50	≤ 50
Endrin	0.10	3.3	0.10	80-140	50-140	65-125	≤ 50	≤ 50
4,4-DDD	0.10	3.3	0.10	70-130	50-145	65-125	≤ 45	≤ 50
Endosulfan II	0.10	3.3	0.10	70-130	40-135	65-125	≤ 50	≤ 50
Endosulfan sulfate	0.10	3.3	0.10	60-140	40-130	65-125	≤ 50	≤ 50
4,4-DDT	0.10	3.3	0.10	70-130	60-140	65-125	≤ 50	≤ 50
Methoxychlor	0.50	16.7	0.50	85-155	30-170	65-125	≤ 50	≤ 50
Endrin ketone	0.10	3.3	0.10	65-130	50-135	65-125	≤ 50	≤ 50
Endrin aldehyde	0.10	3.3	0.10	50-135	20-110	65-125	≤ 50	≤ 50
alpha-Chlordane	0.05	1.7	0.05	70-130	50-130	65-125	≤ 50	≤ 50
gamma-Chlordane	0.05	1.7	0.05	70-130	50-130	65-125	≤ 50	≤ 50
Technical Chlordane	0.50	16.7	0.50	70-130	70-130	65-125	≤ 50	≤ 50
Toxaphene	5.0	167	5.0	70-130	70-130	65-125	≤ 50	≤ 50
Surrogates:								
Tetrachloro-m-xylene	NA	NA	NA	10-130	10-150	65-125	NA	NA
Decachlorobiphenyl	NA	NA	NA	65-110	10-175	65-125	NA	NA

[1] Solid = Solid and Chemical Material and Tissue

[2] The in-house statistical control limits posted in this table are those in effect on the revision date of this SOP. These limits are subject to change based on performance trends.

Table 2: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 3: QC Summary and Recommended Corrective Action

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[1]
Breakdown Check Standard	Prior to initial calibration and each CCV	Degradation <15% for both Endrin and DDT	Correct problem, reanalyze, repeat calibration
Initial Calibration	Initially prior to sample analysis, when calibration verification standards indicate calibration relationship is no longer valid; after major instrument maintenance	See Section 10.2	Correct problem and repeat initial calibration.
ICV	After each initial calibration	%R ±15% from expected value for each analyte	Correct problem and verify second source standard. If that fails, repeat initial calibration.
CCV	Daily prior to sample analysis, every 10 samples and at the end of the analytical sequence	%Drift or %Difference ±15%	Correct problem, reanalyze CCV and all associated samples since last successful CCV
Method Blank	One per extraction batch	No analytes detected > RL DoD: ½ RL	Correct problem, re-extract and reanalyze. Examine project DQO's with PM, if there are no detects in the associated samples re-prep and reanalysis may not be required.
LCS	One per extraction batch	%R within control limits given in Table 1	Correct problem, re-extract, reanalyze along with associated samples Examine project DQO's, flag data if corrective action fails.
MS/MSD	Batch: one pair per extraction batch Client Specific: Per client request	%R & %RPD within control limits given in Table 1	Examine project DQO's with PM, flag data
Sample Duplicate	Per client request	%RPD within precision limit given in Table 1	Examine project DQO's with PM, flag data
Surrogate Spike	All field and QC samples	%R within control limits given in Table 1	Correct problem, re-extract and reanalyze if sufficient sample is available

[1]*The recommended corrective action may include some or all of the items listed in this column. The corrective action taken may be dependent on project data quality objectives and/or analyst judgment but must be sufficient to ensure that results will be valid. If corrective action is not taken or is not successful, data must be flagged with appropriate qualifiers.*

Appendix A: Standard Preparation Tables

The "recipes" given in this Appendix are recommended and are subject to change. If the concentration or volume of any of the components change the recipe must be adjusted accordingly. Unless otherwise noted, and expiration date of 6 months from date of preparation is assigned to all intermediate and working standards. See laboratory SOP LP-LB-002 *Standard Preparation* for further guidance on the preparation of standard solutions.

Table Legend:
Cstock = Concentration of Parent Standard
Vstock = Volume of Parent Standard
Vspike = Volume of Prepared Standard
Cspike = Theoretical Concentration of Prepared Standard

INTERMEDIATE STANDARDS

Toxaphene (50mg/L)

Stock Standard	*Cstock mg/L*	*Vstock mL*	*Vspike mL*	*Cspike mg/L*	*Solvent*
Toxaphene*	1000	1.0	20	50	Hexane

*Restek, Catalog Number 32005 or equivalent.

Technical Chlordane (10mg/L)

Stock Standard	*Cstock mg/L*	*Vstock mL*	*Vspike mL*	*Cspike mg/L*	*Solvent*
Technical Chlordane*	1000	0.400	40	10	Hexane

*Restek Catalog Number 32021 or equivalent.

WORKING STANDARDS

Mirex (10mg/L)

Stock Standard	*Cstock mg/L*	*Vstock mL*	*Vspike mL*	*Cspike mg/L*	*Solvent*
Mirex *	100	1.0	10	10	Hexane

*Ultra Scientific Catalog Number: PST-720S

TCX/DCB (10mg/L)

Stock Standard	*Cstock mg/L*	*Vstock mL*	*Vspike mL*	*Cspike mg/L*	*Solvent*
Pest Surrogate Mix *	200	1.0	20	10	Hexane

*Restek Catalog Number 32000 or equivalent

ICV Standard

Stock Standard	*Cstock mg/L*	*Vstock uL*	*Vspike mL*	*Cspike ug/L*	*Solvent*
Organochlorine Pesticide Mix AB # 2*	8-80	100	40	20-200	Hexane
TCX/DCB Working Standard	10	80		20	

*Restek Catalog Number 32292 or equivalent.

Column Prime Standard

Stock Standard	*Cstock mg/L*	*Vstock uL*	*Vspike mL*	*Cspike ug/L*	*Solvent*
Organochlorine Pesticide Mix AB #2*	8-80	1000	20	400/800	Hexane
TCX/DCB Working Standard	10	800		400	

*Restek Catalog Number 32292 or equivalent

Breakdown Check Standard

Stock Standard	*Cstock mg/L*	*Vstock uL*	*Vspike mL*	*Cspike ug/L*	*Solvent*
Pesticide Performance Evaluation Mix*	10-250	30	30	10-250	Hexane

*Ultra Catalog Number

CALIBRATION STANDARDS

INDAB-5 Pesticide Calibration Level 5

Stock Standard	*Cstock mg/L*	*Vstock mL*	*Vspike mL*	*Cspike ug/L*	*Solvent*
Organochlorine Pesticide Mix AB # 2*	8-80	1.0	100	80-800	Hexane
Mirex Working Standard	10	1.6		160	
TCX/DCB Working Standard	10	0.800		80	

*Restek Catalog Number 32292 or equivalent

Prepare Calibration Standards Level 1-4 in hexane using INDAB-5

(Calibration Level 5) as the parent component and the volumes given in the following table:

INDAB-5 (Calibration Level 5)	INDAB-4	INDAB-3	INDAB-2	INDAB-1
Vstock (mL)	40	20	10	2.5
Vspike (mL)	80	80	80	40

Toxaphene Working Standard (Calibration Level 5)

Stock Standard	*Cstock mg/L*	*Vstock mL*	*Vspike mL*	*Cspike ug/L*	*Solvent*
Toxaphene Intermediate Standard	50	16	100	8000	Hexane
TCX/DCB Working Standard	10	0.80		80	

Prepare the Toxaphene Calibration Standards Level 1-4 in hexane using Toxaphene (Calibration Level 5) as the parent component and the volumes given in the following table:

Toxaphene (CAL Level 5)	Tox 4000	Tox 2000	Tox 1000	Tox 500
Vstock (mL)	20	10	5.0	2.5
Vspike (mL)	40	40	40	40

Technical Chlordane Working Standard (Calibration Level 5)

Stock Standard	*Cstock mg/L*	*Vstock mL*	*Vspike mL*	*Cspike ug/L*	*Solvent*
Technical Chlordane Intermediate	10	8.0	100	800	Hexane
TCX/DCB Working	10	0.800		80	

Prepare the Technical Chloridane Calibration Standards Level 1-4 in hexane using Technical Chlordane (Calibration Level 5) as the parent component and the volumes given in the following table:

Technical Chlordane (Level 5)	T. Chlor 400	T. Chlor 200	T. Chlor 100	T. Chlor 50
Vstock (mL)	20	10	5.0	2.5
Vspike (mL)	40	40	40	40

Final Concentration of Prepared Calibration Standards in Extract*

Analyte*	Level 1 (ug/L)	Level 2 (ug/L)	Level 3 (ug/L)	Level 4 (ug/L)	Level 5 (ug/L)
TCX (surrogate)	5	10	20	40	80
DCB (surrogate)	5	10	20	40	80
Alpha-BHC	5	10	20	40	80
Beta-BHC	5	10	20	40	80
Delta-BHC	5	10	20	40	80
Gamma-BHC	5	10	20	40	80
Heptachlor	5	10	20	40	80
Aldrin	5	10	20	40	80
Heptachlor Epoxide	5	10	20	40	80
Endosulfan I	5	10	20	40	80
Dieldrin	10	20	40	80	160
4-4'-DDE	10	20	40	80	160
Endrin	10	20	40	80	160
Endosulfan II	10	20	40	80	160
4-4'-DDD	10	20	40	80	160
Endosulfan Sulfate	10	20	40	80	160
4,4'-DDT	10	20	40	80	160
Methoxychlor	50	100	200	400	800
Endrin Ketone	10	20	40	80	160
Endrin Aldehyde	10	20	40	80	160
gamma-chlordane	5	10	20	40	80
alpha-chlordane	5	10	20	40	80
Technical Chlordane	50	100	200	400	800
Toxaphene	500	1000	2000	4000	8000

*These concentrations are based on the recipes given in this appendix and are subject to change if the standard preparation changes.

APPENDIX B: EQUATIONS

These equations were taken from reference method SW-846 8081A and from SW-846 8000B, Test Methods for Evaluation of Solid Waste Revision 2, December 1996. USEPA.

Percent Breakdown

% Breakdown of DDT

$$\frac{\text{peak area [or height] (DDE + DDT)}}{\text{peak area [or height] (DDE + DDD + DDT)}} \otimes 100$$

% Breakdown of Endrin

$$\frac{\text{peak area [or height] (endrin aldehyde + endrin ketone)}}{\text{peak area [or height] (endrin aldehyde + endrin ketone + endrin)}} \otimes 100$$

Calibration Factor (CF_i)

$$\frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Extract concentration (ug/L)}}$$

Mean Calibration Factor ($\overline{CF}$)

$$\frac{\sum_{i=1}^{n} CF_i}{n}$$

where:
n = number of calibration levels

Standard Deviation of the Calibration Factor (SD)

$$\sqrt{\frac{\sum_{i=1}^{n}\left(CF_i - \overline{CF}\right)^2}{n-1}}$$

where:
n = number of calibration levels

Percent Relative Standard Deviation (RSD) of the Mean Calibration Factor

$$\frac{SD}{\overline{CF}} \otimes 100$$

Percent Difference (%D)

$$\frac{CF_v - \overline{CF}}{\overline{CF}} \otimes 100$$

where:
CF_v = Calibration Factor from the Continuing Calibration Verification (CCV)

Percent Recovery (%R)

$$\frac{C_s}{C_n} \otimes 100$$

where:
C_s = Concentration of the Spiked Field or QC Sample
C_n = Nominal Concentration of Spike Added

Percent Recovery (%R) for MS/MSD

$$\frac{C_s - C_u}{C_n} \otimes 100$$

where:
C_s = Concentration of the Spiked Sample
C_u = Concentration of the Unspiked Sample
C_n = Nominal Concentration of Spike Added

Relative Percent Difference (%RPD)

$$\frac{C_1 - C_2}{\left(\frac{C_1 + C_2}{2}\right)} \otimes 100$$

where:
C_1 = Measured Concentration of First Sample
C_2 = Measured Concentration of Second Sample

Sample Concentration

Water

$$Concentration_{sample}(ug/L) = Amt_{extract}(ug/L) \otimes \frac{extract\ volume\ (L)}{sample\ volume\ (L)} \otimes DF$$

where:

$$Amt_{extract}(ug/L) = \frac{Peak\ Area\ (or\ Height)}{\overline{CF}}$$

DF = Dilution Factor, if the sample was diluted prior to analysis. If no dilution was made, DF=1. The dilution factor is always dimensionless.

Solids

$$Concentration_{sample}(mg/Kg) = Amt_{extract}(ug/L) \otimes \frac{extract\ volume\ (L)}{sample\ volume\ (Kg)} \otimes \frac{100}{\%\ solids} \otimes DF$$

where:

$$Amt_{extract}(mg/Kg) = \frac{Peak\ Area\ (or\ Height)}{\overline{CF}}$$

DF = Dilution Factor, if the sample was diluted prior to analysis. If no dilution was made, DF=1. The dilution factor is always dimensionless.

Appendix C: Terms & Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

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.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

Calibration: a set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material and the corresponding values realized by the standards.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Calibration Standard: A substance or reference used to calibrate an instrument.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Data Qualifier: a letter designation or symbol appended to an analytical result used to convey information to the data user. (Laboratory)

The EPA-defined qualifiers that are routinely used for this test method are:

U: Compound analyzed for but not detected at a concentration above the reporting limit.

J: Estimated Value

P: There is greater 25 % difference for detected concentrations between two GC columns

C: Postive result whose identification has been confirmed by GC/MS

B: Compound is found in the sample and the associated method blank.

E: Compound whose concentration exceeds the upper limit of the calibration range.

D: Concentration identified from a dilution analysis.

X,Y,Z: Laboratory defined flags that may be used alone or combined as needed. If used, provide a description of the flag in the project narrative.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a <u>range</u> where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogate: a substance with properties that mimic the analyte of interest but that are unlikely to be found in environmental samples.

SEVERN TRENT STL

STANDARD OPERATING PROCEDURE
THE DETERMINATION OF EXTRACTABLE PAH COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY SELECTIVE ION MONITORING (GC/MS-SIM)

Applicable Matrices: Liquids or Solids
Standard Compound List and Reporting Limits: See Table 1

APPROVAL SIGNATURES

Laboratory Director: Michael F. Wheeler, Ph.D. Date: 12/18/03

QA Manager: Kirstin L. McCracken Date: 12-17-03

GC/MS Supervisor: Bryce E. Stearns Date: 12/18/03

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1.0 SCOPE AND APPLICATION

1.1. This method is based on the NOAA Status and Trends Methods for the analysis and determination of low-level polynuclear aromatic hydrocarbons. The analytical method that follows is designed to analyze polynuclear aromatic hydrocarbons in water, soil, sediment, and tissues. See Table 1. Additionally, the alkyl-substituted homologues of these target compounds may be assessed using this method.

1.2. This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to GC/MS.

1.3. This method involves solvent extraction of the matrix sample, characterization to determine the appropriate analytical protocol to be used followed by appropriate cleanup procedure and GC/MS analysis in SIM mode to determine the polynuclear aromatic hydrocarbons present in the sample.

1.4. Target compound concentrations are calculated via the isotopic dilution technique; compound amounts are derived based upon the recovery of spiked analogs. Alternative quantitation via instrument internal standard may be requested.

2.0 SUMMARY OF METHOD

2.1. A one liter aliquot of a liquid sample, 40 g aliquot of a soil or tissue sample is spiked with a surrogate compound mixture and then extracted with methylene chloride. The final extract is concentrated to either 1000 µL (waters) or 2000 µL (soils/tissues). A 2.0 µL aliquot of the concentrated final extract is injected into GC/MS, where it is volatilized in the injection port and swept onto the chromatographic column. A temperature program is used to separate the semivolatile compounds, and they are carried on the gas stream into the ion source of a mass spectrometer. The end of the column is positioned so the eluting compounds are ionized immediately. The ionized molecules are focused and separated according to their mass/charge (m/z) by the quadrupole analyzer. The mass spectrometer is configured to scan only for selected ions specific to the target compounds (SIM mode). The signal is amplified by an electron multiplier and interpreted by the mass spectrometer data system to produce a total ion chromatogram and mass spectra for every data point on the chromatogram.

2.2. The mass spectrometer is calibrated to recognize m/z values in the range of 35-500 amu. Instrument performance is verified by the injection of Decafluorotriphenylphosphine (DFTPP). The ion abundances must meet the criteria shown in Table 2 before analyses can proceed. If the criteria are met, the instrument then must demonstrate acceptable chemical calibration and linearity by the injection of five concentrations of a standard mix containing the analytes of interest, surrogate compounds, and internal standards. If the sensitivity (relative response factor, RRF) and linearity (relative standard deviation, %RSD) criteria shown in Table 3 are met the analysis may proceed. All analyses must occur within 12 hours of the injection of the passing DFTPP. Another analytical sequence may be started by analysis of a passing DFTPP followed by a continuing calibration standard. This standard must meet the sensitivity (RRF) and linearity (difference from the initial calibration , %D) criteria shown in Table 3 before analysis of samples may proceed.

2.3. Analyze all samples within 40 days of extraction. Note that extraction holding times for waters are 7 days from Validated Time of Sample Receipt (VTSR), extraction holding time for soil and tissue samples are 14 days from VTSR. Note: tissue samples are routinely stored as frozen aliquots, holding time for frozen sample aliquots are 14 days from thawing.

3.0 DEFINITIONS

3.1. Definitions are included in Appendix A.

4.0 INTERFERENCES

4.1. Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines. All of these materials routinely must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

4.2. Carryover contamination from the injection port is especially problematic with this analysis due to increased sensitivity. Additional maintenance should be performed to ensure that the analytical system is free of any potential sources of contamination. The late eluting PAHs are particularly susceptible to carryover contamination.

5.0 SAFETY

5.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2. STL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in these methods. Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. STL also has a written environmental health and safety plan.

5.3. The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in these analyses. Specifically, concentrated sulfuric acid presents some hazards and is moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

6.0 EQUIPMENT AND SUPPLIES

- SVOA Autosampler: HP 7673A, or CTC 200AS Liquid Autosampler
- Gas Chromatograph: Hewlett-Packard 5890 GC
- Mass Spectrometer: Hewlett-Packard 5971 MSD, 5972 MSD
- Primary Column: Restek RTx-5 30m x 0.25mm x .25 um, or equivalent

6.1. Hewlett Packard Gas Chromatograph - Mass Spectrometer MSD system

6.1.1. Gas chromatograph- Hewlett-Packard model 5890 Series II, equipped with an CTC autosampler, injection port for split/splitless analysis and all the required accessories, including syringes, septa, injector port liners, and column. Alternatively, a Hewlett-Packard Model 7673A autosampler may be used, with a standard 5890 series II injection port.

6.1.2. Column - Restek, (Rtx-5 30 meter x 0.25 mm ID with 0.25 um film thickness), or equivalent.

6.1.3. Mass Spectrometer-Hewlett-Packard Mass Selective Detector Model 5971 or 5972 operated in SIM mode.

6.1.4. Data System -The analytical system is controlled by the HP Chemstation computer. Target 3.5 software is used for data processing.

6.2. Gas Chromatograph/Mass Spectrometer

6.2.1. GC Maintenance – If required, prior to running DFTPP, replace/clean the injection port liner and septa and also clip about 10 cm off the guard column from the injector end.

6.2.2. GC Conditions-below represents a typical instrument GC Set-up.

Initial column conditions: 35°C for 2 minutes.
Column temperature: 35°C to 320°C at 14°/min.
Final temperature: 320°C for 5.6 min, or until Benzo (g,h,i) perylene has eluted
Injector temperature: 250°C
Transfer line temperature: 300°C
Injector: Grob-like, splitless
Sample volume: 2 µL

6.2.3. MS Conditions

Electron Energy: 70 volts
Mass Range: SIM Mode

7.0 REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Reagent Water –free of compounds of interest.

7.1.2. Sulfuric Acid Solution (H_2SO_4) - (1+1) slowly add 50 mL of concentrated H_2SO_4 (sp. gr. 1.84; 18 N) to 50 mL of reagent water.

7.1.3. Acetone, methanol, methylene chloride, iso-octane, 2-propanol, and toluene - pesticide residue analysis grade or equivalent.

7.1.4. Sodium Sulfate - powdered or granular anhydrous reagent grade, heated at 400°C for four hours in a shallow tray, cooled in a desiccator and stored in a glass bottle. CAUTION: An open container of sodium sulfate may become contaminated during storage in the laboratory.

7.1.5. Sodium sulfite - reagent grade.

7.2. Standards

7.2.1. The laboratory vendor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained in the QA department, or available upon request from the manufacturer.

7.2.2. Stock Standard Solutions

7.2.2.1. Stock standard solutions may be prepared by dissolving approximately 0.0100g of neat material (≥97.0% purity) in methylene chloride or other suitable solvent, and bringing to a known volume in a volumetric flask.

7.2.2.2. When compound purity is assayed to be 97.0 percent or greater, the weight may be used without correction to calculate the concentration of the stock solution. If the compound purity is assayed to be less than 97.0 percent, the weight must be corrected when calculating the concentration of the stock solution.

7.2.2.3. Fresh stock standards must be prepared once every twelve months, or sooner if standards have degraded or concentrated. Stock standards must be checked for signs of degradation or concentration just prior to preparing secondary dilution or working standards.

7.2.2.4. The laboratory typically purchases prepared standard solutions. Dilution of commercially prepared solution are prepared, stored and documented according to the Standards, Preparation and Storage SOP.

7.2.3. Secondary Dilution Standards

7.2.3.1. Using stock standards, prepare secondary dilution standards in hexane that either contain the compounds of interest singly or as a mix.

7.2.3.2. Fresh secondary dilution standards must be prepared once every twelve months or sooner if standards have degraded or concentrated. Secondary dilution standards must be checked for signs of degradation or concentration prior to preparing working standards.

7.2.4. Working Standards

7.2.4.1. Surrogate Standard Spiking Solution: Prepare a surrogate standard spiking solution that contains Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, and Perylene-d_{12} at a concentration of 0.3 ug/mL.

7.2.4.2. The matrix spiking solution consists of all of the target analytes. Prepare a spiking solution that contains each of the target analytes at a concentration of 0.4 ug/mL.

7.2.4.3. Instrument Performance Check Solution. - Prepare a solution of decafluorotriphenylphosphine (DFTPP), such that a 2 μL injection will contain 50 ng of DFTPP.

7.2.4.4. Initial and Continuing Calibration Solutions. - Prepare calibration standards at a minimum of five concentration levels 20, 100, 250, 500, and 1000 pg/uL. The 250 pg/uL calibration standard is the continuing calibration level standard.

7.2.5. Ampulated Standard Extracts - Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date.

7.3. Storage of Standard Solutions

7.3.1. Store the stock and secondary dilution standard solutions at 4 °C (± 2°C) in Teflon-lined screw-cap amber bottles. Fresh standards should be prepared every twelve months at a minimum.

7.3.2. Store the working standards at 4 °C (± 2°C) in Teflon sealed containers. The solution should be checked frequently for stability. These solutions must be replaced after twelve months or sooner if comparison with quality control check samples indicates a problem.

7.3.3. The continuing calibration standard (250 pg/uL) should be prepared weekly, or sooner, and stored at 4 °C (± 2°C).

7.3.4. Protect all standards from light. Samples, sample extracts and standards must be stored separately. Storage of standard solutions in the freezer may cause some compounds to precipitate. This means at a minimum, the standards must be brought to room temperature prior to use, checked for losses and checked that all components have remained in solution. Additional steps may be necessary to ensure all components are in solution.

8.0 SAMPLE HANDLING AND PRESERVATION

8.1. Sample Collection and Preservation

8.1.1. Water samples may be collected in 1 L (or 1 quart) amber glass containers, fitted with screw-caps lined with Teflon. If amber containers are not available, the samples should be protected from light. Soil samples may be collected in glass containers or closed end

tubes (e.g., brass sleeves) in sufficient quantity to perform the analysis. The specific requirements for site sample collection are outlined by the client/ US Regulatory Agencies.

8.1.2. All samples must be iced or refrigerated at 4 °C (±2 °C) from the time of collection until analysis.

8.2. Procedure for Sample Storage

8.2.1. The samples must be protected from light and refrigerated at 4 °C (±2°C) from the time of receipt until 60 days after delivery of a reconciled, complete sample data package to the Agency. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2. Tissue samples may be held as frozen aliquots indefinitely prior to extraction in the absence of specific guidance on tissues sample holding times.

8.2.3. The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3. Procedure for Sample Extract Storage

8.3.1. Sample extracts must be protected from light and stored at 4°C (± 2°C) until 365 days after delivery of a reconciled, complete data package to the Agency.

8.3.2. Samples, sample extracts, and standards must be stored separately.

8.4. Contract Required Holding Times

8.4.1. Extraction of water samples shall be started within 7 days of Validated Time of Sample Receipt (VTSR). Extraction of soil/sediment samples by sonication procedures shall be completed within 14 days of VTSR. Tissue samples are typically frozen and stored but must be extracted within 14 days of thawing.

8.4.2. Extracts of water and soil/sediment/tissue samples must be analyzed within 40 days following extraction.

9.0 QUALITY CONTROL

9.1. A method blank must be extracted with every extraction set, and must meet the most frequent of the following criteria. There must be at least one blank for:

- Each field group or "Case" of field samples received, OR
- Each 7 day calendar period during which samples in a group are received, OR
- Each 20 samples (excluding matrix spikes) in a group that are of similar matrix or concentration (soil only)

The method blank must be analyzed on each instrument which has been used to analyze associated samples, and must not contain any target analytes at concentrations greater than or equal to their CRQL's.

9.2. All surrogates in method blanks and samples must meet the required recovery criteria (shown in Table 4). For sample analysis, if required surrogate criteria are not met, the sample must be reanalyzed. If the sample meets the criteria upon reanalysis, only the passing analysis is submitted. If reanalysis confirms the original failure, the sample must be re-extracted. If a method blank fails recovery criteria, and is confirmed by re-analysis, the blank and all associated samples must be re-extracted. Samples which have been diluted at or more than three to one (i.e., a 25% or lower concentration analysis) may exhibit recovery failures due to the dilution. These samples may require re-analysis at a higher concentration if using the isotopic dilution technique. Each surrogate retention time in a sample must agree within ± 0.06 relative retention time (RRT) units with the continuing calibration standard. Reanalyze to confirm failures of retention time stability. Submit a single passing analysis or both failing analyses.

Individual surrogate component recoveries are calculated with the following equation:

$$Surrogate\ Recovery\ (\%) = \frac{SR}{SA} * 100$$

Where:
SR = Spike Result
SA = Spike Added (concentration)

9.3. Matrix spike (MS) and matrix spike duplicate (MSD) are required for each group of samples of a similar matrix at the most frequent occurrence of the following:

- Each field group or "Case" of field samples received, OR
- Each 20 field samples in a group, OR
- Each 7 day calendar period during which field samples in a group were received, OR
- Each group of field samples of a similar concentration level (soils only)

Before any MS/MSD analysis, analyze the original samples, then analyze the MS and MSD at the same concentration as the most concentrated extract for which the original sample result will be reported. A matrix spike blank may also be requested. If a sample is not used for matrix spike analysis, a matrix spike blank and matrix spike blank duplicate may be requested. Individual component recoveries are calculated with the following equation:

$$MS\ Recovery\ (\%) = \frac{SSR - SR}{SA} * 100$$

Where:
SSR = Spike Sample Results
SR = Sample Results

SA = Spike Added (concentration)

The Relative Percent Difference (%RPD) between matrix spike and matrix spike duplicate analysis is calculated with the following equation:

$$\% \quad RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

Where:
RPD = Relative Percent Difference
D_1 = First Sample Value
D_2 = Second Sample Value (duplicate)

Recovery limits are shown in Table 5.

10.0 CALIBRATION AND STANDARDIZATION

Semivolatile organic standards are received in ampules and are to be stored in the GC-MS preparation laboratory refrigerator. Ampules should only be opened prior to use, and in order of date received (oldest expiration date first). Expired standards must never be used and should be disposed of properly. The expiration date is as provided by the manufacturer. When the manufacturer's expiration date is not provided, the expiration date will be set at 2 years from the preparation date. All primary and intermediate standards are to be maintained at 4± 2°C and all working standards are to be maintained at 4°± 2°C.

10.1. DFTPP

10.1.1. Standard Prep
Injection Volume = 2 µL

A 2 uL injection of DFTPP (25ng/µL) is acquired using a temperature programmed analysis. Spectral evaluation of the DFTPP peak is performed by summing three spectral points (the apex scan, the scan prior to the apex, and the scan immediately following the apex), and subtracting a background scan. Note: the background scan selected for subtraction may not contain a portion of the peak associated with DFTPP. The ion abundances shown in Table 2 must be met before analysis of calibration standards may proceed.

10.1.2. Evaluation and Corrective Action
Before data collection, establish that the GC/MS system meets the standard mass spectral abundance criteria specified in Table 2 above. The initiation of an analysis window begins at the moment of injection of the performance standard (DFTPP) that meets the criteria. Within this window, all calibration standards, method blank analysis, and sample analysis will be performed. DFTPP criteria must be met before any standards, samples or blanks are analyzed. All instrument conditions for standard and

sample analyses, except for the temperature program, must be identical to those used in the acquisition of DFTPP. Whenever corrective action is taken that may affect the tune of the instrument, the tune must be verified with DFTPP regardless of the window status.

Background subtraction is required when tuning the GC/MS system. The background subtraction must be straightforward and eliminate only column bleed or instrument background ions. Background subtraction resulting in spectral distortions for the sole purpose of meeting contract specifications is unacceptable. In such a case, the window would be invalid and all samples analyzed within the window would require reanalysis. In order to obtain a background subtracted spectrum of DFTPP, sum spectral information over a range from one scan before to one scan after the total RIC maxima and subtract the spectral information for a single scan no more than 20 scans prior to the elution of the performance evaluation compound that is representative of background noise.

10.2. Internal Standards

10.2.1. Standard Prep

Volume Added
Add internal standard mixture containing Fluorene-d_{10} and Benzo(a)pyrene-d_{12} to all calibration standards, blanks, and samples to give a final concentration of 0.1 ug/mL. A 1 uL aliquot of the 10 ppm stock is added to 100 uL of standards or extracts prior to analysis.

ISTD ± 2x from last CCAL
Internal standard quantitation ion area must not vary by more than a factor of two (-50% to +100%) from the latest calibration standard. Retention times of internal standards must not vary by more than 0.5 minutes (30 seconds) from the latest calibration standard. If sample analysis fails any single instance of these criteria, the sample must be reanalyzed to determine whether the failure was due to analytical error or matrix effect. If the sample meets the criteria upon reanalysis, only the passing analysis is submitted. If reanalysis confirms the original failure, both analyses are submitted.

10.2.2. Evaluation and Corrective Action
Internal standard responses and retention times in all samples and blanks must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds, the chromatographic system must be checked for malfunctions, and corrections made. If the area of the internal standard compound changes by more than a factor of two from the latest daily calibration standard, then the mass spectrometric system must be checked for malfunction and corrective action taken. Poor spiking technique, evaporation or degradation of the standard stock mixture, or autosampler malfunction can result in erratic internal standard areas. Affected blanks and samples must be reanalyzed; no samples associated with a non-compliant blank are valid.

If a sample has unacceptable internal standard area results, reanalysis of the sample is necessary. If the sample continues to show unacceptable internal standard areas, and intervening samples have been acceptable, then the problem is outside of the laboratory's control, and both analyses are submitted.

10.3. Initial Calibration - Concentrations of organic compounds will be determined by GC/MS using an internal standard and fixed response model. Note: for isotopic dilution analyses the analyte RRF and sample concentration are calculated using the appropriate spiked analog see Table 6 for internal standard, surrogate and target compound associations. Prior to the analysis of samples and blanks, DFTPP tuning requirements must be satisfied according to the method. Once the tune has been established, the GC/MS system will be calibrated to determine the linearity of instrument response. Calibration standards contain all target compounds for the method including surrogate compounds. A relative response factor (RRF) for each compound within the calibration standard is calculated using the following equation:

$$RRF = \frac{(A_x)\,(C_{is})}{(A_{is})\,(C_x)}$$

Where:
A_x = Area of characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the associated internal standard
C_{is} = Concentration of the internal standard (ng/µL)
C_x = Concentration of the compound to be measured (ng/µL)

Relative response factors are calculated for all compounds in the calibration standards. Using the relative response factors, a percent relative standard deviation (%RSD) is calculated for each compound with the following equation:

$$\%\ RSD = \frac{SD}{x} * 100$$

Where:
SD = Standard deviation of initial relative response factors (per compound)
x = Mean of initial relative response factors (per compound)

10.3.1. Standard Preparation

Prepare the initial calibration curve by spiking the appropriate volume of calibration stock solution, surrogate stock solution, and internal standard solution into hexane (100 uL final volume) that yields concentrations of 20, 100, 250, 500, and 1000 pg/uL. All target analytes and surrogates are included in the calibration.

Calibration Criteria
If the minimum RRFs and maximum %RSDs given in Table 3 are met and time remains in the 12 hour window, analysis of samples may proceed.

Chromatography
The analytical run must begin at least 30 seconds before the elution of the first target analyte and must last until at least 3 minutes after the last target analyte.

10.4. Continuing Calibration

A continuing calibration standard of specified concentration containing the compounds of interest, including surrogates must be analyzed every 12 hours or as specified by the method. The relative response factors from the continuing calibration standard are calculated and compared to the average relative response factor from the initial calibration. The percent difference (%D) is calculated with the following equation:

$$\% \ Difference = \frac{RRF_i - RRF_c}{RRF_i} * 100$$

Where:
RRF_i = average relative response factor from initial calibration
RRF_c = relative response factor from current calibration check std.

Continuing Calibration criteria can be found in Table 3.

10.4.1. Standard Preparation - The continuing calibration is prepared from the calibration stock solution.

Volume Added
The final concentration for this standard is at the mid-level concentration of the five point calibration curve (250 pg/uL).

Criteria
A check of the calibration curve must be performed once every 12 hours before sample analysis. Following a successful DFTPP analysis, a 250 pg/uL calibration standard is acquired. If the minimum RRF's and maximum %D's shown in Table 3 are met and time remains in the 12 hour window, analysis of samples may proceed.

11.0 PROCEDURE

11.1. Sample Requirements:

11.1.1. Liquids: A minimum of 1 liter is required for extraction. Additional sample volume is required for Matrix Spike and Matrix Spike Duplicate.

11.1.2. Solids: A minimum of 40 grams of sample is required. Additional sample volume is required for Matrix Spike and Matrix Spike Duplicate.

11.1.3. Tissue: The appropriate aliqout mass needed to achieve project specific reporting levels. Additional sample volume is required for Matrix Spike and Matrix Spike Duplicate.

11.2. Sample Preparation –Pre-analysis screening for all extracts is optional. Please refer to the Sample and Extract Screening SOP. Extracts are received from the extraction analyst and logged into the analytical laboratory. For analysis, add 1 µL of 10 ng/uL Internal Standard Stock to a 100 µL aliquot of sample. To perform a dilution take the appropriate amount of sample and a volume of hexane sufficient to make a 100 µL final volume, and add 1 µL of the Internal Standard Stock. For instance, to perform a 20%

analysis (dilution factor =5), 1 µL of 10 ng/uL Internal Standard Stock, 20 µL of sample, and 80 µL of methylene chloride are combined. A 2 µL injection is required.

11.3. Sample extracts shall be analyzed only after the GC/MS system has met the instrument performance check, initial calibration, and continuing calibration requirements. The same instrument conditions must be employed for the analysis of samples as were used for calibration.

11.4. Prior to the addition of internal standards, make any extract dilution indicated by characterization step. Add internal standards after dilution. Internal standards must be added to maintain the required 0.1 ng/µL of each internal standard in the extract volume. Inject 2 µL of the sample extract into the GC/MS.

11.5. Data Acquisition - Autosamplers should be utilized as much as possible to perform sample analysis. The following procedures are used to set up an autosampler run.

11.5.1. The autosampler is used to position vials for injection, either as single injections or as a sequence. The autosampler needle and rinse vials should be checked daily for cleanliness and proper function. For operation in a sequence, the vial positions in the autosampler tray must correspond to the vial positions in the software sequence.

11.6. If the on-column concentration of any compound in any sample exceeds the initial calibration range, that sample extract must reprepared as a dilution and re-analyzed. Guidance in performing dilution and exceptions to this requirement are given below.

11.7. Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range. The dilution factor chosen should keep the response of the largest peak for a target compound in the upper half of the calibration range of the instrument. Do not submit data for more than two analyses, i.e., the original sample extract and one dilution, or if the semivolatile screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

11.8. Reporting Limits - CRQLs = (See Table 1). Diluted sample reporting limits will be raised by the dilution factor.

11.9. Sample results are verified by their mass spectra. Mass spectra are visually verified by a laboratory staff member experienced in mass spectral interpretation. The following guidelines are used when evaluating mass spectra:

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) are to be present in the sample spectrum.
- The relative intensities of these ions are to agree within plus or minus 20% between the standard and sample spectra.
- Ions greater than 10% in the sample spectrum are considered and accounted for by the analyst making the comparison.

11.10. Guidelines for making tentative identification:

- Due to the nature of this analysis (GC/MS SIM mode), non-target compound identification (TIC) cannot be made.

11.11. Reporting Qualifiers

A = The TIC is a suspected aldol-condensation product.
B = Analyte is found in the associated method blank as well as the sample.
D = Compound is identified in an analysis at a secondary dilution factor.
E = Compound quantitation is above the instrument's calibration range for this analysis.
J = Indicates an estimated quantitation value.
U = Compound was analyzed for but not detected.
X = The reported compound is a suspected laboratory contaminant.
Y = An additional qualifier which will be defined at the time of use by the data reviewer.
Z = The reported result is based on the combined responses from coeluting compounds.
N = This flag is only used for TICs, where the identification is based on a mass spectral library search. It is applied to all TIC results.

12.0 CALCULATIONS

12.1. Identified target compounds are quantitated by the internal standard method. Each compound has a designated internal standard, and characteristic ions, Table 6. Calculation of a target compound concentration is performed with the following fraction and matrix specific equations:

12.1.1. Water:

$$\text{Concentration } \mu\text{g/L} = \frac{(A_x)(I_s)(V_t)(Df)(GPC)}{(A_{is})(RRF)(V_o)(V_i)}$$

Where,
A_x = Area of the characteristic ion for the compound to be measured.
A_{is} = Area of the characteristic ion for the internal standard.
I_s = Amount of internal standard injected in nanograms (ng).
V_o = Volume of water extracted in milliliters (mL).
V_i = Volume of extract injected in microliters (µL).
V_t = Volume of the concentrated extract in microliters (µL) (V_t = 1,000 µL if sample was not subjected to GPC; V_t = 500 µL if sample was subjected to GPC).
RRF = Relative response factor determined from the 12-hour calibration standard.
GPC = GPC factor.
GPC = 1.0 if water sample was not subjected to GPC;
GPC = 2.0 if water sample was subjected to GPC.

Df = Dilution factor. The dilution factor for analysis of water samples for semivolatiles by this method is defined as follows:

$$Df = \frac{\mu L \text{ most conc. extract used to make dilution} + \mu L \text{ clean solvent}}{\mu L \text{ most conc. extract used to make dilution}}$$

If no dilution is performed, Df = 1.0.

12.1.2. Soil/Sediment

$$\text{Concentration } \mu g/Kg \text{ (Dry weight basis)} = \frac{(A_x)\ (I_s)\ (V_t)\ (Df)\ (GPC)}{(A_{is})\ (RRF)\ (V_i)\ (W_s)\ (D)}$$

Where:
A_x, I_s, and A_{is}, are as given for water, above.
V_t = Volume of the concentrated extract in microliters (µL) (V_t = 500 µL).
V_i = Volume of the extract injected in microliters (µL)

$$D = \frac{100 - \%\text{ Moisture}}{100}$$

W_s = Weight of sample extracted in grams (g)
GPC = GPC factor (GPC = 2.0 to account for GPC cleanup).
RRF = Relative response factor determined from the 12-hour calibration standard.
Df = Dilution factor. The dilution factor for analysis of soil/sediment samples for semivolatiles by this method is defined as follows:

If no dilution is performed, Df = 1.0.

$$Df = \frac{\mu L \text{ most conc. extract used to make dilution} + \mu L \text{ clean solvent}}{\mu L \text{ most conc. extract used to make dilution}}$$

The factor of 2.0 in the numerator is used to account for the amount of extract that is not recovered from the mandatory use of GPC cleanup. Concentrating the extract collected after GPC to 0.5 mL maintains the sensitivity of the soil/sediment method.

Calculation of a sample concentration using a secondary ion is done by calculating a new relative response factor,RRF[1], for the secondary ion from the check standard (substitute area of secondary ion where area of primary ion is in the equation for RRF). Secondary ion calculation is used when the primary ion shows matrix interferences in its spectra. In instances where secondary ion calculations are necessary, the narrative will state which samples were affected by interferences and required secondary ion calculations, and show the calculated results. The forms and documentation for the affected samples will reflect primary ion calculations.

Target compounds are verified in Target Review by a data analyst. Each chromatographic peak identified as a target is checked for retention time fit as compared to the continuing calibration standard and its mass spectra is verified using the

guidelines below. Misassignments and interferences that are detected here are corrected. If manual integration is required, "Snap to Data" should be used whenever the peak is baseline resolved for each ion. Surrogates and internal standards should not be manually integrated without the supervision of the Laboratory Section Head or Laboratory Director. Integrations must be reviewed and initialed and dated on the quantitation report next to the "M" qualifier by a second party. A signal integration printout must be submitted for each compound that is manually integrated for any standard, blank, or sample. This is done in target review, using print signals command.

13.0 METHOD PERFORMANCE

13.1. Precision and Accuracy

Laboratory precision and accuracy data were obtained for the method analytes using laboratory control spikes with analytes at concentrations of 125µg/Kg for solid and 0.25µg/L for aqueous matrices. Results were obtained using the analytical instrumentation described in section 6.

13.2. Method Detection Limit Study

This study is a statistically derived assessment of method performance with respect to the variance in the production of extracts and their analysis. Method detection limits are calculated using the formula (3):

$$MDL = S\ t_{(n-1,\ 1\text{-alpha} = 0.99)}$$

$t_{(n-1,\ 1\text{-alpha} = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates
S = the standard deviation of the replicate analyses.

14.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

14.1. Technical acceptance criteria for sample analysis.

14.1.1. The samples must be analyzed on a GC/MS system meeting the DFTPP, initial calibration, continuing calibration and blank technical acceptance criteria.

14.1.2. The sample must be analyzed within the contract required holding time.

14.1.3. The sample must have an associated method blank meeting the blank technical acceptance criteria.

14.1.4. The percent recovery of each of the system monitoring compounds in the sample must be within the acceptance windows in Table 4.

14.1.5. The EICP area for each of the internal standards must be within the inclusive range of 50.0% and 100.0% of the response of the internal standards in the most recent continuing calibration analysis.

14.1.6. The retention time shift for each of the internal standards must be within ± 0.50 minutes (30 seconds) between the sample and the most recent continuing calibration standard analysis.

14.1.7. The RRT of the system monitoring compound in a sample must with in ± 0.06 (RRT) units of its relative retention time in the continuing calibration.

14.1.8. Excluding those ions in the solvent front, no ion may saturate the detector. No target compound concentration may exceed the upper limit of the initial calibration range unless a more dilute aliquot of the sample is also analyzed. Care should be taken in applying the isotopic dilution technique for calculating compound concentrations when large dilution factors are necessary.

14.1.9. After analyzing a sample that exceeds the initial calibration range, the analyst must monitor the samples analyzed immediately after the contaminated sample to assess the extent of carryover, if any. The maximum contamination criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds that exceeded the limits in the contaminated sample. If the maximum criteria is exceeded then all samples affected by the carryover must be re-analyzed.

14.2. Corrective Action for Sample Analysis

14.2.1. Samples must meet technical acceptance criteria before reporting data.

14.2.2. Corrective action for failure to meet instrument performance checks, initial, continuing calibration and method blanks must be completed prior to sample analysis.

14.2.3. Corrective action for system monitoring compounds and internal standard compounds that fail to meet acceptance criteria must be completed prior to sample analysis.

14.3. If any of the system monitoring compounds and internal standard compounds fail to meet acceptance criteria:

14.3.1. Check all calculations, instrument logs, the system monitoring compound, internal standard compound spiking solutions and the instrument operation. If the calculations were incorrect, correct calculations and verify that the system monitoring compound recoveries and internal standard compound responses meet acceptance criteria.

14.3.2. If the instrument log for the amount of internal standard compound spiking solution which was added. If an incorrect amount was spiked reanalyze with the correct amount.

14.3.3. Check the preparation of the internal standards and system monitoring compounds for concentration and expiration.

14.3.4. Verify that the instrument is operating correctly.

14.4. Determine if the problem was a matrix effect.

14.4.1. Check the surrogate recoveries for the MS and MSD.

14.4.2. If the system monitoring compound recoveries and the internal standard compound responses meet the acceptance criteria in the reanalyzed samples the samples are considered in control and the data may be reported.

14.4.3. If the system monitoring compound recoveries and the internal standard compound responses do not meet the acceptance criteria in the reanalyzed samples, then submit data from both analyses.

14.5. Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments defining the nature of the outage. Data qualifiers can be found in Section 11.3. If applicable, a Corrective Action Report will be initiated in order to provide investigation and follow-up.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

15.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

15.3. For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W. Washington D.C. 20036, (202) 872-4477.

15.4. The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes should be characterized and disposed of in a an acceptable manner. The Agency urges laboratories to protect the air, water and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 15.3.

16.0 REFERENCES

16.1. Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, OLM041, USEPA Contract Laboratory Program, September 1998.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

Not Applicable

Table 1. Target Compound List: Reporting Limits and CAS Numbers

Analyte	CAS Number	Aqueous Reporting Limits (ug/L)	Soil/Tissue Reporting Limits (ug/Kg)*
Acenaphthene	83-32-9	0.02	2
Acenaphthylene	208-96-8	0.02	2
Anthracene	120-12-7	0.02	2
C_1-Phenanthrenes/anthracenes		0.02	TBD
C_2-Phenanthrenes/anthracenes		0.02	TBD
C_3-Phenanthrenes/anthracenes		0.02	TBD
C_4-Phenanthrenes/anthracenes		0.02	TBD
Benzo(a)anthracene	56-55-3	0.02	2
Benzo(b)fluoranthene	205-99-2	0.02	2
Benzo(k)fluoranthene	207-08-9	0.02	2
Benzo(g,h,i)perylene	191-24-2	0.02	2
Benzo (a) pyrene	50-32-8	0.02	2
Benzo(e)pyrene	192-97-2	0.02	2
Biphenyl	92-52-4	0.02	2
Chrysene	218-01-9	0.02	2
C_1- Chrysenes		0.02	TBD
C_2- Chrysenes		0.02	TBD
C_3- Chrysenes		0.02	TBD
C_4- Chrysenes		0.02	TBD
Dibenz(a,h)anthracene	53-70-3	0.02	2
2,6 Dimethylnaphthalene	581-42-0	0.02	2
Dibenzothiophene	132-65-0	0.02	2
C_1- Dibenzothiophenes		0.02	TBD
C_2- Dibenzothiophenes		0.02	TBD
C_3- Dibenzothiophenes		0.02	TBD
Fluoranthene	206-44-0	0.02	2
C_1-Fluoranthenes/pyrene		0.02	TBD
Fluorene	86-73-7	0.02	2
C_1- Fluorenes		0.02	TBD

C_2- Fluorenes		0.02	TBD
C_3- Fluorenes		0.02	TBD
Indeno(1,2,3-cd)pyrene	193-39-5	0.02	2
1-Methylnaphthalene	1321-94-4	0.02	2
2-Methylnaphthalene	91-57-6	0.02	2
1 Methylphenanthrene	832-69-9	0.02	2
Naphthalene	91-20-3	0.02	2
C_1- Naphthalenes		0.02	TBD
C_2- Naphthalenes		0.02	TBD
C_3- Naphthalenes		0.02	TBD
C_4- Naphthalenes		0.02	TBD
Phenanthrene	85-01-8	0.02	2
Perylene	198-55-0	0.02	2
Pyrene	129-00-0	0.02	2
2,3,5 Trimethylnaphthalene	2245-38-7	0.02	2

* Reporting Limits based on 40 grams of sample extracted, Final volume 2.0 mL
TBD=To Be Determined

Table 2. DFTPP Criteria

DFTPP Key Ions and Ion Abundance Criteria	
Mass	Ion Abundance Criteria
51	30.0-60.0 percent of mass 198
68	less than 2.0 percent of mass 69
69	Present
70	less than 2.0 percent of mass 69
127	40.0-60.0 percent of mass 198
197	less than 1.0 percent of mass 198
198	base peak, 100 percent relative abundance
199	5.0-9.0 percent of mass 198
275	10.0-30.0 percent of mass 198
365	Greater than 1.0 percent of mass 198
441	Present, but less than mass 443

442	40.0-110.0 percent of mass 198
443	17.0-23.0 percent of mass 442

Table 3. Initial and Continuing Calibration Criteria

Analyte	Minimum RRF	Maximum%RSD	Maximum %Diff
Acenaphthene	0.200	25	25
Acenaphthylene	0.200	25	25
Anthracene	0.200	25	25
Benzo(a)anthracene	0.200	25	25
Benzo(b)fluoranthene	0.200	25	25
Benzo(k)fluoranthene	0.200	25	25
Benzo(g,h,i)perylene	0.200	25	25
Benzo (a) pyrene	0.200	25	25
Benzo(e)pyrene	0.200	25	25
Biphenyl	0.200	25	25
Chrysene	0.200	25	25
Dibenz(a,h)anthracene	0.200	25	25
2,6 Dimethylnaphthalene	0.200	25	25
Dibenzothiophene	0.200	25	25
Fluoranthene	0.200	25	25
Fluorene	0.200	25	25
Indeno(1,2,3-cd)pyrene	0.200	25	25
1-Methylnaphthalene	0.200	25	25
2-Methylnaphthalene	0.200	25	25
1 Methylphenanthrene	0.200	25	25
Naphthalene	0.200	25	25
Phenanthrene	0.200	25	25

Analyte	Minimum RRF	Maximum%RSD	Maximum %Diff
Perylene	0.200	25	25
Pyrene	0.200	25	25
2,3,5 Trimethylnaphthalene	0.200	25	25

Table 4. Surrogate Recoveries

Compound	Water (% Recovery)	Soil (% Recovery)
Naphthalene - d_8	20-130	20-130
Acenaphthene - d_{10}	20-130	20-130
Phenanthrene- d_{10}	20-130	20-130
Chrysene-d_{12}	20-130	20-130
Perylene- d_{12}	20-130	20-130

Table 5. Matrix Spike Recoveries

Compound	% Recovery Water	% Recovery Soil
Acenaphthene	60-140	60-140
Acenaphthylene	60-140	60-140
Anthracene	60-140	60-140
Benzo(a)anthracene	60-140	60-140
Benzo(b)fluoranthene	60-140	60-140
Benzo(k)fluoranthene	60-140	60-140
Benzo(g,h,i)perylene	60-140	60-140
Benzo (a) pyrene	60-140	60-140
Benzo(e)pyrene	60-140	60-140
Biphenyl	60-140	60-140
Chrysene	60-140	60-140
Dibenz(a,h)anthracene	60-140	60-140
2,6 Dimethylnaphthalene	60-140	60-140
Dibenzothiophene	60-140	60-140
Fluoranthene	60-140	60-140
Fluorene	60-140	60-140
Indeno(1,2,3-cd)pyrene	60-140	60-140
1-Methylnaphthalene	60-140	60-140
2-Methylnaphthalene	60-140	60-140
1 Methylphenanthrene	60-140	60-140
Naphthalene	60-140	60-140
Phenanthrene	60-140	60-140
Perylene	60-140	60-140
Pyrene	60-140	60-140
2,3,5 Trimethylnaphthalene	60-140	60-140

Table 6. Quantitation Associations and Masses

Analyte	Quantitation Ion	Confirmation Ions	Associations [a]	Associations [b]
Internal Standards:				
Fluorene - d_{10} **(GC ISA)**	176	174	NA	NA
Benzo (a)pyrene - d_{12} **(GC ISB)**	264	260	NA	NA
Surrogate Standards:				
Naphthalene - d_8 *(IS1)*	136	134	**GC ISA**	**GC ISA**
Acenaphthene - d_{10} *(IS2)*	164	162	**GC ISA**	**GC ISA**
Phenanthrene-d_{10} *(IS3)*	188	184	**GC ISA**	**GC ISA**
Chrysene-d_{12} *(IS4)*	240	236	**GC ISB**	**GC ISB**
Perylene- d_{12} *(IS5)*	264	260	**GC ISB**	**GC ISB**
Target Compounds:				
Acenaphthene	154	153	*IS2*	**GC ISA**
Acenaphthylene	152	153	*IS2*	**GC ISA**
Anthracene	178	176	*IS3*	**GC ISA**
C_1-Phenanthrenes/anthracenes	192	191	*IS3*	**GC ISA**
C_2-Phenanthrenes/anthracenes	206	191	*IS3*	**GC ISA**
C_3-Phenanthrenes/anthracenes	220	205	*IS3*	**GC ISB**
C_4-Phenanthrenes/anthracenes	234	219	*IS3*	**GC ISB**
Benzo(a)anthracene	228	226	*IS4*	**GC ISB**
Benzo(b)fluoranthene	252	253	*IS4*	**GC ISB**
Benzo(k)fluoranthene	252	253	*IS4*	**GC ISB**
Benzo(g,h,i)perylene	276	277	*IS4*	**GC ISB**
Benzo (a) pyrene	252	253	*IS4*	**GC ISB**
Benzo(e)pyrene	252	253	*IS4*	**GC ISB**
Biphenyl	154	152	*IS2*	**GC ISA**
Chrysene	228	226	*IS4*	**GC ISB**
C_1- Chrysenes	242	241	*IS4*	**GC ISB**
C_2- Chrysenes	256	241	*IS4*	**GC ISB**
C_3- Chrysenes	270	255	*IS4*	**GC ISB**
C_4- Chrysenes	284	269	*IS4*	**GC ISB**

Dibenz(a,h)anthracene	278	279	*IS4*	**GC ISB**
2,6 Dimethylnaphthalene	156	141	*IS2*	**GC ISA**
Dibenzothiophene	184	152	*IS3*	**GC ISA**
C_1- Dibenzothiophenes	198	184	*IS3*	**GC ISA**
C_2- Dibenzothiophenes	212	197	*IS3*	**GC ISA**
C_3- Dibenzothiophenes	226	211	*IS3*	**GC ISA**
Fluoranthene	202	101	*IS3*	**GC ISA**
C_1-Fluoranthenes/pyrene	216	215	*IS3*	**GC ISB**
Fluorene	166	165	*IS2*	**GC ISA**
C_1- Fluorenes	180	165	*IS2*	**GC ISA**
C_2- Fluorenes	194	179	*IS2*	**GC ISA**
C_3- Fluorenes	208	193	*IS2*	**GC ISA**
Indeno(1,2,3-cd)pyrene	276	277	*IS4*	**GC ISB**
1-Methylnaphthalene	142	141	*IS1*	**GC ISA**
2-Methylnaphthalene	142	141	*IS1*	**GC ISA**
1 Methylphenanthrene	192	191	*IS3*	**GC ISA**
Naphthalene	128	127	*IS1*	**GC ISA**
C_1- Naphthalenes	142	141	*IS1*	**GC ISA**
C_2- Naphthalenes	156	141	*IS2*	**GC ISA**
C_3- Naphthalenes	170	155	*IS2*	**GC ISA**
C_4- Naphthalenes	184	169	*IS2*	**GC ISA**
Phenanthrene	178	176	*IS3*	**GC ISA**
Perylene	252	253	*IS4*	**GC ISB**
Pyrene	202	101	*IS3*	**GC ISA**
2,3,5 Trimethylnaphthalene	170	155	*IS2*	**GC ISA**

[a] Internal standard, surrogate, and Analyte associations for Isotopic Dilution calculation.
[b] Internal standard, surrogate, and Analyte associations for Internal Standard calculation.

Appendix A: Terms & Definitions

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Concentration Level (low or medium): characterization of soil samples or sample fractions as low concentration or medium concentration is made on the basis of the laboratory's preliminary screen, not on the basis of information entered on the Traffic Report (C-O-C) by the sampler.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Decafluorotriphenylphosphine (DFTPP): compound chosen to establish mass spectral instrument performance for semivolatile analysis.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Extractable: a compound that can be partitioned into an organic solvent from the sample matrix and is amenable to gas chromatography. Extractables include semivolatile (BNA) and pesticide/Aroclor compounds.

GEL Permeation Chromatography (GPC): a size-exclusion chromatographic technique that is used as a cleanup procedure for removing large organic molecules, particularly naturally occurring macro-molecules such as lipids, polymers, viruses, etc.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Initial Calibration Verification (ICV): solution prepared from a separate source from that which is used to prepare the calibration curve.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Internal Standards: compounds added to every standard, blank, matrix spike, matrix spike duplicate, sample at a know concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds.

Isotopic Dilution: a process whereby the determination of the concentration of target analytes is based upon the recovery of spiked analogues.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix: the predominant material of which the sample to be analyzed is composed. For the purpose of this SOW, a sample matrix is either water, soil/sediment, or tissue. Matrix is not synonymous with phase (liquid or solid).

Matrix Duplicate (MD): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate.

Matrix Effect: in general, the effect of a particular matrix (water or soil/sediment) on the constituents with which it contacts. This is particularly pronounced for clay particles, which may adsorb chemicals and catalyze reactions. Matrix effects may prevent extraction of target

analytes, and may affect surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Relative Response Factor (RRF): a measure of the relative mass spectral response of an analyte compared to its internal standard. Relative Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples. See Section 12.0 Calculations.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample. The RL must be minimally at or above the MDL.

Selective Ion Monitoring (SIM): a mass spectrometer acquisition mode in which the instrumentation is configured to selectively scan and acquire only those ions necessary for identification and quantitation of the target compounds. The limited mass range enables greater dwell times per mass than can be accomplished with full scan mode thereby enabling greater instrument sensitivity.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogates (Surrogate Standards): for semivolatiles and pesticides/Aroclors compounds added to every blank, sample, matrix spike, matrix spike duplicate, and standard; used to evaluate analytical efficiency by measuring recovery. Surrogates are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

STL KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Analysis of Polychlorinated Biphenyl Congeners Based on SW-846 Method 8082

(SUPERSEDES: KNOX-GC-0011, Rev. 3

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1. Scope and Application

1.1. This SOP describes procedures to be used when SW-846 Method 8082 is applied to the analysis of polychlorinated biphenyl (PCB) congeners by gas chromatography/electron capture detection (GC/ECD). It is applicable to extracts derived from any matrix which are prepared according to the sample extraction SOP, KNOX-OP-0014, current revision.

1.2. Table 1 lists compounds that are routinely determined by this method and gives the reporting limits (RL) for each matrix. RLs given are based on the low-level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

2. Summary of Method

2.1. This method presents conditions for the analysis of prepared extracts for PCB congeners. The congeners are separated by dual fused silica capillary columns and detected by electron capture detection. Quantitation is performed using the internal standard method.

2.1.1. Aqueous samples are extracted with methylene chloride using continuous liquid / liquid extraction. Solid samples are extracted with methylene chloride/acetone using Soxhlet extraction. Waste dilution is used for samples that are miscible with the solvent.

2.1.2. Extracts are dried and concentrated to a volume of 10 ml. The extracts are then cleaned using a sulfuric acid wash. When necessary, extracts are cleaned using mercury treatment or tetrabutyl ammonium (TBA) sulfite treatment to remove elemental sulfur. Extracts are washed with a 5% NaCl solution, dried and concentrated to final volume using nitrogen evaporation.

2.1.3. After the initial preparation step, the sample is introduced into the GC and concentrations of target analytes are measured by the detector response, within a defined retention time window, relative to the response to standard concentrations.

3. Definitions

3.1. Definitions of terms used in this SOP may be found in the glossary of the Laboratory Quality Manual (LQM).

4. Interferences

4.1. Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Elemental sulfur, often associated with sediments from sites with anaerobic conditions, may result in analytical signal suppression. Sulfur is removed using mercury cleanup or treatment with TBA sulfite.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including Florisil® cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and sulfur cleanup (Method 3660).

5. Safety

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Specific Safety Concerns or Requirements

5.2.1. The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.2.2. There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.3. Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the

MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Mercury	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3.1. PCBs have been classified as potential carcinogens under OSHA. Concentrated solutions of PCBs must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.4. Exposure to chemicals will be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. Opened containers of neat standards will be handled in a fume hood.

5.6. Sample extracts and standards that are in a flammable solvent shall be stored in an explosion-proof refrigerator.

5.7. When using hydrogen gas as a carrier, all precautions listed in the STL Corporate Safety Manual shall be observed.

6. Equipment and Supplies

6.1. An analytical system complete with a gas chromatograph and a ^{63}Ni electron capture detector is required. A data system capable of measuring peak area and/or height is required.

6.2. Refer to Table 2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. Reagents and Standards

7.1. Calibration Standards: A calibration curve with at least five points is prepared at nominal concentrations ranging from 1 to 50 ng/ml for each compound of interest in hexane. Some compounds may be prepared at higher levels due to chromatographic performance, stability, and sensitivity. Refer to Table 3 for analytes and calibration levels.

7.2. Surrogate Standards: A 100 ng/mL surrogate spiking solution is prepared in methanol. Tetrachloro-m-xylene and 2,3,3',5,5',6-Hexachlorobiphenyl (BZ 165) are used as surrogate standards. Refer to Table 3 for the calibration levels for surrogate standards and to Table 4 for the typical spiking levels.

7.3. Internal Standards: A 250 ng/mL internal standard (IS) solution is prepared in hexane. Compounds in the IS solution are 2,4,5-Trichlorobiphenyl (BZ 29) and 2,3,3',4,5,6-Hexachlorobiphenyl (BZ 160). Internal standards are added to all standards and extracts at 25 ng per mL of extract. For example, if the volume of an extract used is 100 µL, 10 µL of the 250 ng/mL internal standard solution would be added. Refer to Table 3.

7.4. Quality Control (QC) Standards: The LCS and MS/MSD spiking solution is prepared to contain a final concentration of 100 ng/mL for all analytes except BZ1, BZ3 and BZ15. The concentrations of BZ1 and BZ3 are 2000 ng/mL and the concentration of BZ15 is 500 ng/mL. Refer to Table 4 for typical spiking levels.

7.5. Initial Calibration Verification Standard (2nd Source Standard): The mid level ICV standard includes all analytes. The standard is prepared from a stock independent from the calibration standards.

7.6. The standards listed in sections 7.1 to 7.5 are stored at $\leq 6^{o}$C. All standards must be protected from light. Standard solutions must be brought to room temperature before using.

7.6.1. Expiration times for all standards are measured from the time the standard is prepared or one year from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If a vendor supplied standard has an earlier expiration date, then that date is used.

7.6.2. Stock standards are purchased as certified solutions or prepared from pure solutions. Stock standard solutions must be replaced or demonstrated to be valid by comparison to a second source standard after one year.

7.6.3. Calibration standards, ICV standards and spiking solutions are prepared as dilutions of the stock standards. The standards must be replaced or demonstrated to be valid by comparison to a second source standard after six months.

8. Sample Collection, Preservation and Storage

8.1. Extracts must be refrigerated at $\leq 6^{o}C$ and should be stored in suitable glass containers with Teflon lined caps. (Extracts will normally be stored for 30 days after invoicing.)

8.2. Water samples are extracted within seven days of sampling and the extracts are analyzed within 40 days of the end of the extraction.

8.3. Solids and waste samples are extracted within fourteen days of sampling and the extracts are analyzed within 40 days of the end of the extraction.

9. Quality Control

9.1. Initial Demonstration of Capability: The initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin.

9.2. Batch Definition: Batches are defined at the sample preparation stage. Batches should be kept together through the entire analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the QC Program document (QA-003) for further details of the batch definition.

9.2.1. Quality Control Batch: The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike/matrix spike duplicate (MS/MSD), a laboratory control sample (LCS) and a method blank. Laboratory generated QC samples (blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC

samples are included in the batch count. Upon client request, the MS/MSD may be replaced with a matrix spike and a sample duplicate. If insufficient sample is available for a MS/MSD, a LCS duplicate may be substituted.

9.3. Control Limits: In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples. These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations, unless those limits are tighter than the calibration criteria, in which case limits may be widened. Refer to policy QA-003 for more details.

9.3.1. These limits do not apply to dilutions greater than 5X. Surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.3.2. All surrogate, LCS, and MS recoveries must be entered into QuantIMS so that accurate historical control limits can be generated.

9.3.3. Refer to the QC Program document (QA-003) for further details of control limits.

9.4. Surrogates

9.4.1. Every sample, blank and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 4.

9.4.2. If only one surrogate in a sample extract is outside the control limit, and all of the method blank and LCS surrogates and spikes are in control, the outlier may be attributed to matrix effects.

9.4.3. If both sample surrogates are outside limits, the following corrective actions must take place (except for dilutions greater than 5X):

9.4.4. Check all calculations for error.

9.4.5. Ensure that instrument performance is acceptable.

9.4.6. Recalculate the results and/or reanalyze the extract if either of the above checks reveal a problem.

9.4.7. If none of the above resolves the problem, reprepare and reanalyze the sample or flag the data as "Estimated Concentration". Repreparation is not necessary if there is an obvious chromatographic interference.

Note: The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to a matrix effect (unless the analyst believes that the repeated out of control results are not due to a matrix effect).

9.4.8. If dual column analysis is used, the choice of which result to report is made in the same way as for the samples (Section 12.1.2) unless one column is out of control, in which case the in-control result is reported.

9.4.9. If the surrogates are out of control for the original sample, MS and MSD, then a matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then repreparation or flagging of the data is required.

9.4.10. Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.5. Method Blanks

9.5.1. For each batch of samples, analyze a method blank. The method blank consists of reagent water for aqueous samples, and reagent sand and sodium sulfate for soil samples (refer to SOP KNOX-OP-0014 for details). Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must meet the following acceptance criteria:

9.5.1.1. If the concentration of a target analyte in the method blank is greater than the MDL but less than the reporting limit, corrective action is required, but the associated data may be reported. The corrective action must include the addition of "B" qualifiers to the results for the associated samples with the corresponding analytes detected in the method blank above the MDL.

9.5.1.2. If the concentration of a target analyte in the method blank is above the reporting limit and the associated sample values are more than 20 times the concentration present in the method blank, corrective action is required, but the associated data may be reported. The corrective action must include the addition of "B" qualifiers to the results for the

associated samples with the corresponding analytes detected in the method blank above the reporting limit.

9.5.1.3. If the concentration of a target analyte in the method blank is greater than the reporting limit, and the concentration of that analyte in an associated sample is less than 20 times the method blank concentration, the sample batch must be reextracted and reanalyzed.

9.5.1.4. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with a narrative statement that describes the issue.

9.6. Instrument Blanks

9.6.1. An instrument blank must be analyzed prior to sample analysis during any 12 hour period of analysis that does not contain a method blank.

9.6.2. An instrument blank consists of the appropriate solvent with internal standards added.

9.6.3. Control criteria are the same as for the method blank, except that only reanalysis of affected samples would be required, not re-extraction.

9.7. Laboratory Control Samples

9.7.1. A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. The LCS contains the analytes shown in Table 4 and must contain the same analytes as the matrix spike.

9.7.2. If any control analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch.

9.7.3. Refer to the QC Program document (QA-003) for further details of the corrective action.

9.7.4. If dual column analysis is used, the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in-control result is reported.

9.8. Matrix Spikes/Matrix Spike Duplicates: A matrix spike and matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of samples. Spiking compounds and levels are given in Table 4. Compare the percent recovery and relative percent difference (RPD) to the laboratory control limits.

9.8.1. If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed.

9.8.2. If the recovery for any component is outside QC limits for both the matrix spike/matrix spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.

9.8.3. If a matrix spike/matrix spike duplicate is not possible due to limited sample, then a laboratory control sample duplicate should be analyzed.

9.8.4. The matrix spike/matrix spike duplicate must be analyzed at the same dilution as the unspiked sample.

9.8.5. If dual column analysis is used, the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in-control result is reported.

9.9. STL QC Program: Further details of QC and corrective action guidelines are presented in the QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. Calibration and Standardization

10.1. Refer to Table 2 for details of GC operating conditions. The conditions listed should result in resolution of all analytes listed in Table 7. Chromatographic resolution is defined in section 10.9.

10.2. Refer to Table 5 for initial calibration and continuing calibration analytical sequences.

10.3. Refer to Appendix II for a calibration and spike summary.

10.4. Internal standard calibration is recommended unless the sample matrix is likely to interfere with the quantitation of the internal standard. Prepare standards containing each analyte of interest at a minimum of five concentration levels. The low level standard should be at or below the reporting limit. The other standards define the working range of the detector. Recommended calibration levels are given in Table 3.

10.5. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns or replacing the electron capture detector. A new calibration is not required after clipping the column, replacing the septum or syringe or other minor maintenance.

10.6. With the exception of Section 10.7, it is not acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve and the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve.

10.7. A level may be removed from the calibration if the reason can be clearly documented, for example a broken vial. A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration. All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.8. Internal standard calibration

10.8.1. The internal standard approach assumes that variations in instrument sensitivity, amount injected, etc., can be corrected by determining the ratio of the response of the analyte to the response of an internal standard that has been added to the extract. The internal standards are similar in analytical behavior to the compounds of interest. Typical internal standards are listed in Table 3. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences (i.e., the magnitude of the internal standard area or height must be within 50 to 150% of the response in the mid-level of the initial calibration). If the sample matrix interferes with quantitation of the internal standard, then the external standard approach must be used instead. (Refer to SOP KNOX-GC-0015 for the external standard calculations.) In this event, use the response factors from the previous continuing calibration to quantitate the analytes in the sample with the interference (applies only to the sample with the interference).

10.8.2. Introduce each calibration standard into the GC using the technique that will be used for samples. Response factors (RF) for each compound are calculated as follows:

$$RF = \frac{H_s \text{ x } C_{is}}{H_{is} \text{ x } C_s}$$

Where:
H_s = Response for the analyte to be measured, height
H_{is} = Response for the internal standard, height
C_{is} = Concentration of internal standard
C_s = Concentration of the analyte to be determined in the standard

10.8.3. Average response factor

The average response factor may be used if the percent relative standard deviation (%RSD) of the response factors is $\leq$ 20%.

The equation for average response factor is:

$$Average\ response\ factor = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where: n = Number of calibration levels

$\sum_{i=1}^{n} RF_i$ = Sum of response factors for each calibration level

10.9. The following requirements must be met for any calibration to be used:

- All analytes must be adequately resolved chromatographically to perform separate integrations for compounds shown as resolved in Table 7. The resolution must be achieved on the highest level standard used in the most recent calibration. Chromatographic resolution is defined as having at least 0.04 minutes between all retention times, and with a distinguishable valley between the two peaks.
- Response must increase with increasing concentration.

10.10. Initial Calibration Verification Standard (2nd Source Standard)

10.10.1. A mid-level standard from a second source is analyzed as the initial calibration verification (ICV). The ICV shall be analyzed with each initial calibration.

10.10.2. The ICV must be within +/- 25% of its expected value with allowance for up to two analytes within +/- 35%.

10.11. Calibration Verification (CCV)

10.11.1. 12 Hour Calibration

10.11.1.1. The RF is verified by the analysis of a mid-level calibration standard at the beginning, after every 12 hours and at the end of the analysis sequence. The center of each retention time window is updated with each 12-hour calibration at the discretion of the analyst.

10.11.1.2. The analytical shift starts with the injection of the mid-level standard. The data associated with any sample that is injected > 12 hours after the start of the analytical shift is not valid. The extract must be reanalyzed within a valid shift.

10.11.2. Continuing Calibration

10.11.2.1. It may be appropriate to analyze a mid point standard more frequently than every 12 hours. If these calibration verification standards are analyzed, requirements are the same as the 12 hour calibration with the exception that retention times need not be updated.

10.11.2.2. The mid-level calibration mix (CS-4 or CS-5 in Table 3) is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse, analyze the 12-hour standard sequence instead. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.11.3. % Drift calculation

% Drift is used for evaluating calibration verification.

$$\%\,Drift = \frac{Calculated\ Conc.\ -\ Theoretical\ Conc.}{Theoretical\ Conc.} \times 100\%$$

10.11.4. Any individual compounds with %D $\leq$15% meet the calibration criteria.

10.11.5. Closing calibration standards are not necessary for internal standard methods.

10.11.6. The internal standard response in a calibration verification standard must be within 50 to 150% of the response in the mid-level of the initial calibration.

10.11.7. If the analyst notes that a CCV failed and can document the reason for failure (e.g., broken vial, carryover from the previous sample, etc.), then a second CCV may be analyzed without any adjustments to the instrument.

10.11.8. If routine corrective action procedures fail to produce a second consecutive (immediate) calibration verification within acceptance criteria, then the laboratory has to demonstrate performance after corrective action with two consecutive successful calibration verifications. If the laboratory has not demonstrated acceptable performance, sample analyses must not occur until a new initial calibration curve is established and verified. However, sample data associated with an unacceptable calibration verification may be reported as qualified data under the following special conditions:

10.11.8.1. When the acceptance criteria for the continuing calibration verification is exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise, the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.

10.11.9. If highly contaminated samples are expected, it is acceptable to analyze blanks or primers at any point in the run.

10.11.10. Corrective Action for Samples: For this internal standard method, any samples injected after a standard not meeting the calibration criteria must be reinjected.

11. Procedure

11.1. Extraction: The extraction procedure is described in SOP KNOX-OP-0014.

11.2. Cleanup: Appendix III contains instructions for sulfur removal using elemental mercury. Other cleanup procedures are described in SOP KNOX-OP-0014.

11.3. Gas Chromatography: Typical gas chromatographic conditions are given in Table 2.

11.4. Sample Introduction: Analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure. Allow extracts to warm to ambient temperature before injection. Add the internal standard solution to the extract (1:10 ratio).

11.5. Analytical Sequence: An analytical sequence starts with an initial calibration or CCV. The typical analytical sequence is given in Table 5. If there is a break in the analytical sequence of greater than 12 hours, a 12-hour calibration verification standard must be analyzed before proceeding with the sequence.

11.6. Retention Time Windows

11.6.1. Retention time windows must be determined for all analytes. Make three injections of all analytes of interest over the course of a 72 hour period. Calculate the standard deviation of the three retention times for each analyte (relative retention times may also be used). Plus or minus three times the standard deviation of the retention times of each analyte defines the retention time window.

11.6.2. The centers of the windows are updated with the mid-point of the initial calibration. The windows may also be updated at the discretion of the analyst, on the basis of the12-hour calibration verification.

11.6.3. If the retention time window as calculated above is less than +/- 0.03 minutes, use +/- 0.03 minutes as the retention time window. This allows for slight variations in retention times caused by sample matrix.

11.6.4. The laboratory must calculate new retention time windows each time a new column is installed. The new windows must be generated within one week of the installation of the new column. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.

11.6.5. Corrective Action for Retention Times: The retention times of all compounds in each continuing calibration must be within the most recently updated retention time windows. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed unless the following conditions are met for any compound that elutes outside the retention time window:

- The retention time of that compound in the standard must be within a retention time range equal to twice the original window.
- No peak that would be reportable may be present on the sample chromatogram within an elution time range equal to three times the original retention time window.

11.7. Percent Moisture: Analytical results are reported as dry weight. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP KNOX-WC-0012 for determination of percent moisture.

11.8. Procedural Variations: Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA manager. If contractually required, the client shall be notified. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. Data Analysis and Calculations

12.1. Qualitative Identification

12.1.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmation column, at a concentration greater than the reporting limit (MDL if J flag confirmation is required by the client).

Note: All NFESC or Navy samples must be reported to the MDL unless otherwise specified by the client.

12.1.2. Dual column quantitation: The lower of the two results is normally reported. The lower result is considered better because the higher result is generally higher because of chromatographic interference. However, the higher result is reported if any of the following three bulleted possibilities are true:

- There is obvious chromatographic interference on the column with the lower result.
- The continuing calibration on the column with the lower result fails. (If the higher result is > 40% higher and the calibration on the column with the lower result fails, then the sample must be evaluated for reanalysis.)
- There is no interference and the RPD between the two results is >40%.

12.1.3. If the RPD between the response on the two columns is greater than 40%, the confirmation is suspect and the results are qualified. RPD is calculated using the following formula:

$$RPD = \frac{R1 - R2}{\frac{1}{2}(R1 + R2)} \text{ x } 100$$

Where: R=Result

12.2. Surrogate recovery results are calculated and reported as described in Section 9.4.

12.3. Calibration Range: If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the mid-level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

12.4. Dilutions: Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits above 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample should be reanalyzed at a dilution targeted to bring the largest hit into the upper half of the calibration range.

12.4.1. Guidance for Dilutions Due to Matrix: If the sample is initially run at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination.

12.4.2. Reporting Dilutions: The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12.5. Interferences: If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.6. Calculations

12.6.1. Internal Standard Calculations Using Calibration Factors

12.6.1.1. Aqueous Samples

$$\text{Concentration}\,(ug/L) = \frac{H_x \text{ x } C_{is} \text{ x } V_f \text{ x } D_f}{H_{is} \text{ x RF x } V_s} \text{ x Split Factor}$$

Where:

H_x = Response for the analyte in the sample, height
C_{is} = Concentration of internal standard added, ng/mL
V_f = Final volume of extract, mL
D_f = Bench dilution factor
H_{is} = Response of the internal standard, height
RF = Response factor for analyte
V_s = Volume of sample extracted, mL

$$\text{Split Factor} = \frac{\text{Total volume of extract prior to final concentration, mL}}{\text{Volume of extract taken for final concentration, mL}}$$

Example 1: TCX in Aqueous Sample (1000 mL sample extracted and concentrated to 10 mL; no split taken)

H_x = 351,469
C_{is} = 25 ng/mL
V_f = 10 mL
D_f = 2
H_{is} = 151,548
RF = 1.706843
V_s = 1000 mL
Split Factor = 1

$$\frac{351{,}469 \text{ x } 25\,\text{ng/mL x } 10\,\text{mL x } 2}{151{,}548 \text{ x } 1.706843 \text{ x } 1000\,\text{mL}} \text{ x } 1 = 0.679 \text{ ng/mL (ppb)}$$

Example 2: TCX in Low-level Aqueous Sample (1000 mL sample extracted and concentrated to 10 mL; 5 mL taken and concentrated to 0.5 mL)

H_x = 272,035
C_{is} = 25 ng/mL
V_f = 0.5 mL
D_f = 2
H_{is} = 153,024
RF = 1.706843
V_s = 1000 mL
Split Factor = 10 mL/5 mL

$$\frac{272{,}035 \text{ x } 25\,\text{ng/mL x } 0.5\,\text{mL x } 2}{153{,}024 \text{ x } 1.706843 \text{ x } 1000\,\text{mL}} \text{ x } \frac{10\text{mL}}{5\,\text{mL}} = 0.052 \text{ ng/mL (ppb)}$$

12.6.1.2. Non-aqueous Samples

$$\text{Concentration (ug/kg)} = \frac{H_x \text{ x } C_{is} \text{ x } V_f \text{ x } D_f}{H_{is} \text{ x RF x } W_s} \text{ x Split Factor}$$

Where:

W_s = Weight of sample extracted, g

Example 3: TCX in Soil (18.2 g sample extracted and concentrated to 10 mL; no split is taken)

H_x = 59,321
C_{is} = 25 ng/mL
V_f = 10 mL
D_f = 1
H_{is} = 152,301
RF = 1.706843
V_s = 18.2 g
Split Factor = 1

$$\frac{59{,}321 \text{ x } 25\,\text{ng/mL x } 10\,\text{mL x } 1}{152{,}301 \text{ x } 1.706843 \text{ x } 18.2\,\text{g}} \text{ x } 1 = 3.13 \text{ ng/g (ppb)}$$

Note: RLs and MDLs in the QuantIMS reference data are based on extracting 10 g of soil. Therefore, the QuantIMS dilution factor must be used to adjust the RLs and MDLs when a sample weight other than 10 g is extracted.

$$\text{QuantIMS Dilution Factor (DF)} = \frac{10\,\text{g, nominal weight}}{\text{Actual Weight Extracted, g}} \text{ x Bench dilution factor}$$

Example 4: Actual weight of sample extracted = 18.2 g
Bench dilution factor = 1

$$\text{QuantIMS DF} = \frac{10\,\text{g}}{18.2\text{ g}} \text{ x } 1 = 0.549$$

QuantIMS will only accept two decimal places in the dilution factor field, therefore, 0.55 must be entered.

12.6.2. The internal standard response in the samples must be within 50%-150% of the response in the mid-point of the previous ICAL. If the internal standard response is within acceptance criteria on one column, but outside criteria on the second column, the sample results will be reported using the column with acceptable results. If the internal standard response

exceeds this criteria on both columns, the following corrective action must be taken:

- Verify that the instrument is working properly.
- Reinject the sample extract.

12.6.3. Surrogate Recovery: Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factors from the initial calibration are used. Surrogate recovery is calculated using the following equation:

$$\%\,\text{Recovery} = \frac{\text{Concentration found}}{\text{Concentration spiked}} \text{ x } 100$$

13. Method Performance

13.1. Method Detection Limit: Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy # QA-005.

13.2. Initial Demonstration: Each analyst must complete a successful initial demonstration of capability (IDOC). This requires analysis of QC check samples containing all of the standard analytes for the method.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid-level calibration.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in Table 6.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. Pollution Prevention

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. Waste Management

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Procedure: The following waste streams are produced when this method is carried out.

- Expired primary and working PCB standards are stored in metal closed-top containers.
- Vials containing sample extracts are stored in plastic or metal containers resistant to solvents.

16. References

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Section 8000B.

16.2. SW846, Update III, December 1996, Method 8082.

17. Miscellaneous

17.1. Modifications from Reference Method: None

17.2. Appendix I: Tables

17.2.1. Table 1 - Standard Analyte List

17.2.2. Table 2 - Gas Chromatographic Conditions

17.2.3. Table 3 – Typical Calibration Levels

17.2.4. Table 4 - Typical OPR, LCS, MS & MSD Spiking Levels

17.2.5. Table 5 - Typical Analytical Sequence

17.2.6. Table 6 - Performance Criteria for Four Replicate Initial Demonstrations of Capability

17.2.7. Table 7 - Resolution with Typical Chromatographic Conditions

17.3. Appendix II: Calibration and Spike Summary

17.4. Appendix III: Sulfur Removal using Elemental Mercury

17.5. Appendix IV: Example Data Review Checklist

Table 1 Standard Analyte List

Analyte			Reporting Limit				
CAS Number	BZ[1]	Compound Name	Aqueous ug/L	Low-level Aqueous (ug/L)	Solid ug/kg (Dry)	Tissue ug/kg (Total)	Waste ug/kg
2051-60-7	1	2-Chlorobiphenyl	0.2	0.02	20	20	2000
2051-62-9	3	4-Chlorobiphenyl	0.2	0.02	20	20	2000
16605-91-7	5	2,3-dichlorobiphenyl	0.01	0.001	1	1	100
34883-43-7	8	2,4'-Dichlorobiphenyl	0.01	0.001	1	1	100
2050-68-2	15	4,4'-Dichlorobiphenyl	0.05	0.005	5	5	500
37680-65-2	18	2,2',5-Trichlorobiphenyl	0.01	0.001	1	1	100
7012-37-5	28	2,4,4'-Trichlorobiphenyl	0.01	0.001	10	10	100
16606-02-3	31	2,4',5-trichlorobiphenyl	0.01	0.001	10	10	100
38444-90-5	37	3,4,4'-Trichlorobiphenyl	0.01	0.001	1	1	100
41464-39-5	44	2,2',3,5'-Tetrachlorobiphenyl	0.01	0.001	1	1	100
41464-40-8	49	2,2',4,5'-Tetrachlorobiphenyl	0.01	0.001	1	1	100
35693-99-3	52	2,2',5,5'-Tetrachlorobiphenyl	0.01	0.001	1	1	100
32598-10-0	66	2,3',4,4'-Tetrachlorobiphenyl	0.01	0.001	1	1	100
32598-11-1	70	2,3',4',5-Tetrachlorobiphenyl	0.01	0.001	1	1	100
32690-93-0	74	2,4,4',5-Tetrachlorobiphenyl	0.01	0.001	1	1	100
32598-13-3	77	3,3',4,4'-Tetrachlorobiphenyl	0.01	0.001	1	1	100
70362-50-4	81	3,4,4',5-Tetrachlorobiphenyl	0.01	0.001	1	1	100
38380-02-8	87	2,2',3,4,5'-Pentachlorobiphenyl	0.01	0.001	1	1	100
68194-07-0	90	2,2',3,4',5-Pentachlorobiphenyl	0.01	0.001	1	1	100
38380-01-7	99	2,2',4,4',5-Pentachlorobiphenyl	0.01	0.001	1	1	100
37680-73-2	101	2,2',4,5,5'-Pentachlorobiphenyl	0.01	0.001	1	1	100
32598-14-4	105	2,3,3',4,4'-Pentachlorobiphenyl	0.01	0.001	1	1	100
38380-03-9	110	2,3,3',4',6-Pentachlorobiphenyl	0.01	0.001	1	1	100
74472-37-0	114	2,3,4,4',5-Pentachlorobiphenyl	0.01	0.001	1	1	100
74472-38-1	115	2,3,4,4',6-Pentachlorobiphenyl	0.01	0.001	1	1	100
31508-00-6	118	2,3',4,4',5-Pentachlorobiphenyl	0.01	0.001	1	1	100
56558-17-9	119	2,3',4,4',6-Pentachlorobiphenyl	0.01	0.001	1	1	100
65510-44-3	123	2,3',4,4',5'-Pentachlorobiphenyl	0.01	0.001	1	1	100
57465-28-8	126	3,3',4,4',5-Pentachlorobiphenyl	0.01	0.001	1	1	100
38380-07-3	128	2,2',3,3',4,4'-Hexachlorobiphenyl	0.01	0.001	1	1	100
35065-28-2	138	2,2',3,4,4',5'-Hexachlorobiphenyl	0.01	0.001	1	1	100
52712-04-6	141	2,2',3,4,5,5'-hexachlorobiphenyl	0.01	0.001	1	1	100
38380-04-0	149	2,2',3,4',5',6-Hexachlorobiphenyl	0.01	0.001	1	1	100
52663-63-5	151	2,2',3,5,5',6-Hexachlorobiphenyl	0.01	0.001	1	1	100
35065-27-1	153	2,2',4,4',5,5'-Hexachlorobiphenyl	0.01	0.001	1	1	100
38380-08-4	156	2,3,3',4,4',5-Hexachlorobiphenyl	0.01	0.001	1	1	100
69782-90-7	157	2,3,3',4,4',5'-Hexachlorobiphenyl	0.01	0.001	1	1	100
74472-42-7	158	2,3,3',4,4',6-Hexachlorobiphenyl	0.01	0.001	1	1	100
52663-72-6	167	2,3',4,4',5,5'-Hexachlorobiphenyl	0.01	0.001	1	1	100
59291-65-5	168	2,3',4,4',5',6-Hexachlorobiphenyl	0.01	0.001	1	1	100
32774-16-6	169	3,3',4,4',5,5'-Hexachlorobiphenyl	0.01	0.001	1	1	100
35065-30-6	170	2,2',3,3',4,4',5-Heptachlorobiphenyl	0.01	0.001	1	1	100
52663-70-4	177	2,2',3,3',4,5',6'-Heptachlorobiphenyl	0.01	0.001	1	1	100
35065-29-3	180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	0.01	0.001	1	1	100
52663-69-1	183	2,2',3,4,4',5',6-Heptachlorobiphenyl	0.01	0.001	1	1	100
74472-48-3	184	2,2',3,4,4',6,6'-Heptachlorobiphenyl	0.01	0.001	1	1	100
52663-68-0	187	2,2',3,4',5,5',6-Heptachlorobiphenyl	0.01	0.001	1	1	100
39635-31-9	189	2,3,3',4,4',5,5'-Heptachlorobiphenyl	0.01	0.001	1	1	100
35694-08-7	194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	0.01	0.001	1	1	100
52663-78-2	195	2,2',3,3',4,4',5,6-Octachlorobiphenyl	0.01	0.001	1	1	100
40186-71-8	200	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	0.01	0.001	1	1	100
52663-75-9	201	2,2',3,3',4,5,5',6'-Octachlorobiphenyl	0.01	0.001	1	1	100
2136-99-4	202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl	0.01	0.001	1	1	100
40186-72-9	206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	0.01	0.001	1	1	100
52663-79-3	207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	0.01	0.001	1	1	100
2051-24-3	209	2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	0.01	0.001	1	1	100

[1] PCB congener number originally assigned by Ballschmiter & Zell ("BZ Number"), 1980. (K. Ballschmiter and M. Zell. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. Fresenius Z. Anal. Chem. 302:20-31. 1980.)

Table 2 Gas Chromatographic Conditions

Parameter	Recommended Conditions
Injection Port Mode	Pulse Split: 40 psi for 0.25 min
Injection Port Temperature	250°C
Detector Temperature	330°C
Column Temperature Program	160°C for 0.25 min, 5°C/min to 210°C, 1°C/min to 215°C, 4°C/min to 270°C, 1 min hold.
Column 1	RTX-CLPesticides, 30m x 0.25mm id, 0.25 µm df, or equivalent
Column 2	RTX-CLPesticides II, 30m x 0.25 mm id, 0.20 µm df, or equivalent
Gas Flow Split Ratio	1/25
Split Vent Flow Rate	20 mL/min
Linear Velocity	50 cm/sec
Column Flow	1.5 mL/min
Injection	1 µL
Carrier Gas	Hydrogen
Make-up Gas	Nitrogen
Y Splitter Type	Restek or J&W or Supelco glass tee

Table 3 Typical Calibration Levels

CAS Number	BZ-1993	Compound Name	CS1 ng/mL	CS2 ng/mL	CS3 ng/mL	CS4 ng/mL	CS5 ng/mL	CS6 ng/mL
2051-60-7	1	2-Chlorobiphenyl	20	40	100	200	500	1000
2051-62-9	3	4-Chlorobiphenyl	20	40	100	200	500	1000
16605-91-7	5	2,3-dichlorobiphenyl	1	2	5	10	25	50
34883-43-7	8	2,4'-Dichlorobiphenyl	1	2	5	10	25	50
2050-68-2	15	4,4'-Dichlorobiphenyl	5	10	25	50	125	250
37680-65-2	18	2,2',5-Trichlorobiphenyl	1	2	5	10	25	50
7012-37-5	28	2,4,4'-Trichlorobiphenyl	1	2	5	10	25	50
16606-02-3	31	2,4',5-trichlorobiphenyl	1	2	5	10	25	50
38444-90-5	37	3,4,4'-Trichlorobiphenyl	1	2	5	10	25	50
41464-39-5	44	2,2',3,5'-Tetrachlorobiphenyl	1	2	5	10	25	50
41464-40-8	49	2,2',4,5'-Tetrachlorobiphenyl	1	2	5	10	25	50
35693-99-3	52	2,2',5,5'-Tetrachlorobiphenyl	1	2	5	10	25	50
32598-10-0	66	2,3',4,4'-Tetrachlorobiphenyl	1	2	5	10	25	50
32598-11-1	70	2,3',4',5-Tetrachlorobiphenyl	1	2	5	10	25	50
32690-93-0	74	2,4,4',5-Tetrachlorobiphenyl	1	2	5	10	25	50
32598-13-3	77	3,3',4,4'-Tetrachlorobiphenyl	1	2	5	10	25	50
70362-50-4	81	3,4,4',5-Tetrachlorobiphenyl	1	2	5	10	25	50
38380-02-8	87	2,2',3,4,5'-Pentachlorobiphenyl	1	2	5	10	25	50
68194-07-0	90	2,2',3,4',5-Pentachlorobiphenyl	1	2	5	10	25	50
38380-01-7	99	2,2',4,4',5-Pentachlorobiphenyl	1	2	5	10	25	50
37680-73-2	101	2,2',4,5,5'-Pentachlorobiphenyl	1	2	5	10	25	50
32598-14-4	105	2,3,3',4,4'-Pentachlorobiphenyl	1	2	5	10	25	50
38380-03-9	110	2,3,3',4',6-Pentachlorobiphenyl	1	2	5	10	25	50
74472-37-0	114	2,3,4,4',5-Pentachlorobiphenyl	1	2	5	10	25	50
74472-38-1	115	2,3,4,4',6-Pentachlorobiphenyl	1	2	5	10	25	50
31508-00-6	118	2,3',4,4',5-Pentachlorobiphenyl	1	2	5	10	25	50
56558-17-9	119	2,3',4,4',6-Pentachlorobiphenyl	1	2	5	10	25	50
65510-44-3	123	2,3',4,4',5'-Pentachlorobiphenyl	1	2	5	10	25	50
57465-28-8	126	3,3',4,4',5-Pentachlorobiphenyl	1	2	5	10	25	50
38380-07-3	128	2,2',3,3',4,4'-Hexachlorobiphenyl	1	2	5	10	25	50
35065-28-2	138	2,2',3,4,4',5'-Hexachlorobiphenyl	1	2	5	10	25	50
52712-04-6	141	2,2',3,4,5,5'-hexachlorobiphenyl	1	2	5	10	25	50
38380-04-0	149	2,2',3,4',5',6-Hexachlorobiphenyl	1	2	5	10	25	50
52663-63-5	151	2,2',3,5,5',6-Hexachlorobiphenyl	1	2	5	10	25	50
35065-27-1	153	2,2',4,4',5,5'-Hexachlorobiphenyl	1	2	5	10	25	50
38380-08-4	156	2,3,3',4,4',5-Hexachlorobiphenyl	1	2	5	10	25	50
69782-90-7	157	2,3,3',4,4',5'-Hexachlorobiphenyl	1	2	5	10	25	50
74472-42-7	158	2,3,3',4,4',6-Hexachlorobiphenyl	1	2	5	10	25	50
52663-72-6	167	2,3',4,4',5,5'-Hexachlorobiphenyl	1	2	5	10	25	50
59291-65-5	168	2,3',4,4',5',6-Hexachlorobiphenyl	1	2	5	10	25	50
32774-16-6	169	3,3',4,4',5,5'-Hexachlorobiphenyl	1	2	5	10	25	50
35065-30-6	170	2,2',3,3',4,4',5-Heptachlorobiphenyl	1	2	5	10	25	50
52663-70-4	177	2,2',3,3',4,5',6'-Heptachlorobiphenyl	1	2	5	10	25	50
35065-29-3	180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	1	2	5	10	25	50
52663-69-1	183	2,2',3,4,4',5',6-Heptachlorobiphenyl	1	2	5	10	25	50
74472-48-3	184	2,2',3,4,4',6,6'-Heptachlorobiphenyl	1	2	5	10	25	50
52663-68-0	187	2,2',3,4',5,5',6-Heptachlorobiphenyl	1	2	5	10	25	50
39635-31-9	189	2,3,3',4,4',5,5'-Heptachlorobiphenyl	1	2	5	10	25	50
35694-08-7	194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	1	2	5	10	25	50
52663-78-2	195	2,2',3,3',4,4',5,6-Octachlorobiphenyl	1	2	5	10	25	50
40186-71-8	200	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	1	2	5	10	25	50
52663-75-9	201	2,2',3,3',4,5,5',6'-Octachlorobiphenyl	1	2	5	10	25	50
2136-99-4	202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl	1	2	5	10	25	50
40186-72-9	206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	1	2	5	10	25	50
52663-79-3	207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	1	2	5	10	25	50
2051-24-3	209	2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	1	2	5	10	25	50
Surrogates								
877-09-8	TCMX	Tetrachloro-m-xylene	1	2	5	10	25	50
74472-46-1	165	2,3,3',5,5',6-Hexachlorobiphenyl	1	2	5	10	25	50
Internal Stds								
15862-07-4	29	2,4,5-Trichlorobiphenyl	25	25	25	25	25	25
41411-62-5	160	2,3,3',4,5,6-Hexachlorobiphenyl	25	25	25	25	25	25

Table 4 Typical LCS, MS/MSD and Surrogate Spiking Levels

CAS Number	BZ	Compound Name	Control Analytes	Aqueous ug/L	Low-level Aqueous ug/L	Solid ug/kg dry	Tissue ug/kg	Waste ng/kg
2051-60-7	1	2-Chlorobiphenyl		2.0	0.5	200	200	20000
2051-62-9	**3**	**4-Chlorobiphenyl**	**Y**	2.0	0.5	200	200	20000
16605-91-7	5	2,3-dichlorobiphenyl		0.10	0.025	10	10	1000
34883-43-7	8	2,4'-Dichlorobiphenyl		0.10	0.025	10	10	1000
2050-68-2	**15**	**4,4'-Dichlorobiphenyl**	**Y**	0.50	0.125	50	50	5000
37680-65-2	**18**	**2,2',5-Trichlorobiphenyl**	**Y**	0.10	0.025	10	10	1000
7012-37-5	28	2,4,4'-Trichlorobiphenyl		0.10	0.025	10	10	1000
16606-02-3	31	2,4',5-trichlorobiphenyl		0.10	0.025	10	10	1000
38444-90-5	37	3,4,4'-Trichlorobiphenyl		0.10	0.025	10	10	1000
41464-39-5	44	2,2',3,5'-Tetrachlorobiphenyl		0.10	0.025	10	10	1000
41464-40-8	49	2,2',4,5'-Tetrachlorobiphenyl		0.10	0.025	10	10	1000
35693-99-3	**52**	**2,2',5,5'-Tetrachlorobiphenyl**	**Y**	0.10	0.025	10	10	1000
32598-10-0	**66**	**2,3',4,4'-Tetrachlorobiphenyl**	**Y**	0.10	0.025	10	10	1000
32598-11-1	70	2,3',4',5-Tetrachlorobiphenyl		0.10	0.025	10	10	1000
32690-93-0	74	2,4,4',5-Tetrachlorobiphenyl		0.10	0.025	10	10	1000
32598-13-3	77	3,3',4,4'-Tetrachlorobiphenyl		0.10	0.025	10	10	1000
1000	81	3,4,4',5-Tetrachlorobiphenyl		0.10	0.025	10	10	1000
1000	87	2,2',3,4,5'-Pentachlorobiphenyl		0.10	0.025	10	10	1000
1000	90	2,2',3,4',5-Pentachlorobiphenyl		0.10	0.025	10	10	1000
1000	99	2,2',4,4',5-Pentachlorobiphenyl		0.10	0.025	10	10	1000
1000	101	2,2',4,5,5'-Pentachlorobiphenyl		0.10	0.025	10	10	1000
32598-14-4	105	2,3,3',4,4'-Pentachlorobiphenyl		0.10	0.025	10	10	1000
38380-03-9	110	2,3,3',4',6-Pentachlorobiphenyl		0.10	0.025	10	10	1000
74472-37-0	114	2,3,4,4',5-Pentachlorobiphenyl		0.10	0.025	10	10	1000
74472-38-1	115	2,3,4,4',6-Pentachlorobiphenyl		0.10	0.025	10	10	1000
31508-00-6	**118**	**2,3',4,4',5-Pentachlorobiphenyl**	**Y**	0.10	0.025	10	10	1000
56558-17-9	119	2,3',4,4',6-Pentachlorobiphenyl		0.10	0.025	10	10	1000
65510-44-3	123	2,3',4,4',5'-Pentachlorobiphenyl		0.10	0.025	10	10	1000
57465-28-8	126	3,3',4,4',5-Pentachlorobiphenyl		0.10	0.025	10	10	1000
38380-07-3	**128**	**2,2',3,3',4,4'-Hexachlorobiphenyl**	**Y**	0.10	0.025	10	10	1000
35065-28-2	138	2,2',3,4,4',5'-Hexachlorobiphenyl		0.10	0.025	10	10	1000
52712-04-6	141	2,2',3,4,5,5'-hexachlorobiphenyl		0.10	0.025	10	10	1000
38380-04-0	149	2,2',3,4',5',6-Hexachlorobiphenyl		0.10	0.025	10	10	1000
52663-63-5	151	2,2',3,5,5',6-Hexachlorobiphenyl	**Y**	0.10	0.025	10	10	1000
35065-27-1	**153**	**2,2',4,4',5,5'-Hexachlorobiphenyl**		0.10	0.025	10	10	1000
38380-08-4	156	2,3,3',4,4',5-Hexachlorobiphenyl		0.10	0.025	10	10	1000
69782-90-7	157	2,3,3',4,4',5'-Hexachlorobiphenyl		0.10	0.025	10	10	1000
74472-42-7	158	2,3,3',4,4',6-Hexachlorobiphenyl		0.10	0.025	10	10	1000
52663-72-6	167	2,3',4,4',5,5'-Hexachlorobiphenyl		0.10	0.025	10	10	1000
59291-65-5	168	2,3',4,4',5',6-Hexachlorobiphenyl		0.10	0.025	10	10	1000
32774-16-6	169	3,3',4,4',5,5'-Hexachlorobiphenyl		0.10	0.025	10	10	1000
35065-30-6	170	2,2',3,3',4,4',5-Heptachlorobiphenyl		0.10	0.025	10	10	1000
52663-70-4	177	2,2',3,3',4,5',6'-Heptachlorobiphenyl		0.10	0.025	10	10	1000
35065-29-3	**180**	**2,2',3,4,4',5,5'-Heptachlorobiphenyl**	**Y**	0.10	0.025	10	10	1000
52663-69-1	183	2,2',3,4,4',5',6-Heptachlorobiphenyl		0.10	0.025	10	10	1000
74472-48-3	184	2,2',3,4,4',6,6'-Heptachlorobiphenyl		0.10	0.025	10	10	1000
52663-68-0	**187**	**2,2',3,4',5,5',6-Heptachlorobiphenyl**	**Y**	0.10	0.025	10	10	1000
39635-31-9	189	2,3,3',4,4',5,5'-Heptachlorobiphenyl		0.10	0.025	10	10	1000
35694-08-7	194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl		0.10	0.025	10	10	1000
52663-78-2	**195**	**2,2',3,3',4,4',5,6-Octachlorobiphenyl**	**Y**	0.10	0.025	10	10	1000
40186-71-8	200	2,2',3,3',4,5',6,6'-Octachlorobiphenyl		0.10	0.025	10	10	1000
52663-75-9	201	2,2',3,3',4,5,5',6'-Octachlorobiphenyl		0.10	0.025	10	10	1000
2136-99-4	202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl		0.10	0.025	10	10	1000
40186-72-9	**206**	**2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl**	**Y**	0.10	0.025	10	10	1000
52663-79-3	207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl		0.10	0.025	10	10	1000
2051-24-3	**209**	**2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl**	**Y**	0.10	0.025	10	10	1000
Surrogates								
877-09-8	TCMX	Tetrachloro-m-xylene		0.10	0.025	10	10	1000
74472-46-1	165	2,3,3',5,5',6-Hexachlorobiphenyl		0.10	0.025	10	10	1000

Table 5 Typical Analytical Sequence

Step Number	Action
1	Initial Calibration
2	Initial Calibration Verification
3	Solvent blank (optional)
4	Instrument or Method Blank
5	Up to 20 samples (unless 12 hours comes first)
6	Solvent blank (optional)
7	Continuing calibration
8	Instrument or Method Blank
9	Up to 20 samples (unless 12 hours comes first)
	Repeat steps 7-9 as needed
10	Instrument or Method Blank
11	Up to 20 samples (unless 12 hours comes first)
12	Solvent blank (optional)
13	Continuing calibration
14	Instrument or Method Blank
15	Up to 20 samples unless 12 hours comes first)
	Repeat steps 13-15 as needed

Table 6 Performance Criteria for Four Replicate Initial Demonstrations of Capability

CAS Number	BZ	Compound Name	Mean Recovery Limits	RSD Limit
2051-60-7	1	2-Chlorobiphenyl	50-130	30
2051-62-9	3	4-Chlorobiphenyl	60-140	30
16605-91-7	5	2,3-dichlorobiphenyl	60-140	30
34883-43-7	8	2,4'-Dichlorobiphenyl	60-140	30
2050-68-2	15	4,4'-Dichlorobiphenyl	60-140	30
37680-65-2	18	2,2',5-Trichlorobiphenyl	60-140	30
7012-37-5	28	2,4,4'-Trichlorobiphenyl	60-140	30
16606-02-3	31	2,4',5-trichlorobiphenyl	60-140	30
38444-90-5	37	3,4,4'-Trichlorobiphenyl	60-140	30
41464-39-5	44	2,2',3,5'-Tetrachlorobiphenyl	60-140	30
41464-40-8	49	2,2',4,5'-Tetrachlorobiphenyl	60-140	30
35693-99-3	52	2,2',5,5'-Tetrachlorobiphenyl	60-140	30
32598-10-0	66	2,3',4,4'-Tetrachlorobiphenyl	60-140	30
32598-11-1	70	2,3',4',5-Tetrachlorobiphenyl	60-140	30
32690-93-0	74	2,4,4',5-Tetrachlorobiphenyl	60-140	30
32598-13-3	77	3,3',4,4'-Tetrachlorobiphenyl	60-140	30
70362-50-4	81	3,4,4',5-Tetrachlorobiphenyl	60-140	30
38380-02-8	87	2,2',3,4,5'-Pentachlorobiphenyl	60-140	30
68194-07-0	90	2,2',3,4',5-Pentachlorobiphenyl	60-140	30
38380-01-7	99	2,2',4,4',5-Pentachlorobiphenyl	60-140	30
37680-73-2	101	2,2',4,5,5'-Pentachlorobiphenyl	60-140	30
32598-14-4	105	2,3,3',4,4'-Pentachlorobiphenyl	60-140	30
38380-03-9	110	2,3,3',4',6-Pentachlorobiphenyl	60-140	30
74472-37-0	114	2,3,4,4',5-Pentachlorobiphenyl	60-140	30
74472-38-1	115	2,3,4,4',6-Pentachlorobiphenyl	60-140	30
31508-00-6	118	2,3',4,4',5-Pentachlorobiphenyl	60-140	30
56558-17-9	119	2,3',4,4',6-Pentachlorobiphenyl	60-140	30
65510-44-3	123	2,3',4,4',5'-Pentachlorobiphenyl	60-140	30
57465-28-8	126	3,3',4,4',5-Pentachlorobiphenyl	60-140	30
38380-07-3	128	2,2',3,3',4,4'-Hexachlorobiphenyl	60-140	30
35065-28-2	138	2,2',3,4,4',5'-Hexachlorobiphenyl	60-140	30
52712-04-6	141	2,2',3,4,5,5'-hexachlorobiphenyl	60-140	30
38380-04-0	149	2,2',3,4',5',6-Hexachlorobiphenyl	60-140	30
52663-63-5	151	2,2',3,5,5',6-Hexachlorobiphenyl	60-140	30
35065-27-1	153	2,2',4,4',5,5'-Hexachlorobiphenyl	60-140	30
38380-08-4	156	2,3,3',4,4',5-Hexachlorobiphenyl	60-140	30
69782-90-7	157	2,3,3',4,4',5'-Hexachlorobiphenyl	60-140	30
74472-42-7	158	2,3,3',4,4',6-Hexachlorobiphenyl	60-140	30
52663-72-6	167	2,3',4,4',5,5'-Hexachlorobiphenyl	60-140	30
59291-65-5	168	2,3',4,4',5',6-Hexachlorobiphenyl	60-140	30
32774-16-6	169	3,3',4,4',5,5'-Hexachlorobiphenyl	60-140	30
35065-30-6	170	2,2',3,3',4,4',5-Heptachlorobiphenyl	60-140	30
52663-70-4	177	2,2',3,3',4,5',6'-Heptachlorobiphenyl	60-140	30
35065-29-3	180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	60-140	30
52663-69-1	183	2,2',3,4,4',5',6-Heptachlorobiphenyl	60-140	30
74472-48-3	184	2,2',3,4,4',6,6'-Heptachlorobiphenyl	60-140	30
52663-68-0	187	2,2',3,4',5,5',6-Heptachlorobiphenyl	60-140	30
39635-31-9	189	2,3,3',4,4',5,5'-Heptachlorobiphenyl	60-140	30
35694-08-7	194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	60-140	30
52663-78-2	195	2,2',3,3',4,4',5,6-Octachlorobiphenyl	60-140	30
40186-71-8	200	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	60-140	30
52663-75-9	201	2,2',3,3',4,5,5',6'-Octachlorobiphenyl	60-140	30
2136-99-4	202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl	60-140	30
40186-72-9	206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	60-140	30
52663-79-3	207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	60-140	30
2051-24-3	209	2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	60-140	30
Surrogates				
877-09-8	TCMX	Tetrachloro-m-xylene	NA	30
74472-46-1	165	2,3,3',5,5',6-Hexachlorobiphenyl	NA	30

Table 7 Resolution with Typical Chromatographic Conditions

CAS Number	BZ	Compound Name	Resolved on Column A	Resolved on Column B
2051-60-7	1	2-Chlorobiphenyl	Y	Y
2051-62-9	3	4-Chlorobiphenyl	Y	Y
16605-91-7	5	2,3-dichlorobiphenyl	N (8)	Y
34883-43-7	8	2,4'-Dichlorobiphenyl	N (5)	Y
2050-68-2	15	4,4'-Dichlorobiphenyl	Y	Y
37680-65-2	18	2,2',5-Trichlorobiphenyl	Y	Y
7012-37-5	28	2,4,4'-Trichlorobiphenyl	Y	Y
16606-02-3	31	2,4',5-trichlorobiphenyl	Y	Y
38444-90-5	37	3,4,4'-Trichlorobiphenyl	Y	Y
41464-39-5	44	2,2',3,5'-Tetrachlorobiphenyl	Y	Y
41464-40-8	49	2,2',4,5'-Tetrachlorobiphenyl	Y	Y
35693-99-3	52	2,2',5,5'-Tetrachlorobiphenyl	Y	Y
32598-10-0	66	2,3',4,4'-Tetrachlorobiphenyl	Y	Y
32598-11-1	70	2,3',4',5-Tetrachlorobiphenyl	Y	Y
32690-93-0	74	2,4,4',5-Tetrachlorobiphenyl	Y	Y
32598-13-3	77	3,3',4,4'-Tetrachlorobiphenyl	Y	Y
70362-50-4	81	3,4,4',5-Tetrachlorobiphenyl	Y	N (87)
38380-02-8	87	2,2',3,4,5'-Pentachlorobiphenyl	Y	N (81)
68194-07-0	90	2,2',3,4',5-Pentachlorobiphenyl	Y	N (101)
38380-01-7	99	2,2',4,4',5-Pentachlorobiphenyl	Y	Y
37680-73-2	101	2,2',4,5,5'-Pentachlorobiphenyl	Y	N (90)
32598-14-4	105	2,3,3',4,4'-Pentachlorobiphenyl	Y	N (141)
38380-03-9	110	2,3,3',4',6-Pentachlorobiphenyl	Y	Y
74472-37-0	114	2,3,4,4',5-Pentachlorobiphenyl	Y	Y
74472-38-1	115	2,3,4,4',6-Pentachlorobiphenyl	Y	Y
31508-00-6	118	2,3',4,4',5-Pentachlorobiphenyl	Y	Y
56558-17-9	119	2,3',4,4',6-Pentachlorobiphenyl	Y	Y
65510-44-3	123	2,3',4,4',5'-Pentachlorobiphenyl	Y	N (149)
57465-28-8	126	3,3',4,4',5-Pentachlorobiphenyl	Y	Y
38380-07-3	128	2,2',3,3',4,4'-Hexachlorobiphenyl	Y	Y
35065-28-2	138	2,2',3,4,4',5'-Hexachlorobiphenyl	Y	N (158)
52712-04-6	141	2,2',3,4,5,5'-hexachlorobiphenyl	Y	N (105)
38380-04-0	149	2,2',3,4',5',6-Hexachlorobiphenyl	Y	N (123)
52663-63-5	151	2,2',3,5,5',6-Hexachlorobiphenyl	Y	Y
35065-27-1	153	2,2',4,4',5,5'-Hexachlorobiphenyl	Y	Y
38380-08-4	156	2,3,3',4,4',5-Hexachlorobiphenyl	Y	Y
69782-90-7	157	2,3,3',4,4',5'-Hexachlorobiphenyl	Y	Y
74472-42-7	158	2,3,3',4,4',6-Hexachlorobiphenyl	Y	N (138)
52663-72-6	167	2,3',4,4',5,5'-Hexachlorobiphenyl	Y	Y
59291-65-5	168	2,3',4,4',5',6-Hexachlorobiphenyl	Y	Y
32774-16-6	169	3,3',4,4',5,5'-Hexachlorobiphenyl	Y	Y
35065-30-6	170	2,2',3,3',4,4',5-Heptachlorobiphenyl	Y	N (201)
52663-70-4	177	2,2',3,3',4,5',6'-Heptachlorobiphenyl	Y	Y
35065-29-3	180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	Y	Y
52663-69-1	183	2,2',3,4,4',5',6-Heptachlorobiphenyl	Y	Y
74472-48-3	184	2,2',3,4,4',6,6'-Heptachlorobiphenyl	Y	Y
52663-68-0	187	2,2',3,4',5,5',6-Heptachlorobiphenyl	Y	Y
39635-31-9	189	2,3,3',4,4',5,5'-Heptachlorobiphenyl	Y	Y
35694-08-7	194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	Y	Y
52663-78-2	195	2,2',3,3',4,4',5,6-Octachlorobiphenyl	N (207)	Y
40186-71-8	200	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	Y	Y
52663-75-9	201	2,2',3,3',4,5,5',6'-Octachlorobiphenyl	Y	N (170)
2136-99-4	202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl	Y	Y
40186-72-9	206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	Y	Y
52663-79-3	207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	N (195)	Y
2051-24-3	209	2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	Y	Y
Surrogates				
877-09-8	TCMX	Tetrachloro-m-xylene	Y	Y
74472-46-1	165	2,3,3',5,5',6-Hexachlorobiphenyl	Y	Y

Appendix II: Calibration and Spike Summary

	CS1	CS2	CS3	CS4	CS5	CS6
	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL
All BZ except 1,3,15	1	2	5	10	25	50
BZ 15	5	10	25	50	125	250
BZ 1, 3	20	40	100	200	500	1000
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Aqueous	0.01	0.02	0.05	0.10	0.25	0.50
Initial Sample Volume=1000mL	0.05	0.10	0.25	0.50	1.25	2.50
Final Extract Volume=10mL	0.20	0.40	1.00	2.00	5.00	10.00
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Low-Level Aqueous	0.001	0.002	0.005	0.010	0.025	0.050
Initial Sample Volume=1000mL	0.005	0.010	0.025	0.050	0.125	0.250
Final Extract Volume=1mL	0.020	0.040	0.100	0.200	0.500	1.000
	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg
Soil 10 g dry weight	1	2	5	10	25	50
Initial Sample Weight=10g dry	5	10	25	50	125	250
Final Extract Volume=10mL	20	40	100	200	500	1000
	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg
Waste	100	200	500	1000	2500	5000
Initial Sample Weight=0.1g	500	1000	2500	5000	12500	25000
Final Extract Volume=10mL	2000	4000	10000	20000	50000	100000

LCS, MS/MSD Spike Concentration (ng/mL)

All BZ except 1,3,15	100
BZ 15	500
BZ 1, 3	2000

Aqueous 1.0 mL x (100/500/2000 ng/mL) / 1000 mL = 0.10/0.50/2.0 ng/mL
Low-Level Aqueous 0.25 mL x (100/500/2000 ng/mL) / 1000 mL = 0.025/0.125/0.50 ng/mL
Soil 10 g dry weight 1.0 mL x (100/500/2000 ng/mL) / 10.0 g = 10/50/200 ng/g dry weight
Waste 1.0 mL x (100/500/2000 ng/mL) / 0.1 g = 1000/5000/20000 ng/g

Surrogate Standard Concentration (ng/mL)

BZ 165	100
Tetrachloro-m-xylene	100

Surrogate Spike Concentration (ng/mL)

Aqueous 1.0 mL x 100 ng/mL / 1000 mL = 0.10 ng/mL
Low-Level Aqueous 0.25 mL x 100 ng/mL / 1000 mL = 0.025 ng/mL
Soil 10 g dry weight 1.0 mL x 100 ng/mL / 10.0 g = 10 ng/g dry weight
Waste 1.0 mL x 100 ng/mL / 0.1 g = 1000 ng/g

Appendix III: Sulfur Removal using Elemental Mercury

Sulfur Removal: Sulfur can be removed using mercury. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipet, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

Sulfur Removal with Elemental Mercury:

- **Note**: Use Mercury sparingly in order to minimize exposure and disposal costs.
- Transfer 500-1000 uL of sample extract into a clean Teflon sealed vial.
- Add one to three drops of mercury to the extract vial and seal.
- Shake well for 15-30 seconds, then swirl in a Vortex-Genie™.
- Remove the extract from the mercury using a disposable pipette and transfer to a clean vial.
- If black precipitate forms, sulfur was present. Shake again, then swirl. Transfer the supernate to a clean test tube and repeat. Do this until relatively little precipitate remains, or screening indicates that the cleanup is complete.
- Properly dispose of the mercury waste.

Appendix IV: Example Data Review Checklist

STL Knoxville GC PCB Congeners Initial Calibration Data Review / Narrative Checklist
Method 8082, SOP KNOX -GC-0011, Rev. 3
Page 1 of 1

Analysis Date:		**Instrument/File ID:**	
2nd Source Verification Filename:			

Review Items **A. Continuing Calibration**	**Yes**	**No**	**N/A**	**2nd Level**	**If No, why is data reportable?**
1. Were at least **5 levels** analyzed?					
2. Were **all ICAL standards used** for calibration?					
3. Is **low** level standard concentration **≤ RL**?					
4. Are all **%RSDs ≤ 20%** ?					
5. Was the response factor for each analyte calculated using the correct internal standard?					
6. Was each run checked for **saturation**?					
7. Are all analytes in the highest calibration standard adequately resolved? (≥0.04 min & a distinguishable valley between all peaks)					
8. Is **integration** acceptable and were all manual integrations clearly identified, initialed, dated and reason given?					Reasons: 1) Corrected split peak; 2) Unresolved peak; 3) Tailing; 4) RT shift; 5) Wrong peak selected; 6) Other
9. Was ICAL method file processed using the **correct result files**? (Compare peak heights-areas in method file to heights-areas of calibration standards.)					
10. Is the 2nd source standard within +/- 25 % of the expected value?					❑ ≤2 analytes within +/- 35 % of the expected value: _____

Analyst:	**Date:**	**2nd Level Reviewer :**	**Date:**
Comments:		**Comments:**	

Appendix IV: Example Data Review Checklist, continued

STL Knoxville GC PCB Congeners Continuing Calibration Data Review / Narrative Checklist
Method: 8082 - KNOX-GC-0011 Rev 3
Page 1 of 1

Analysis Date:		**Sequence ID:**		**ICAL File ID:**		**Scanned file verified as correct** _____

Review Items **A. Continuing Calibration**	**Yes**	**No**	**NA**	**2nd ✔**	**If No, why is data reportable?**
1. Was the ***correct ICAL*** used for quantitation?					
2. Were the ***same process parameters*** used for the CCAL standards and the ICAL?					
3. Were ***CCAL standards*** run at proper frequency ***(before all samples and after no more than 20 injections/12 hrs of sample analysis)*** ?					
4. Were RTs within ***RT windows (+/- 0.03 minutes) ?***					
5. Is ***%D*** for each analyte ***≤ 15%*** for each CCAL?					❑ [Avg] Average %D ≤15% and all individual %D's 30% for _____ _____
6. Are ***internal standards*** within 50-150% of ICAL midpoint?					
7. Is **integration** acceptable and were all manual integrations clearly identified, initaled, dated and reason given?					Reasons: 1) Corrected split peak; 2) Unresolved peak; 3) Tailing; 4) RT shift; 5) Wrong peak selected; 6) Other

Analyst:	**Date:**	**2nd Level Reviewer :**	**Date:**
Comments:		**Comments:**	

Appendix IV: Example Data Review Checklist, continued

STL Knoxville GC PCB Congeners Data Review / Narrative Checklist **LOT #_____**
Method: 8082, SOP: KNOX-GC-0011 Rev. 3 **Page 1 of 1**

Sequence No.:						
Scanned File:						

Review Items **A. Continuing Calibration (CCAL)**	**Yes**	**No**	**N/A**	**2nd √**	**If No, why is data reportable?**
1. **CCAL Checklist** completed for each analytical batch?					
B. Client Sample and QC Sample Results					
1. Were all **special project requirements** met?					
2. Were **Turbochrom** sample IDs, DFs, prep **factors verified**?					
3. Sample analyses done within preparation and analytical **holding time** (HT)? *If no, list samples and NCM#:* _____					□ *[ht1] HT expired upon receipt.* □ *[ht2] Client requested analysis after HT expired.** □ **Re-extraction done after HT expired.**
4. Same **process file** used for samples and ICAL? (2nd Level - Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF or curve.)					
5. Are **sample and MS/MSD surrogates** within QC limits?					□ [sur1] MS/MSD surr.%R showed same effect. □ [sur2] Re-extraction demonstrated same effect. □ **[sur3] Not enough sample for re-extraction.** □ [sur7] Obvious matrix interference. □ **[sur12] Surr.%R high and all targets ND.** □ **[sur16] 1 Surr. out, but blank & LCS surrogates in control - matrix effect.**
6. Are internal standards within 50-150% of ICAL midpoint?					
7. Do positive hits meet identification criteria? (**RT and 2nd column confirmation** for single peak analytes)					
8. Are positive results **within calibration range**?					
9. Were peaks checked for **saturation**?					
10. Were **integrations** acceptable and are all manual integrations clearly identified, initialed, dated and reason given?					Reasons: 1) Corrected split peak; 2) Unresolved peak; 3) Tailing; 4) RT shift; 5) Wrong peak selected; 6) Other
11. Is largest analyte **diluted to 20-100%** of the calibration range?					□ [dil1] Dilution required to prevent contamination of instrument due to non-target compounds.
12. Were runs checked for **carryover**?					
13. Were soil results calculated using the **dry sample weight**?					
13. Final **report acceptable**? (Results correct, RLs calculated correctly, units correct, surrogate %R correct, appropriate flags used, deviations noted in narrative, dilution factor correct, and extraction/ analysis dates correct.)					
C. Preparation/Matrix QC					
1. **LCS** done per prep batch and all analytes and surrogates within laboratory established QC limits?					□ **[lcs2] Insufficient sample for reanalysis.*** □ **[lcs3] LCS %R high and all analyte(s) were <RL in associated samples.**
2. **Method blank** done per prep batch, method blank or instrument blank run with each sequence, and all analytes <RL?					□ **[mb3] No analyte > RL in associated samples.*** □ **[mb4] Sample results > 20x higher than blank.** □ **[mb5] Insufficient sample for reanalysis.***
3. **Method blank surrogate recoveries** within QC limits?					□ **[mb1] Sample surrogates OK and there is no analyte >RL in samples associated with blank.***
4. **MS/MSD** done per batch?					□ [lcsd] Insufficient sample. LCS/LCSD analyzed.
4. **MS/MSD recoveries and RPDs** within laboratory generated control limits?					□ [ms1] LCS acceptable - sample matrix effects. □ [ms2] LCS acceptable. High native analyte concentration relative to spike level. □ [ms3] Spikes diluted out. LCS acceptable. □ [rpd] LCS acceptable. RPD out due to lack of sample homogeneity.
5. Were **MS run #'s** assigned correctly?					
D. Other					
1. Are all **nonconformances** documented appropriately?					

Analyst:	**Date:**	**2nd Level Reviewer:**	**Date:**
Comments:		**Comments:**	

* Such action must be taken in consultation with client. GC033R5.DOC, 2/5/04
NOTE: Nonconformance memos are required for **bold** and *italicized* autotext statements: **Bold** = deficiency, *italicized* = anomoly.

STL KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Analysis of Polychlorinated Dioxins/Furans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Based on Methods 8290, 1613B, 23, 0023A, and TO-9A

(SUPERSEDES: KNOX-ID-0004, Rev. 4)

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1. Scope and Application

1.1 This procedure is used for the determination of tetra- through octa- chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in water, soils, solids, sediments, wipes, biological samples, fly ash, XAD resin, filters, still bottoms, waste oils, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). This procedure is designed to meet analytical program requirements where US EPA Method 8290, 1613B, 23, 0023A, or TO-9A is specified.

1.2 The seventeen 2,3,7,8-substituted PCDDs/PCDFs listed in Table 1 may be determined by this procedure. Specifications are also provided for separate determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). In addition, total homologs (i.e Total TCDD, Total TCDF, etc.) may be identified by this method.

1.3 The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) in Table 2 are the levels at which the PCDDs/PCDFs can be quantitated with no interferences present.

1.4 This procedure is designed for use by analysts who are experienced with residue analysis and skilled in HRGC/HRMS.

1.5 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2. Summary of Method

2.1 This procedure uses high resolution capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS) techniques.

2.2 Samples are spiked with a solution of known amounts of the isotopically labeled internal standards listed in Table 13 and Table 15. The samples are then extracted using matrix specific extraction procedures.

2.2.1 Water samples are extracted using separatory funnel techniques with methylene chloride as the extraction solvent.

2.2.2 Solid samples are extracted by Soxhlet extraction with the appropriate solvent.

2.2.3 Organic liquid waste samples are diluted in solvent.

2.3 After extraction, the sample is concentrated and solvent exchanged with hexane. The extract is then subjected to one or more cleanup steps to rid the sample of interferences. The final extract is prepared by adding a known amount of the labeled recovery standards (13C12-1,2,3,4-TCDD and 13C12-1,2,3,7,8,9-HxCDD) and concentrating to the final volume.

2.4 The acid-base cleanup of the sample is used before column chromatography for samples that contain large amounts of basic and acid coextractables. If such interferences are not removed

before column chromatography, they may cause a shift in the predicted elution pattern. Conditions which may indicate the need for this procedure are: samples which are highly colored, samples which contain lipids or other oxidizable compounds or samples which contain known large amounts of polar organics.

2.5 Silica gel is effective in removing chlorophenoxy herbicide residues, while alumina partitions PCBs, 2,4,5-trichlorophenol and hexachlorophene.

2.6 When the above cleanup techniques do not completely remove interferences, an activated carbon cleanup is used to remove interferences.

2.7 An aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high resolution (≥10,000) mass spectrometer. Two exact m/z's are monitored for each analyte.

2.8 The identification of the target 2,3,7,8 substituted isomers is based on their retention time relative to the labeled internal standards as established during routine calibration and the simultaneous detection of the two most abundant ions in the molecular ion region. All other PCDD/PCDF congeners are identified by their retention times falling within retention time windows as established during routine calibration, and the simultaneous detection of the two most abundant ions in the molecular ion region. Confirmation of identification is based on comparing the calculated ion ratios with the theoretical ion abundances. The identification of 2,3,7,8-TCDF is confirmed on an isomer specific (DB-225) GC column.

2.9 Quantitation of the 2,3,7,8-substituted PCDD/PCDF isomers, total PCDDs, and total PCDFs is based on their relative response to the internal standards. A multipoint calibration is performed to establish mean response factors for the target analytes. The instrument performance is routinely checked by the analysis of continuing calibration standards. Method performance is demonstrated by the analysis of method blanks, initial precision and recovery samples, and ongoing precision and recovery samples.

3. Definitions

3.1 Analyte: A PCDD or PCDF tested for by this method. The analytes are listed in Table 1.

3.2 Calibration Standard: A solution prepared from a secondary standard and/or stock solution and used to calibrate the response of the instrument with respect to analyte concentration.

3.3 Calibration Verification Standard (VER): The mid-point calibration standard (CS3) that is used to verify calibration. See Table 5 and Table 6.

3.4 Cleanup Standard: 37Cl4-2,3,7,8-TCDD which is added to samples, blanks, quality control samples, and calibration solutions. It is added to the samples after extraction but prior to extract cleanup, and is used to judge the efficiency of the cleanup procedures.

3.5 Column Performance Solution Mixture (CPSM): A mixture of TCDD or TCDF isomers (including the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer) known to elute close to the retention time of 2,3,7,8-TCDD or 2,3,7,8-TCDF on the analytical column being used. It is used to demonstrate acceptable

resolution between the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer and all other TCDD or TCDF isomers on analytical column (percent valley < 25%).

3.6 Congener: Any member of a particular homologous series, for example, 1,2,3,7,8-pentachlorodibenzofuran.

3.7 CS1, CS2, CS3, CS4, CS5: See Calibration Standard and Table 5 and Table 6.

3.8 Detection Limit (DL): The minimum concentration of the target analyte that can be detected. Sample specific detection limits are calculated from the instrument noise level and internal standard response.

3.9 Estimated Detection Limit (EDL): The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level.

3.10 Estimated Maximum Possible Concentration (EMPC): The calculated concentration of a signal in the same retention time region as a target analyte but which does not meet the other qualitative identification criteria defined in the procedure.

3.11 GC: Gas chromatograph or gas chromatography

3.12 Homologous Series: A series of compounds in which each member differs from the next member by a constant amount. The members of the series are called homologs.

3.13 HRGC: High resolution GC

3.14 HRMS: High resolution MS

3.15 ICV: Initial Calibration Verification Standard. A calibration standard from a second source, traceable to a national standard if possible. The ICV is analyzed after the initial calibration to verify the concentration of the Initial Calibration Standards.

3.16 Internal Standards: Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes or detection limits.

3.17 IPR: Initial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

3.18 Isomer: Chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.

3.19 Laboratory Blank: See Method Blank.

3.20 Laboratory Control Sample: See Ongoing Precision and Recovery Standard (OPR).

3.21 Maximum Level (MaxL): The concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.22 Method Blank: An aliquot of reagent water, sand, sodium sulfate, or other representative matrix, free of the targets of interest and interferences, that is extracted and analyzed along with the samples to monitor for laboratory contamination.

3.23 Minimum Level (MinL): The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.24 MS: Mass spectrometer or mass spectrometry.

3.25 Multiple Ion Detection (MID): A MS operational mode in which only selected ions are monitored rather than scanning the instrument to obtain a complete mass spectrum.

3.26 OPR: Ongoing precision and recovery standard; a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

3.27 PAR: Precision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

3.28 PCDD: Polychlorinated dibenzo-p-dioxins.

3.29 PCDF: Polychlorinated dibenzofurans.

3.30 PFK: Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.31 Recovery Standard: 13C12-1,2,3,4-TCDD and 13C12-1,2,3,7,8,9-HxCDD which are added to every sample, blank, and quality control spike sample extract prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standard.

3.32 Relative Percent Difference (RPD): A measure of the difference between two values normalized to one of the values. It is used to determine the accuracy of the concentration measurements of second source verification standards.

3.33 Relative Response Factor (RRF): The ratio of the response of the mass spectrometer to a known amount of a compound relative to that of a known amount of a reference standard as measured in the initial and continuing calibrations. It is used to determine instrument performance and it is used to calculate the concentration of target analytes, internal standard recoveries, or detection limits in samples, blanks, and quality control samples.

3.34 Signal to Noise Ratio: The ratio of the mass spectrometer response of a GC peak to the background noise signal.

3.35 Split Ratio (S): The decimal expression of the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards.

3.36 Window Defining Mix: A solution which contains the first and last eluting isomers of each homologue group and is used to verify that the switching times between the MID descriptors have been appropriately set.

3.37 Additional definitions can be found in the STL Knoxville LQM glossary and in the STL Quality Management Plan.

4. Interferences

4.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using PVC gloves, powdered gloves, or gloves with measurable levels of phthalates.

4.2 The use of high purity reagents and solvents helps minimize interference problems. Where necessary, reagents are cleaned by extraction or solvent rinse.

4.3 Interferences coextracted from the samples will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans that may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

5. Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the STL Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

5.2.1 Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. For the operations described herein, Nitrile clean room gloves are worn. For operations using solvents that splash, silver shield gloves are recommended. Silver shield gloves protect against breakthrough for most of the solvents used in this procedure

5.3 Finely divided dry soils contaminated with PCDDs and PCDFs may be particularly hazardous because of the potential for inhalation and ingestion. Such samples are to be processed in a confined environment, such as a hood or a glove box.

5.4 The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.5 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them or use thermal protection when working on them while they are above room temperature.

5.6 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source. Alternatively, the source may be removed from the vacuum manifold through a vacuum interlock.

5.7 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power. If the work involved requires measurement of voltage supplies, the instrument may be left on.

5.8 Hearing protection must be worn when using mechanical systems to grind fish or tissue samples.

5.9 When using a scalpel, cut away from yourself. If you are holding something, cut away from your hand.

5.10 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid (1)	Corrosive, Oxidizer, Dehydradator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Sodium Hydroxide	Corrosive, Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.

Hydrochloric Acid	Corrosive, Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Methylene Chloride	Carcinogen, Irritant	25 ppm-TWA, 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable, Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable, Poison, Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Toluene	Flammable, Poison, Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Cyclohexane	Flammable, Irritant	300 ppm TWA	Inhalation of vapors causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. High concentrations have a narcotic effect.
Tetradecane	Irritant	None established	Inhalation of vapors may cause difficulty breathing, headache, intoxication and central nervous system damage.

Benzene	Flammable, Toxic, Carcinogen	PEL: 1 ppm TWA ; 5 ppm, 15 min. STEL	Causes skin irritation. Toxic if absorbed through skin. Causes severe eye irritation. Toxic if inhaled. Vapor or mist causes irritation to mucous membranes and upper respiratory tract. Exposure can cause narcotic effect. Inhalation at high concentrations may have an initial stimulatory effect on the central nervous system characterized by exhileration, nervous excitation and/or giddiness, depression, drowsiness or fatigue. Victim may experience tightness in the chest, breathlessness, and loss of consciousness.
Nonane	Flammable	None established	Harmful if inhaled/swallowed. Vapor/mist is irritating to eyes, mucous memebranes and upper respiratory tract. Causes skin irritiation.
Potassium Hydroxide	Corrosive, Poison	2 mg/m3 ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on the severity of exposure. Symptoms may include coughing, sneezing, damage to the nasal or respiratory tract. High concentrations can cause lung damage. Corrosive! Contact with skin can cause irritation or severe burns and scarring with greater exposures.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.10.1 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include benzene and methylene chloride, 2,3,7,8-TCDD and all other 2,3,7,8- substituted PCDD or PCDF isomers.

Note: The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.11 Exposure to chemicals will be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.12 The preparation of all standards and reagents and glassware cleaning procedures that involve solvents such as acetone, toluene, methylene chloride, and hexane will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.13 All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported immediately to a laboratory supervisor.

5.14 Training: Workers must complete the employee Corporate Safety Manual safety orientation prior to working in the laboratory.

5.15 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch, and shifts).

5.16 Confinement: Work areas should be isolated and posted with signs. Glassware and tools should be segregated. Benchtops should be covered with plastic backed absorbent paper.

5.17 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

5.18 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

6. Equipment and Supplies

6.1 Sample Extraction Equipment.

Note: All glassware used in extraction and cleanup procedures is solvent rinsed twice before use with acetone, toluene, methylene chloride and hexane in that order. Pre-extract the soxhlet apparatus with toluene for at least 4 hours. Rinse glassware with all 4 solvents once. See SOP KNOX-QA-0002, current revision, "Glassware Cleaning", for details.

6.1.1 Aqueous Sample Extraction

6.1.1.1 Multi-position separatory funnel rotator.

6.1.1.2 2000 mL separatory funnels with PFTE stopcocks and PFTE stoppers.

6.1.1.3 100 mm glass funnel with short stem.

6.1.1.4 Class A 1 mL pipettes.

6.1.1.5 1000 mL graduated cylinders.

6.1.1.6 PFTE squirt bottles, 500 mL.

6.1.1.7 Syringes.

6.1.1.8 Glass wool, precleaned with methylene chloride.

6.1.1.9 Buchner funnels, filter flasks, rubber stopper and GF/D filters

6.1.1.10 Vacuum source

6.1.2 Soxhlet Extraction

6.1.2.1 Analytical balance, capable of weighing to 0.01 g.

6.1.2.2 Stainless steel spatula.

6.1.2.3 Stainless steel tweezers.

6.1.2.4 Soxhlet extractor or Dean-Stark soxhlet extractor.

6.1.2.5 Heating mantles with temperature controls.

6.1.2.6 500 mL evaporative flask, round bottom.

6.1.2.7 Glass condenser, compatible with the dean-stark extractor.

6.1.2.8 Class A 1 mL pipettes.

6.1.2.9 Glass wool, precleaned with methylene chloride.

6.1.2.10 High purity glass fiber soxhlet thimble.

6.1.2.11 Boiling beads, 6 mm glass.

6.1.2.12 PFTE boiling chips.

6.1.3 Waste Dilution

6.1.3.1 Analytical balance, capable of weighing to 0.01 g.

6.1.3.2 40 mL vial, with PFTE lined cap.

6.1.3.3 5 3/4 inch borosilicate glass pipets.

6.1.3.4 Rubber bulbs.

6.1.3.5 1 ml Class A pipette.

6.2 Sample Cleanup Equipment.

6.2.1 Acid-base cleanup

6.2.1.1 Disposable Pasteur pipets and rubber bulbs.

6.2.1.2 Graduated cylinder, 100 mL volume.

6.2.1.3 Vials, 40 mL volume, with PFTE lined caps.

6.2.2 Dual column cleanup

6.2.2.1 Disposable glass columns.

6.2.2.1.1 20mm x 240mm custom glass column with support ring and tapered tip.

6.2.2.1.2 16mm x 240mm custom glass column with support ring and tapered tip.

6.2.2.2 Aluminum support rack for custom columns.

6.2.2.3 Amber-colored glass jar with a PFTE lined screw cap, 250mL.

6.2.2.4 Volumetric flask, 100 mL volume.

6.2.2.5 Disposable Pasteur pipets and rubber bulbs.

6.2.2.6 Bottletop solvent dispenser.

6.2.2.7 40 mL vials with PFTE lined screw caps.

6.2.2.8 Volumetric flask, 100mL

6.2.2.9 Graduated cylinder, 100 ml.

6.2.2.10 Solvent waste collection jars, 125mL.

6.2.2.11 Marking pen.

6.2.3 Activated carbon cleanup

6.2.3.1 10 mL disposable pipet for use as the column.

6.2.3.1.1 All disposable carbon columns are solvent rinsed before use. The solvents used are acetone, toluene, methylene chloride and hexane (in this order).

6.2.3.2 Glass wool, precleaned with methylene chloride.

6.2.3.3 25 mL graduated cylinder

6.2.3.4 40 mL vials.

6.3 Sample Concentration Equipment.

6.3.1 Macro Concentration Equipment – Rapid-Vap

6.3.1.1 Labconco Rapid-Vap concentrator

6.3.1.2 600 mL sample concentrator tubes, Labconco or equivalent.

6.3.1.3 Borosilicate 5.75 inch and 9.0 inch disposable pipettes.

6.3.1.4 Rubber bulbs.

6.3.1.5 Borosilicate 40 mL disposable vials with PFTE lined screwcaps.

6.3.2 Macro Concentration – Snyder Column

6.3.2.1 Heating mantles with temperature controls.

6.3.2.2 Three-ball macro Snyder column.

6.3.2.3 Rubber bulbs.

6.3.2.4 Nine inch borosilicate glass pipets.

6.3.2.5 40 mL vial, with PFTE lined cap.

6.3.2.6 PFTE boiling chips.

6.3.3 Micro Concentration – N-Evap

6.3.3.1 Nitrogen blowdown apparatus (N-EVAP or equivalent).

6.3.3.2 Mini vials, 1.1 mL capacity with a tapered bottom; with PFTE faced, rubber septa and screw caps.

6.4 Sample Analysis Equipment.

6.4.1 Gas Chromatograph --- Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specification in Section 10.

6.4.1.1 GC column for PCDDs/PCDFs and for isomer specificity for 2,3,7,8-TCDD --- 60m x 0.32mm ID x 0.25µm film thickness DB-5 or RTX-5 fused silica capillary column (J&W No. 123-5062, Restek No.10227 or 10227-125 IntegraGuard) or equivalent.

6.4.1.2 GC column for isomer specificity for 2,3,7,8-TCDF --- 30m x 0.32mm ID x 0.25µm film thickness DB-225 or RTX-225 fused silica capillary column (J&W No. 123-2232 or Restek No.14024) or equivalent.

6.4.2 Mass Spectrometer --- Electron impact ionization with the filament eV's optimized for best instrument sensitivity, stability and signal to noise ratio. Shall be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period of approximately 1 second and shall meet all of the performance specifications in Section 10.

6.4.3 GC/MS Interface --- The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beam

6.4.4 Data System --- Capable of collecting, recording, and storing MS data.

7. Reagents and Standards

7.1 Sample Pre-Treatment

7.1.1 Hydrochloric acid (HCl), concentrated 37% wt in water (ACS), Mallinkcrodt AR Select or equivalent.

7.1.2 1N HCl - Carefully add 83mL of concentrated HCl to 917 mL of reagent water in a glass container.

7.2 Aqueous Extraction

7.2.1 Acetone, pesticide quality or equivalent.

7.2.2 Toluene, pesticide quality or equivalent.

7.2.3 Methylene chloride, pesticide quality or equivalent.

7.2.4 Hexane, pesticide quality or equivalent.

7.2.5 Tetradecane, pesticide quality or equivalent.

7.2.6 Reagent water must be produced by a Millipore DI system or equivalent, being able to produce water with 18 mega ohm resistance. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2.7 Sodium sulfate (ACS), granular anhydrous. Heated at 450 ºC for a minimum of four (4) hours. After cooling, store in a desiccator.

7.3 Soxhlet extraction

7.3.1 Acetone, pesticide quality or equivalent.

7.3.2 Toluene, pesticide quality or equivalent.

7.3.3 Methylene chloride, pesticide quality or equivalent.

7.3.4 Hexane, pesticide quality or equivalent.

7.3.5 Benzene, pesticide quality or equivalent.

7.3.6 Tetradecane, pesticide quality or equivalent.

7.3.7 Sand, prepared by extracting with methylene chloride and/or baking at 450 °C for a minimum of 4 hours. After cooling store in a dessicator.

7.3.8 Sodium sulfate (ACS), granular anhydrous. Heated at 450 ºC for a minimum of four (4) hours. After cooling, store in a desiccator.

7.3.9 Dry Ice.

7.3.10 Reagent water must be produced by a Millipore DI system or equivalent, being able to produce water with 18 MΩ resistance. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.4 Waste Dilution

7.4.1 Hexane, pesticide quality or equivalent.

7.4.2 Benzene, pesticide quality or equivalent.

7.5 Acid-Base Cleanup

7.5.1 Sulfuric acid, concentrated, ACS grade, specific gravity 1.84.

7.5.2 Potassium hydroxide, 20% aqueous. Prepare by cautiously adding, 100 g of potassium hydroxide pellets to 400 mL of deionized water. This solution is stored at room temperature in a plastic bottle.

7.5.3 Sodium chloride, NaCl, analytical reagent, 5 percent (w/v) in reagent grade water.

7.5.4 Hexane, pesticide quality or equivalent.

7.5.5 Benzene, pesticide quality or equivalent.

7.5.6 Sodium sulfate (ACS), granular anhydrous. Heated at 450 ºC for a minimum of four (4) hours. After cooling, store in a desiccator.

7.6 Silica Gel/Alumina Column Cleanup

7.6.1 Sodium sulfate (ACS), granular anhydrous. Heated at 450 ºC for a minimum of four (4) hours. After cooling, store in a desiccator.

7.6.2 Methylene chloride pesticide quality or equivalent.

7.6.3 Hexane, pesticide quality or equivalent.

7.6.4 Acetone, pesticide quality or equivalent.

7.6.5 Toluene, pesticide quality or equivalent.

7.6.6 Silica gel, Davisil Grade 923, 100-200 mesh or equivalent. Prepare by Soxhlet extraction with methylene chloride for at least 6 hours. Transfer to an aluminum foil-covered Pyrex glass container then air dry and activate in an oven at 110 ± 10 °C for a minimum of four (4) hours. Store in labeled glass jars in desiccator until use.

7.6.7 3.3% Deactivated silica gel – To prepare add 3. 3mL of reagent water to 100 g of silica gel (section 7.6.6) in a 250 mL amber-colored glass jar with a PFTE lined screw cap. Mix thoroughly by shaking until no lumps are visible, and the silica gel is free flowing and no longer sticks to the side of the jar.

7.6.8 Acidic silica gel - To prepare, add 19 mL of concentrated sulfuric acid to 60 g silica gel (section 7.6.6) in a 250 mL amber-colored glass jar with a PFTE lined screw cap. Mix thoroughly by shaking until no lumps are visible, and the silica gel is free flowing and no longer sticks to the side of the jar.

7.6.9 Alumina, Neutral - Super I - Scientific Absorbents. Purchase and use only activated alumina. Store in an oven at 110 ± 10 °C when not in use.

7.6.9.1 Each new lot of alumina must be tested upon receipt and before use. Elute a solution containing all of the ^{13}C internal standards and native analytes through a column packed with the new lot of alumina. Collect the 5% and 60% fractions together and analyze by HRMS. Archive the 80 mL of hexane in a separate container. The target analytes and internal standard recoveries must be greater than 85% in the final fraction. If the recovery is less than 85% for any compound or internal standard, the ratios and volumes of the elution solvents must be optimized and the test repeated until all compounds meet the recovery criteria.

7.6.10 5% methylene chloride in hexane. Add 15 mL methylene chloride to 285 mL hexane. Store in an amber-colored glass bottle at room temperature until use.

7.6.11 60% methylene chloride in hexane - add 390 mL methylene chloride to 210 mL hexane. Store in an amber-colored glass bottle at room temperature until use.

7.7 Activated Carbon Cleanup

7.7.1 Thoroughly mix 5% (by weight) active carbon AX-21 and 95% (by weight) silica gel (Davisil Grade 923, 100-200 mesh). Activate in an oven at 130 °C for 6 hours. Store in a dessicator in an amber colored bottle with a foil lined lid until use. Do not label the bottle until oven activation is complete to avoid heat damage to the label.

7.7.2 Toluene, pesticide quality or equivalent.

7.7.3 Methylene Chloride, pesticide quality or equivalent.

7.7.4 Benzene, pesticide quality or equivalent.

7.7.5 Methanol, pesticide quality or equivalent.

7.7.6 Cyclohexane, pesticide quality or equivalent.

7.7.7 Tetradecane, pesticide quality or equivalent.

7.7.8 Hexane, pesticide quality or equivalent.

7.7.9 Acetone, pesticide quality or equivalent.

7.8 Standards and Calibration Solutions: Certified Reference Standard purchased from Cambridge Isotope Laboratories (CIL, Andover Massachusetts), and Wellington Laboratories (Guelph, Ontario, Canada). If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with PFTE-lined caps.

7.8.1 Nonane, pesticide quality or equivalent.

7.9 Stock Solutions: Standards are used as received after being sonicated and transferred to 1.0 mL amber glass vials with PFTE lined caps.

7.9.1 Initial Calibration Standards:

7.9.1.1 1613B/8290: CS1-CS5. CIL Catalog No. EDF-9999. (See Table 5).

7.9.1.2 23/0023A/TO-9A: CS1-CS5. CIL Catalog No. EDF-4052. (See Table 6)

7.9.2 Initial Calibration Verification Standard: Wellington Laboratories Catalog No. EPA-1613-CS3.

7.9.3 Daily Calibration Verification Standards

7.9.3.1 1613B/8290: CS3. CIL Catalog No. EDF-9999-3. (See Table 7).

7.9.3.2 1613B/8290: CS3. CIL Catalog No. EDF-4141. (See Table 7).

Note: This standard may be used as both the Continuing Calibration Standard and the DB/Rtx-5 GC Window Defining Mix/Column Performance Check Solution.

7.9.3.3 23/0023A/TO-9A: CS3. CIL Catalog No. EDF-4052-3. (See Table 8)

7.9.4 PAR Native Standard Stock Solution: CIL Catalog No. EDF-7999 (see Table 11) 40-400 ng/mL in nonane, 200 µL.

7.9.5 Internal Standard Stock Solution

7.9.5.1 1613B/8290: CIL Catalog No. EDF-8999, (see Table 13), 100 ng/mL ($^{13}C_{12}$-OCDD 200 ng/mL) in nonane, 500 µL.

7.9.5.2 23/0023A/TO-9A: CIL Catalog No. EDF-4053, (see Table 15), 1000 ng/mL ($^{13}C_{12}$-OCDD 2000 ng/mL) in nonane, 1.2 mL.

7.9.6 23/0023A/TO-9A Surrogate Standard Stock Solution: CIL Catalog No. EDF-4054, (see Table 16), 1000 ng/mL in nonane, 1.2 mL.

7.9.7 Cleanup Standard Stock Solution: CIL Catalog No. ED-907, (see Table 14), 50 µg/mL in nonane, 1.2 mL.

7.9.8 $^{13}C_{12}$-2,3,7,8-TCDD Labeled Standard Stock Solution: CIL Catalog No. ED-900, 50 µg/mL in nonane, 1.2 mL.

7.9.9 $^{13}C_{12}$-2,3,7,8-TCDF Labeled Standard Stock Solution: CIL Catalog No. EF-904 50 µg/mL in nonane, 1.2 mL.

7.9.10 $^{13}C_{12}$-1,2,3,4-TCDD Labeled Standard Stock Solution: CIL Catalog No. ED-911, 50 µg/mL in nonane, 1.2 mL.

7.9.11 $^{13}C_{12}$-1,2,3,7,8,9-HxCDD Labeled Standard Stock Solution: CIL Catalog No. ED-996, 50 µg/mL in nonane, 1.2 mL.

7.9.12 PCDD/PCDF Window Defining and Isomer Specificity Mixture: CIL Catalog No. EDF-4147 (see Table 18 and Table 19). This standard is used for qualitative purposes only and is not considered quantitative.

7.10 Secondary Stock Solutions

7.10.1 Cleanup Standard Secondary Stock Solution: Dilute 0.100 mL of the stock solution in section 7.9.7 to 1.0 mL in a volumetric flask with nonane to a final concentration of 5.0 µg/mL.

7.10.2 Cleanup Standard Working Stock Solution: Dilute 0.200 mL of the stock solutions in section 7.10.1 to 5.0mL in a volumetric flask with nonane to a final concentration of 200 ng/mL.

7.10.3 $^{13}C_{12}$ TCDD/TCDF Internal Standard Secondary Stock Solution: Dilute 0.100 mL of the stock solutions in sections 7.9.8 and 7.9.9 to 10 mL in a volumetric flask with nonane to a final concentration of 500 ng/mL.

7.10.4 Recovery Standard Secondary Stock Solution: Dilute 1.0 mL of the stock solutions in sections 7.9.10 and 7.9.11 to 10 mL in a volumetric flask with nonane to a final concentration of 5.0 µg/mL.

7.11 Standards and Spiking Solutions

7.11.1 PCDD/PCDF Window Defining and Isomer Specificity Standard: Combine 25 µL of the standard solution in section 7.9.12, 5 mL of the IS spiking solution in section 7.11.3, 5 µL of the RS stock solution in section 7.10.4, and 500 µL of nonane in a 10 mL vial. Concentrate the solution to 500 µL with a stream of nitrogen and transfer to 1.0 mL amber glass vials with PFTE lined cap.

7.11.2 PAR Native Standard Spiking Solution: Dilute 200 µL of the stock solution in section 7.9.4 to 40 mL in a graduated cylinder with acetone to a final concentration of 0.2-2.0 ng/mL. 1.0 mL of this solution is added to each IPAR, OPR, LCS or MS/MSD sample. See Table 11 for a complete list of compounds and their concentrations.

7.11.3 1613B/8290 Internal Standard Spiking Solution: Dilute 500 µL of the stock solution in section 7.9.5.1 to 50 mL in a graduated cylinder with acetone to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank, and QC sample. See Table 13 for a complete list of compounds and their concentrations.

7.11.4 23/0023A/TO-9A Internal Standard Spiking Solution: Dilute 100 µL of the stock solution in section 7.9.5.2 to 100 mL in a graduated cylinder with acetone to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank, and QC sample. See Table 13 for a complete list of compounds and their concentrations.

7.11.5 23/0023A/TO-9A Surrogate Standard Spiking Solution: Dilute 500 µL of the stock solution in section 7.9.6 to 25 mL in a graduated cylinder with nonane to a final concentration of 20 ng/mL. 100 µL of this solution is added to each sample train components before sampling. See Table 16 for a complete list of compounds and their concentrations.

7.11.6 Cleanup Standard Spiking Solution: Dilute 100 µL of the stock solution in section 7.10.2 to 100 mL in a volumetric graduate with hexane to a final concentration of 0.20 ng/mL. 1.0 mL of this solution is added to each sample, method blank, and QC sample extract prior to cleanup. See Table 14 for a complete list of compounds and their concentrations.

7.11.7 $^{13}C_{12}$ TCDD/TCDF Internal Standard Spiking Solution: Dilute 200 µL of the stock solution in section 7.10.3 to 100 mL in a volumetric flask with acetone to a final concentration of 1.0 ng/mL. 1.0 mL of this solution is added to each sample, method blank, and QC sample extract that are extracted for TCDD and/or TCDF analysis only.

7.11.8 Recovery Standard Spiking Solution: Dilute 200 µL of the stock solution in section 7.10.4 to 10 mL in a volumetric flask with nonane to a final concentration of 0.1 µg/mL. 20 µL of this solution is added to each sample, method blank, and QC sample extract.

7.12 Stability of Solutions: Standards have an expiration of ten (10) years from date of receipt unless otherwise specified by the manufacturer. Standard solutions used for quantitative purposes should be analyzed periodically, and should be assayed against reference standards before further use.

7.13 Perfluorokerosene (PFK) is used in neat form to tune and calibrate the mass spectrometer. Fluka (Catalog No. - 77275) has been found to be superior to other sources of PFK.

8. Sample Collection, Preservation and Storage

8.1 Sampling is not performed for this method by STL Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, Receipt and Log In of Commercial Samples, current revision. Sample container and preservation recommendations are listed in the table below.

Sample Holding Times, Containers, and Preservation

	1613B	8290[1]	23	0023A	TO-9A
Holding Times	Samples -1 year Extracts – 1 year	Samples -30 days from collection Extracts –45 days from extraction Tissue Extracts - 45 days from collection	Samples -30 days from collection Extracts –45 days from extraction	Samples -30 days from collection Extracts –45 days from extraction	Samples -7 days from collection Extracts –40 days from extraction
Containers	Amber Glass	Amber Glass	See KNOX-ID-0012	See KNOX-ID-0012	See KNOX-ID-0012
Preservation:					
Aqueous Samples	0-4 °C in the dark If residual chlorine is present, add 80 mg/L sodium thiosulfate. If pH > 9, adjust to pH 7-9 with sulfuric acid	4 °C ± 2 °C in the dark	N/A	N/A	N/A
Solid Samples	<-10 °C in the dark	4 °C ± 2 °C in the dark	N/A	N/A	N/A
Tissue Samples	<-10 °C in the dark	<-20 °C in the dark[2]	N/A	N/A	N/A
Air Samples	N/A	4 °C ± 2 °C in the dark	4 °C ± 2 °C in the dark	4 °C ± 2 °C in the dark	≤4 °C in the dark

Note:

1 For method 8290 and 0023A the holding times listed are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed may be as high as a year for certain matrices. The results of samples analyzed after the holding time expiration date should be considered to be minimum concentrations and should be identified as such in the final report. Sample extracts, however, should always be analyzed within 45 days of extraction. (For the State of South Carolina – The holdings times for 8290 are as listed in the table and are not considered recommendations.)

2 If the freezer used to store 8290 samples is not capable of reaching a temperature of <-20 °C when the temperature control is set to its maximum limit, a storage higher temperature is acceptable as long as it is <-10 °C.

8.2 Extracts should be stored in the dark at room temperature in amber or clear glass vials prior to analysis.

9. Quality Control

9.1 Initial Demonstration of Capability

9.1.1 Initial precision and recovery (IPR) samples are analyzed to demonstrate the ability to generate acceptable precision and accuracy.

9.1.2 For aqueous samples, extract, concentrate, and analyze four 1-L aliquots of reagent water spiked with labeled internal standards and the precision and recovery standard according to the procedures in section 11. For non-aqueous samples, extract, concentrate, and analyze four aliquots of sand or sodium sulfate spiked with labeled internal standards and the precision and recovery standard according to the procedures in section 11. It is recommended that a method blank be prepared with the IPR samples.

9.1.3 Using the results of the set of four analyses, compute the average concentration (X) of the extracts in ng/mL and the standard deviation of the concentration (s) in ng/mL for each compound.

9.1.4 For each compound, compare s and X with the corresponding limits for initial precision and recovery in Table 9 for method 1613B and Table 10 for methods 8290, 23, 0023A, and TO-9A. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test.

9.2 The method detection limit (MDL) study described in Section 13 must be completed with acceptable results before analysis of samples may begin.

9.3 A laboratory method blank must be run along with each analytical batch of 20 (10, including field blank if provided, for TO-9A) or fewer samples. The method blank is normally analyzed immediately after the calibration standards. The method blank consists of reagent water for aqueous samples, and a clean solid matrix (sand or sodium sulfate) for solid samples. The method blank must meet the following acceptance criteria;

- The concentration of target analytes in the method blank must be less than the MDL.
- If the concentration of target analytes in the method blank is greater than the MDL but less than the minimum level (ML), corrective action is required but the associated samples may be reported. At a minimum, corrective must include the addition of "B" qualifiers to all associated samples with analytes detected in the method blank above the MDL.
- If the concentration of target analytes in the method blank is greater than minimum level (ML) but less than 5% of the concentration in the associated samples, corrective action is required but the associated data may be reported. At a minimum, corrective must include the addition of "B" qualifiers to all associated samples with analytes detected in the method blank above the ML and documentation in the case narrative.
- If the method blank sample fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the

problem and corrective action. The problem and corrective action is documented in the project narrative.

- If there is no target analyte greater than the minimum levels (ML) in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be done in consultation with the client.

9.3.1 The method blank internal standard recoveries must be within the established control limits. If internal standard recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If internal standard recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. If the method blank internal standard recoveries are outside the QC limits and the decision is made to report the sample results, an NCM must be initiated and the reason for accepting the sample results clearly documented. Consultation with the client before acceptance must take place.

9.3.2 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," an NCM is initiated and appropriate comments made in the report narrative to provide further documentation.

9.3.3 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.4 Instrument Blank

9.4.1 Instruments must be evaluated for contamination during each 12 hour analytical run. This is accomplished by analysis of a method blank if available. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of solvent with the internal standards and recovery standards added. It is evaluated in the same way as the method blank.

9.5 Laboratory Control Sample (LCS) or Ongoing Precision and Pecovery (OPR)

9.5.1 An LCS/OPR sample is analyzed along with each analytical batch of 20 (10, including field blank if provided, for TO-9A) or fewer samples. LCS/OPR spike components, concentrations, and control limits are given in Table 11.

9.5.2 If any analyte in the LCS is outside the control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the LCS/OPR sample fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the problem and corrective action. The problem and corrective action is documented in the project narrative.

- If the batch is not re-extracted and reanalyzed, an NCM must be initiated and the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of an acceptable reason for not reanalyzing might be that the

matrix spike and matrix spike duplicate recoveries are within control limits, the method blank and sample internal standard recoveries are within limits, and the data clearly demonstrates that the problem was confined to the LCS/OPR).

- For method TO-9A calculate the precision (%D) relative to the previous TO-9A LCS. The precision must be within ± 30%.

9.5.3 Ongoing monitoring of the LCS/OPR provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.6 Internal Standards.

Internal standards are spiked into all samples, blanks, and laboratory control samples to assess method performance on the sample matrix. The recovery of each labeled internal standard must be within the limits in Table 13 for methods 1613B and 8290 or in Table 15 for methods 23, 0023A, and TO-9A.

9.6.1 If the recovery is outside these limits the following corrective action should be taken:

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- If the recovery of any internal standard is less than the lower control limit, calculate the S/N ratio of the internal standard. If the S/N is > 10 and the estimated detection limits (EDLs) are less than the minimum levels (ML's), report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the estimated detection limits (EDLs) are greater than the minimum levels (ML's), re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample may be re-extracted or additional clean-ups may be employed. The decision to reanalyze or flag the data should be made in consultation with the client.

9.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Method 8290 only.

When method 8290 is performed a matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every 20 samples of a given matrix. The MS/MSD is spiked with the same subset of analytes as the LCS (See Table 12). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented in the report narrative.

- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the analysis is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.
- If a MS/MSD is not possible due to limited sample, then a LCSD should be analyzed. The LCSD is evaluated using the same acceptance criteria as the LCS. The RPD of the LCS and LCSD are compared to the acceptance limits in Table 12.
- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.8 Surrogate Standards – Methods 23, 0023A, TO-9A

Field surrogate standards are added to the collection media prior to sample collection when performing methods 23, 0023A, or TO-9A. The surrogate recoveries are calculated relative to the internal standards and are a measure of sampling efficiency. The recovery of the surrogate standards should be within the limits specified in Table 16. Poor recoveries of the surrogate standards may indicate breakthrough in the sampling train.

9.8.1 If the recovery is outside these limits the following corrective action should be taken:

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- Flag the results that are outside control limits and notify the Project Manager. The client must be notified and consulted for additional corrective action.

10. Calibration and Standardization

10.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The other type, continuing calibration, consists of analyzing the column performance check solution and a calibration solution (CS3). No samples are to be analyzed until acceptable calibration as described in sections 10.2 and 10.2.9.1 is demonstrated and documented.

10.2 Initial Calibration

10.2.1 Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 5 for methods 1613B and 8290 or in Table 6 for methods 23, 0023A, or TO-9A. Store calibration standards at room temperature in the dark. Calibration standard solutions have an expiration date of ten (10) years from date of receipt unless otherwise specified by the manufacturer/supplier.

10.2.2 Establish operating parameters for the GC/MS system (suggested operating conditions are displayed in Figure 1 and Figure 2). For method 1613B adjust the GC conditions to meet the relative

retention times for the PCDDs/PCDFs listed in Table 3. The cycle time for MID descriptors must be ≤ 1 sec.

10.2.3 By using a PFK molecular leak, tune the instrument to meet the minimum resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to the m/z 303.9016 (from TCDF). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Document that the resolving power at reduced accelerating voltage of m/z 380.9760 is greater than 10,000 (10 percent valley).

10.2.4 Analyze 2µL of the Window Defining Mixture and set the switchpoints for the MID descriptors. The switchpoints must be set to encompass the retention time window of each congener group.

10.2.5 If the initial calibration is being performed on the DB-5 or RTX-5 column, analyze 2µL of the Column Performance solution or Mixture Solution. The chromatographic peak separation between 2,3,7,8-TCDD and the closest eluting non-2,3,7,8-TCDD isomer must be resolved with a % Valley of ≤ 25, where

$$\%\ \text{Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8-TCDD}} \times 100$$

If the initial calibration is being performed on the DB-225 or RTX-225 column, analyze 2µL of the TCDF Column Performance solution. The chromatographic peak separation between 2,3,7,8-TCDF and the closest eluting non-2,3,7,8-TCDF isomer must be resolved with a % Valley of ≤ 25, where

$$\%\ \text{Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8-TCDF}} \times 100$$

10.2.6 Analyze 2µL of each of the five calibration standards and calculate the RRF of each analyte vs. the appropriate internal standard listed in Table 3 for methods 1613B and 8290 or in Table 4 for methods 23, 0023A, and TO-9A using the following equation;

$$\text{RRF} = \frac{\text{As} \times \text{Cis}}{\text{Ais} \times \text{Cs}}$$

where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Cis = concentration of the appropriate internal standard
Cs = concentration of the compound of interest

10.2.7 Calculate the mean relative response factor and the standard deviation of the relative response factors using the equations in the LQM for each calibration standard solution.

10.2.8 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met for each initial calibration standard before sample analyses are performed. If acceptable initial

calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to problems with an individual analysis within the calibration series, follow the procedure in STL Policy P-T-001(see reference section 16.9).

10.2.8.1 The percent relative standard deviation (RSD) for the mean relative response factors must be within the acceptance criteria listed in Table 5 for methods 1613B and 8290 or in Table 6 for methods 23, 0023A, and TO-9A.

10.2.8.2 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standards must have signal-to-noise ratios (S/N) ≥ 10.

10.2.8.3 The ion abundance ratios must be within the specified control limits in Table 22.

10.2.8.4 For method 1613B the absolute retention time of $^{13}C_{12}$-1234-TCDD must exceed 25.0 minutes on the DB/Rtx-5 column and 15.0 minutes on the DB/Rtx-225 column.

10.2.9 Analyze 2µL of the Initial Calibration Verification (ICV) Standard in section 7.9.2. Calculate the concentration of the ICV using the RRF's from the CS3 standard analyzed in section 10.2.6. Calculate the percent difference (%D) between the expected and the calculated ICV concentration using the following formula.

$$\%D = \frac{\left(C_{Exp} - C_{Calc}\right)}{C_{Exp}} \times 100$$

Where:
C_{Exp} = The expected concentration of the ICV Standard.
C_{Calc} = The calculated concentration of the ICV Standard.

10.2.9.1 The general criteria for percent difference acceptance limits is less than or equal to ±35% for all native and labeled compounds. The warning limits for percent difference is ±35 - 55%.

10.2.9.2 All data associated with compounds with percent differences in the warning limits must be reviewed before acceptance.

10.2.9.3 All data associated with compounds with percent differences outside the warning limits shall be documented as an NCM. Corrective action must be taken and may include the following

- Reanalyze the ICV Standard
- Replace and reanalyze the ICV Standard
- Evaluate the instrument performance
- Evaluate the Initial Calibration Standards

10.3 Continuing Calibration

10.3.1 Continuing calibration is performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks. A calibration check is also required at the end of a 12 hour period when performing method 8290 or 0023A.

10.3.2 Document the mass resolution performance as specified in section 10.2.3. The mass resolution checks must be performed at the beginning and at the end of each 12-hour shift.

10.3.3 Analyze 2µL of the Window Defining Mixture and or Column Performance Solution Mixture under the same instrument conditions used to perform the initial calibration. Determine and document acceptable column performance as described in section 10.2.4 and 10.2.5.

10.3.4 Analyze 2µL of the Daily Calibration Standard Solution (CS3). Calculate the concentrations using the formulas in section 12.3.

> Note: The combined Continuing Calibration Standard/Window Defining Mix/Column Performance Solution specified in section 7.9.3.2 may be used in section 10.3.2, 10.3.4, and 10.3.6.

10.3.5 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met at the beginning of each 12 hour period that samples are analyzed. If acceptable beginning continuing calibration criteria is not met, identify the root cause, perform corrective action and repeat the continuing calibration. If the second consecutive beginning continuing calibration does not meet acceptance criteria, additional corrective action must be performed. Acceptable performance must be demonstrated after two consecutive failing beginning continuing calibrations by the analysis of two consecutive acceptable beginning continuing calibrations or by analysis of a new initial calibration.

10.3.5.1 The measured concentration or percent difference for each compound must be within the acceptance criteria limits in Table 7 for methods 1613B and 8290 or in Table 8 for methods 23, 0023A, and TO-9A.

10.3.5.2 For method 1613B the relative retention times of PCDDs/PCDFs and labeled compounds in the standard must be within the limits in Table 3.

10.3.5.3 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standard must have signal-to-noise ratios (S/N) ≥ 10.

10.3.5.4 The ion abundance ratios must be within the specified control limits in Table 22.

10.3.5.5 When performing method 8290 or 0023A, if the continuing calibration fails at the beginning of a 12-hour shift, the instructions in section 10.3.5 must be followed. If the continuing calibration check performed at the end of a 12 hour period fails by no more than ±25 percent RPD for unlabeled native analytes and ±35 percent RPD for labeled standards, the closing standard may not be used as a beginning calibration standard for the next 12-hour shift and the requirements in section 10.3.5 must be met before analysis may continue. Use the mean RRF from the two daily continuing calibration runs to compute the analyte concentrations, instead of the RRFs obtained from the initial calibration. If the continuing calibration check performed at the end of a 12 hour period fails by more than ±25 percent RPD for unlabeled native analytes and ±35 percent RPD for labeled standards initiate corrective action and reanalyze all positive sample extracts analyzed during the 12 hour period encompassing the failed end of shift calibration check.

> It is realized that it may not always be possible to achieve all RF criteria. For example, the RF criteria for 13C12-HpcDD and 13C12-OCDD were not met, however the RF values for

the corresponding unlabeled compounds were within the criteria established in this procedure. The data quality for the unlabeled HpCDD and OCDD values were not compromised as a result of the calibration event. In these situations, the analyst must consult with the group manager and the project manager to assess the impact on the data quality objectives on the affected samples. Corrective action must be taken and any decision to report sample data in this situation must be made in conjunction with the client. An NCM must be initiated if the data is to be reported.

10.3.6 Daily calibration must be performed every 12 hours of instrument operation. The 12 hour shift begins with the documentation of the mass resolution followed by the injection of the Window Defining Mixture or Column Performance Solution Mixture and the Daily Calibration Standard.

10.3.6.1 For methods 1613B, 23, TO-9A The mass resolution documentation must also be performed at the end of the 12 hour shift. If the lab is operating consecutive 12 hour shifts, the mass resolution check from the end of the previous period can be used for the beginning of the next period.

10.3.6.2 For method 8290, 0023A - The Continuing Calibration Standard check and mass resolution documentation must also be performed at the end of the 12 hour shift. If the lab is operating consecutive 12-hour shifts, the Window Defining Mixture and/or Column Performance Solution Mixture must be analyzed at thebeginning of each 12-hour period. The mass resolution and continuing calibration checks from the previous period can be used for the beginning of the next period.

11. Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variations in the procedure, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager, and QA Manager. If contractually required, the client shall be notified.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2 Sample Pretreatment

11.2.1 Tissue Samples

11.2.1.1 If the sample matrix is tissue and has not been homogenized prior to sample receipt, the entire sample is blended to provide a homogeneous sample. At least 20 g of tissue should be homogenized if possible to allow for reanalysis if necessary.

11.2.1.2 Cut tissue into pieces of a uniform size (approximately 1 inch square). Homogenize the tissue sample in a laboratory blender.

11.2.1.3 Weigh out 10 grams of the homogenized tissue sample. Add the 10 g sample along with 20 g of sodium sulfate to a laboratory blender. Blend the tissue/sodium sulfate mixture, while adding dry ice as necessary, to achieve a powder like consistency.

11.2.1.4 Record the sample and weight on the sample prep sheet or in a logbook.

11.2.2 Fly Ash Samples

11.2.2.1 If the sample matrix is fly ash and is to be analyzed by method 8290, pretreat the sample with HCl as follows:

11.2.2.2 Weigh 10±0.05 g of the fly ash sample and transfer to a 240 mL glass jar. Record the sample and weight on the sample prep sheet. If a sample is designated for MS/MSD analysis, prepare two additional portions of the sample and label them as the MS and MSD samples.

11.2.2.3 Add 1.0 mL of the internal standard spiking solution (see section 7.11.3) to the sample. Record the standard solution ID and volume spiked on the sample prep sheet. Initial and date the entry. Add 150 mL of 1N HCl to the sample. Seal the jar with a PFTE lined screw cap and shake for 3 hours at room temperature.

11.2.2.4 Rinse a glass fiber filter with reagent water, and filter the sample through the filter paper, placed in a Buchner funnel, into a 1 L flask. Rinse the sample bottle twice with small amounts of reagent water, making sure that all particulate matter is transferred onto the glass fiber filter. Wash the fly ash cake with approximately 500 mL organic-free reagent water.

11.2.2.5 Extract the sample and glass fiber filter by Dean-Stark Soxhlet extraction in section 11.4.

11.3 Aqueous Sample Extraction

11.3.1 Remove the samples from the refrigerator several hours before extraction and allow them to come to room temperature before measuring the volume or performing the extraction. Inspect the sample for solids or biphasic sample characteristics. If either condition exists, document the observation on the sample tracking sheet and consult the project manager for further instructions (see 11.3.6.1 – 11.3.6.4.4 below). If visible solids are present determine the percent solids using the following procedure

11.3.1.1 Add 10 mL of the well shaken sample to a pre-weighed aluminum weighing dish. Weigh the dish to three significant figures. Dry the dish overnight in an oven at 105 °C. Reweigh the dish and calculate the percent solids using the following equation.

$$\%solids = \frac{\text{weight of dish plus sample after drying} - \text{weight of dish}}{\text{weight of dish plus sample before drying} - \text{weight of dish}} \times 100$$

11.3.1.2 If the sample contains >1 percent suspended solids, a sample aliquot sufficient to provide 10 grams of dry solids is used and the sample is extracted following the procedure in section 11.4. If excess liquid is present, the sample may be filtered and the solids and filter extracted as in section 11.3.6.4.

11.3.1.3 If the sample contains ≤1 percent suspended solids the sample is filtered through a Buchner funnel with a 2.7 um glass fiber filter following the procedure in section 11.3.6.4.

11.3.2 Refer to Knoxville SOP, KNOX-QA-0002, current revision, for information on glassware cleaning procedures for extraction glassware. Visually inspect all glassware prior to use for scratches or cracks. Retire and replace any glassware found to be damaged.

11.3.3 Place separatory funnels, one for each sample, the method blank, and the OPR, in the positions in the rotary extractor.

11.3.4 Place a 600 mL concentration tube directly beneath each separatory funnel in the tube holder.

11.3.5 Plug a glass funnel with glass wool and pour in some sodium sulfate (about 1 to 2 inches from the top). Rinse the sodium sulfate with methylene chloride. After the funnel stops dripping, place the funnel on top of the concentrator tube.

11.3.6 If solids are not observed in the sample, mark the level of the sample on the sample bottle in order to measure the volume later and carefully add the sample to the separatory funnel, taking care not to spill any sample. Using a 1000 mL graduated cylinder measure out 1000 mL of reagent water and add to the separatory funnels marked for the method blank , LCS/OPR, and LCSD (if required).

11.3.6.1 If the sample exhibits biphasic characteristics, the sample can either be mixed and extracted as an aqueous sample or the phases can be separated and extracted individually. The decision as to which approach to use should be made in consultation with the Project Manager and the Client. Document the decision process as well as the characteristics and relative volumes of each sample phase.

11.3.6.2 For method 8290, if the sample appears to have a solids content of >1% or is biphasic, the project manager is contacted to determine if the client wants the sample filtered. If so, follow the procedure in section 11.3.6.3. The particulates on the filter and the filter itself may be extracted by soxhlet extraction following the procedure section 11.4. The resulting extract is combined with the extract of the aqueous portion during the concentration step.

11.3.6.3 For method 1613B, if the visible solids appear to be ≤1 percent (≤10g/L of sample) follow the procedure in section 11.3.6.4. If the visible solids appear to be >1 percent follow the procedure in section 11.3.6.4.5.

11.3.6.4 Sample Filtration

11.3.6.4.1 Assemble a Buchner funnel with a rubber stopper on top of a clean filter flask. Insert a 2.7 um glass fiber filter into the funnel. Wet the filter paper with a few mL's of reagent water and apply vacuum to the filter flask.

11.3.6.4.2 Apply vacuum to the flask, mark the level of the sample on the sample bottle in order to measure the volume later and carefully add the sample to the Buchner funnel, swirling the sample remaining in the bottle to suspend any particles.

11.3.6.4.3 Rinse the sample bottle twice with approximately 10 mL portions of reagent water to transfer any remaining particles onto the filter. Rinse any particles off the sides of the Buchner funnel with small quantities of reagent water.

11.3.6.4.4 If the percent solids is ≤1 percent, extract the filtrate in a separatory funnel by proceeding to section 11.3.7. Extract the solids on the filter and the filter itself following the procedure in section

11.4. **Do not add internal standards to this portion of the sample, only add internal standards to the aqueous portion of the sample!** The resulting extract is combined with the extract of the aqueous portion during the macro concentration step in section 11.6.

11.3.6.4.5 If the percent solids is not ≤1 percent, extract the particulates on the filter and the filter itself following the procedure in section 11.4 otherwise follow the instructions in section 11.3.6.4.4.

11.3.7 Using a Class A 1 mL volumetric pipet, add 1 mL of the ^{13}C labeled internal standard spiking solution, as specified in section 7.11.3, to each sample, the method blank, LCS/OPR, LCSD, and MS/MSD (8290 only) samples . Record the amount of spike used and the spike solution number in the standards logbook and on the benchsheet.

11.3.8 Using a Class A 1 mL volumetric pipet, add 1 mL of the PAR native spiking solution, as specified in section 7.11.2, to the designated LCS/OPR, LCSD (if required), and MS/MSD (8290 only) samples. Record the amount of spike used and the spike solution number in the standards logbook and on the benchsheet.

Note: If the volume of standard in the stock container is less than 10mL after use, discard the remaining portion and prepare a new batch as specified in section 7.11.2.

11.3.9 Add 60 mL of methylene chloride to the sample bottle and shake. Then add the methylene chloride to the separatory funnel. Add 60 mL of methylene chloride to the method blank, LCS/OPR , and LCSD (if required) as well.

11.3.10 Securing the separatory funnel with the rotator retaining straps and rotate for 2 minutes.

CAUTION: Care should be used while performing this operation. Vent the separatory funnel frequently. Goggles may be worn when performing this procedure.

11.3.11 Allow the water and the methylene chloride to separate for 10 minutes. If it is not separated after 10 minutes, try to break up the emulsion by gently swirling the sample or tilting the separatory funnel on its side.

11.3.12 Drain the methylene chloride from the separatory funnel into the glass funnel that is filled with sodium sulfate, allowing the extract to drip into the concentrator tube. Be careful not to allow water to escape the separatory funnel or the sodium sulfate will harden and block the flow of the extract. When an emulsion is present, do not drain the emulsion until the third methylene chloride shake has been completed. If at least 10 minutes has elasped and other ways of breaking up or reducing the size of the emulsion have failed the following steps may be tried to reduce the impact of the emulsion on the sodium sulfate.

11.3.12.1 Place a large piece of pre-cleaned glass wool in the funnel containing the sodium sulfate.

11.3.12.2 Spread the glass wool out, covering the entire surface of the sodium sulfate to about a depth of about 5 to 10mm. If the emulsion is hard to break up and persistent, a small, additional layer of sodium sulfate may be added on top of the glass wool.

11.3.12.3 Drain the solvent and emulsion layer into the funnel being careful to drain no more than 60 mL of volume if a clear phase layer cannot be determined.

11.3.12.4 If this procedure is used the funnel should be rinsed with an extra 30ml of methylene chloride to ensure all analytes are rinsed into the concentrator tube after the third portion of methylene chloride has drained through the sodium sulfate in section 11.3.14.

11.3.13 Repeat steps 11.3.9 through 11.3.12 two more times.

11.3.14 After the third methylene chloride portion has filtered through the sodium sulfate, rinse the funnel with approximately 40 mL of methylene chloride.

11.3.15 Remove the separatory funnel from the hood and pour the extracted water into the extracted waters waste carboy.

11.3.16 Fill the empty sample bottle to the marked level with tap water. Pour the tap water into a 1000 mL graduated cylinder. Record the volume of sample used on the benchsheet.

11.3.17 Proceed to Macro Extract Concentration by Rapid-Vap in section 11.7.

11.4 Soxhlet Extraction

11.4.1 Prepare and label the required number of Soxhlet systems.

NOTE: If samples have a high water content (e.g., sludges, pulp samples, etc.) or are to be extracted by method 1613B, a Dean-Stark extractor should be used to remove the water from the sample. The Dean-Stark apparatus is installed between the Soxhlet body and the condenser when the components are assembled.

11.4.1.1 The Soxhlet is prepared by cleaning and rinsing per section 6.1.

11.4.2 Transfer 10±0.05 g of the solid sample (wet weight) into a glass fiber extraction thimble or glass fiber filter paper and put the thimble or filter inside the Soxhlet. If tissue samples are being extracted, add the entire sample and sodium sulfate mixture prepared in section 11.2.1.3. Record the sample and weight on the sample prep sheet. Initial and date the entry. If a sample is designated for MS/MSD analysis (8290 only), prepare two additional portions of the sample and label them as the MS and MSD samples.

Note: The MS and MSD samples must be prepared at the same weight as the OS to avoid calculation errors in the RPD values.

11.4.2.1 For the method blank, LCS/OPR and LCSD (if required) add 10±0.05 g of sand or sodium sulfate to a glass fiber extraction thimble.

11.4.2.2 If the matrix is tissue samples, sodium sulfate and dry ice are used for method blank, LCS/OPR, and LCSD (if required). Transfer 20±0.5 g of the sodium sulfate and several small chips of dry ice into an extraction thimble.

11.4.2.3 Record the blank matrix type and lot number on the bench sheet.

11.4.3 Pour approximately 350 mL toluene into a 500 mL round bottom flask. Place the flask in the heating mantle. Add 10-15 boiling beads and several PFTE boiling chips.

11.4.4 Place the extraction thimble in the glass Soxhlet extractor.

11.4.5 Assemble the Soxhlet system and secure to the lab supports.

11.4.5.1 Place the method blank and QC samples in random postions within the available prep positions in the hood (i.e do not use the same positions each time the method blank and QC samples are prepared). Record the condenser postion and soxhlet set number for the method blank.

11.4.6 Spike each sample with 1.0 ml of the internal standard spiking solution (see section 7.11.3) and add a small amount of glass wool if needed to the top of the extraction thimble. Record the standard solution ID and volume spiked on the sample prep sheet. Initial and date the entry.

Note: Omit this step if internal standards have been previously added to fly ash samples during acid pre-treatment (section 11.2.2.3).

11.4.6.1 Spike the LCS/OPR, LCSD (if required), and MS/MSD (8290 only) samples with 1.0 ml of the PAR native spiking solutions (see section 7.11.2) prior to adding the glass wool. Record the standard solution ID and volume spiked on the sample prep sheet. Initial and date the entry.

Note: If the volume of standard in the stock container is less than 10mL after use, discard the remaining portion and prepare a new batch as specified in section 7.11.2.

11.4.7 Adjust the temperature of the heating mantle to bring the toluene in the round bottom flask to a rolling boil. There should be a steady drip from the condensers so that the solvent should completely cycle at least 5 times an hour. Record the date and time that the soxhlet extraction was started on the benchsheet and initial and date.

11.4.8 Soxhlet extract the sample in the above manner for a minimum of 16 hours. At the end of the extraction period turn off the heating mantles. Record the date and time that the soxhlet extraction was completed on the benchsheet and initial and date.

11.4.9 Remove the condensers and empty the Soxhlet extractor chamber, then remove the Soxhlet extractor from the 500 mL round bottom flask.

11.4.10 Add several (2-3) fresh boiling chips to the flasks. Insert a three-ball macro Snyder column into the top of the 500 mL round flask.

11.4.11 Place the 500 mL flask back into the heating mantle and reduce the extract volume to approximately 10-15 mL.

11.4.12 Transfer the extract into a 40 mL vial containing 100 uL of tetradecane, rinsing the 500 mL flask 3 times with 3 mL of toluene. Add the rinsings to the 40 mL vial.

11.4.13 Place the 40 mL vials into the nitrogen concentration device and reduce the volume to near dryness. Add 4 mL of hexane and swirl the vial. Reduce the volume of hexane to near dryness again to complete the solvent exchange. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipet to the vial to aid in dissolving the residue. Adjust the final volume of the extract with hexane to 12 mL for acid-base cleanup or 2 mL for column cleanup. Proceed to sample cleanup in section 11.8.

11.5 Waste Dilution

11.5.1 Organic wastes, oil, solids that will dissolve in solvent, and non-aqueous sludge samples may be prepared by the waste dilution technique.

11.5.2 Tare a clean 40 mL VOA vial on a laboratory balance. Add an appropriate amount of sample (e.g., 1.0 g) to the VOA vial. If a sample is designated for MS/MSD analysis (8290 only), prepare two additional portions of the sample and label them as the MS and MSD samples. Prepare method blank, LCS/OPR, and LCSD (if required) samples by adding 12 mL of hexane to a 40 mL VOA vial.

11.5.3 Record the weights and volumes used on the laboratory bench sheets and initial and date.

11.5.4 Add 1.0 ml of the internal standard spiking solution (see section 7.11.3) to the samples, method blanks, and QC samples. Record the spike solution number and the volume spiked on the sample prep sheet. Initial and date the entry. Add hexane to bring the volume to 12 mL. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipet to the vial to aid in dissolving the sample.

11.5.5 Add 1.0 ml of the PAR native spiking solutions (see section 7.11.2) to the LCS/OPR, LCSD (if required), and MS/MSD (8290 only) samples. Record the spike solution identification number and the volume spiked on the sample prep sheet. Initial and date the entry.

11.5.6 Proceed to sample extract cleanup in section 11.8.

11.6 Air Sampling Trains

11.6.1 For media and sample preparation of air sampling trains refer to Knoxville SOP, KNOX-ID-0012.

11.7 Macro Extract Concentration by Rapid-Vap

11.7.1 Preheat the unit to the appropriate temperature for the solvent used in the extraction.

11.7.2 Set the operating parameters on the programmer. For example, if there is 300 ml of a methylene chloride extract, the following parameters may be used and should be adjusted as needed:

Temperature	30 °C
Vortex Speed	30%, to be increased at a later time
Nitrogen	7-9 psi
Timer Set	30 minutes

11.7.3 Place 600 ml concentrator tubes containing the extract in the Rapid-Vap. Begin concentrating the extract, adjust the vortex speed for the proper rate of concentration.

11.7.4 When the extract has been concentrated to less than 20 mL, add approximately 60 mL of hexane. Concentrate the extract to a final volume of approximately 2 ml. Shut off the nitrogen flow and turn off the Rapid-Vap or remove the 600 mL concentrator tube to prevent further concentration.

11.7.5 Transfer the extract to a 40 ml vial with a 9” disposable pipet, rinsing the sample tube three times with 3 ml of hexane. Reduce the volume in the 40 mL vial using the N-Evap to approximately 2 ml and proceed to extract cleanup in section 11.8. If no additional cleanups are to be performed continue with the the follwing steps to dry the extract.

11.7.6 Prepare a small funnel by putting a small plug of pre-cleaned glass wool to the bottom of the funnel and adding a layer of sodium sulfate on top of the glass wool.

11.7.7 Pipet the extract from the Rapi-Vap concentrator tube and through the funnel containing the sodium sulfate into a 40ml vial.

11.7.8 Rinse the concentrator tube 3 times with approximately 3ml of hexane for each rinse. The sodium sulfate funnel then should be rinsed with an additional 2ml of hexane. Proceed to micro concentration in section 11.9.

11.8 Sample Extract Cleanup

11.8.1 For 1613B samples, add 1.0 mL of the ^{37}Cl-,2,3,7,8-TCDD cleanup standard (see section 7.11.6) to each sample extract as well as the method blank and OPR sample extracts.

11.8.2 Acid-Base Cleanup

The acid-base cleanup is employed when sample extracts are colored and/or oily in appearance, or if specified by the client or project manager.

11.8.2.1 Bring the extract volume up to ~15 mL with hexane in a 40 ml vial.

NOTE: If the extracts are from fish tissue, omit sections 11.8.2.2 and 11.8.2.3.

11.8.2.2 Wash the extract by adding 10 mL of 20% aqueous potassium hydroxide to the vial and gently shaking for 20 seconds. If an emulsion begins to form, discontinue shaking. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer with a glass pipet, taking care not to remove any of the solvent layer or remaining emulsion. Repeat the base washing until no color is visible in the base layer (perform a maximum of four base washings).

11.8.2.3 Add 10 mL of 5% (w/v) aqueous sodium chloride to the vial and gently shake for 20 seconds. If an emulsion forms, discontinue shaking. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer with a glass pipet, taking care not to remove any of the solvent layer or remaining emulsion.

11.8.2.4 Slowly add 15 mL of concentrated sulfuric acid to the vial and shake for 30 seconds. If an emulsion forms, discontinue shaking. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer with a glass pipet, taking care not to remove any of the solvent layer or remaining emulsion. Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

11.8.2.5 Add 10 mL 5% (w/v) aqueous sodium chloride to the vial and gently shake for 20 seconds. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer with a glass pipet, taking care not to remove any of the solvent layer or remaining emulsion. Dry the hexane extract by adding 1 to 2 grams of sodium sulfate and swirling the vial.

11.8.2.6 Reduce the extract volume to approximately 2 ml.

11.8.2.7 Proceed to section 11.8.3, silica gel/alumina column cleanup.

11.8.3 Silica gel/alumina column cleanup

Silica gel/alumina column cleanup is employed when sample extracts are clear or after other cleanup techniques have been employed. If treated drinking water samples are being analyzed, further cleanup may not be necessary.

11.8.3.1 Prepare a 20mm diameter column and a 16mm diameter column for each extract by rinsing, in order, with acetone, toluene, methylene chloride and hexane. Place a large ball of pre-cleaned glass wool in the bottom of each column.

11.8.3.2 Mark the level to which the column packings will be added with a marking pen starting at the top of the glass wool plug and proceeding from bottom to top. The levels for each type column are as follows;

20 mm Silica Gel column
- 12 mm – 2g of 3.3% deactivated silica gel
- 16 mm – 4g of acidic silica gel
- 12 mm - 2g of 3.3% deactivated silica gel
- 10 mm – sodium sulfate

16 mm Alumina Column
- 40 mm – 6 g of neutral alumina
- 10 mm – sodium sulfate

11.8.3.3 Place the columns to the lab supports in the hood so that the 20 mm silica gel column is above the 16 mm alumina column. Offset the columns slightly so that the packings can be added and the columns rinsed.

11.8.3.4 Add the column packing in the order listed above while tapping with a marking pen to column to settle the contents to prevent channeling. When the columns have been completely packed, remove the lower columns from the support rack and remove the ink markings with a paper towel moistened with methylene chloride. Replace the columns in the rack.

11.8.3.5 Place a 125ml glass jar under the lower alumina column to catch the solvent wastes and eluants as they filter through the column.

11.8.3.6 Measure out 60ml of Hexane using a graduated cylinder and pour it into a 100ml volumetric flask, one flask for each set of columns, to be used later in the procedure. Do not use this hexane for the column rinsing in the next section.

11.8.3.7 Add 20 ml of hexane to each column to rinse the packing. Collect the hexane from the columns in the 125 mL glass jar, the columns must be aligned so that the waste does not drip on the surface of the hood. When the level of solvent in the silica gel column approaches the top of the packing, move the upper column support so that the tips of the upper columns are inserted into the tops of the lower columns and the solvent will drip into the lower columns.

11.8.3.8 Just as the level of hexane reaches the top of the packing in the silica gel column transfer the sample extract into the top of the column. Rinse the extract vial 3 times with 1.5ml of Hexane and add each of these rinsings to the silica gel column.

11.8.3.9 Just as the solvent level reaches the top of the column packing pour the 60ml of hexane into the top of the silica gel column and allow this to drip into and through the alumina column and into the collection jar. When the hexane has completely drained from the silica gel column, remove the column from the support rack and dispose of it in the appropriate waste container.

11.8.3.10 Just as the level of hexane reaches the top of the packing in the alumina column using a solvent dispenser add 10ml of 5% methylene chloride/hexane mixture. Immediately after adding the 5% mixture replace the 125 mL glass jar containing the solvent waste with 40ml vial which has been labeled with the sample workorder number. Dispose of the solvent waste in the 125 mL glass jar in the appropriate waste collection container.

11.8.3.11 Just as the level of the 5% mixture reaches the top of the packing in the alumina column add 30ml of 65% methylene chloride/hexane using a solvent dispenser and continue to catch the eluants in the 40ml vial.

11.8.3.12 When the solvent has completely drained from the alumina column, cap the 40 mL vial containing the eluant and dispose of the alumina column in the appropriate waste container.

11.8.3.13 If no further cleanup is to be performed, proceed to final extract micro concentration. Otherwise, reduce the volume of the extract to approximately 2ml using the nitrogen micro concentration apparatus and proceed to the next cleanup.

11.8.4 Activated carbon cleanup

Carbon column cleanups should be performed when site history indicates carbon columns are necessary for removal of interferences. Carbon columns should also be run if, when running the extracts through dual columns, it is noticed that the acid silica layer becomes colored along the entire length of the acid silica.

11.8.4.1 Prepare a 10 mL disposable pipette by cutting off the tapered end to achieve a 12-cm column. Insert a glass-wool plug of about 1 cm in length at one end and pack the column with 4.1 cm of the of the AX-21 Carbon/Silica Gel mixture. Hold the packing by inserting an additional glass wool plug, again about 1 cm in length, in the other end.

11.8.4.2 Pre-elute the column with 10 mL of cyclohexane/methylene chloride (50:50 v/v). Turn the column over and pre-elute in the opposite direction with another 5 mL of cyclohexane/methylene chloride (50:50 v:v).

11.8.4.3 When the solvent reaches the glass wool, add the sample extract. Rinse the sample vial 2 times with 2 ml of 50/50 cyclohexane/methylene chloride. Add these rinses to the column. Elute the column with the following sequence of solvents:

11.8.4.3.1 6 mL of cyclohexane/methylene chloride (50:50 v/v).

11.8.4.3.2 5 mL of methylene chloride/methanol/benzene (75:20:5 v/v).

11.8.4.4 Allow the 75:20:5 methylene chloride/methanol/benzene to drain completely. Turn the column over and in the direction of reverse flow elute the PCDD/ PCDF fraction with 25 mL toluene into a 40 mL vial containing 100 uL of tetradecane.

11.8.4.5 Place vials containing the extract in the nitrogen concentration apparatus and reduce the solvent volume to approximately 0.3 ml.

11.9 Micro Extract Concentration by Nitrogen Blowdown.

11.9.1 When all cleanups have been completed on the sample, add 20 ul of the labeled recovery standard spiking solution (see section 7.11.8) to an empty clean 1.1 ml tapered minivial that has been labeled with the sample ID. Mark the level of the recovery standard on the minivial (mark half the level, 10 µL, if the extracts are from treated drinking waters). Record the volume of recovery standard added on the benchsheet.

11.9.2 Transfer the concentrated extract into the mini-vial. Rinse the 40 ml vial at least twice with a small amount of hexane and add the rinses to the minivial. Put the minivial on the N-EVAP nitrogen blowdown and reduce the volume to the mark on the vial. Put the cap with PFTE-faced septa securely on the vial. Record the final extract volume on the benchsheet.

11.9.3 All items listed on the data review check list must be checked by both the prep analyst who performed the extraction and cleanups and the prep analyst who performed the second level review. An example data review check list is shown in Figure 4.

11.9.4 Transfer the extracts and paperwork to the GC/MS group for analysis.

11.10 Sample Extract Analysis

11.10.1 Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 2 µL into the GC/MS and acquire data until OCDF has eluted from the column.

11.10.2 Record analysis information in the instrument logbook. The following information is required:

Date of analysis
Time of analysis
Instrument data system filename
Analyst
Lab sample identification

Additional information may be recorded in the logbook if necessary.

11.10.3 Generate ion chromatograms for the masses listed in Table 21 that encompass the expected retention windows of the PCDD and PCDF homologous series.

12. Data Analysis and Calculations

12.1 Refer to Figure 4 for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.2 Qualitative identification criteria for PCDDs and PCDFs. For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

12.2.1 The ion current response for both ions used for quantitative purposes must reach maximum simultaneously (± 2 seconds).

12.2.2 The signal-to-noise ratio (S/N) for each GC peak at each exact m/z must be ≥ 2.5 for positive identification of a PCDD/PCDF compound.

12.2.3 The ratio of the integrated areas of the two exact m/z's specified in Table 21 must be within the limits specified in Table 22, or alternatively when performing method 1613B, within ±10 percent of the ratio in the midpoint (CS3) calibration or the calibration verification (VER), whichever is most recent.

12.2.4 Method 1613B only - The relative retention time of the peak for a 2,3,7,8-substituted PCDD or PCDF must be within the limits in Table 3.

12.2.5 Method 8290 and 0023A only - For 2,3,7,8-substituted isomers, which have an isotopically labeled internal standard or recovery standard present in the sample extract, the retention time of the two ions used for quantitation purposes must be within -1 to +3 seconds of the isotopically labeled standard.

12.2.6 Method 23 and TO-9A only - For 2,3,7,8-substituted isomers, which have an isotopically labeled internal standard or recovery standard present in the sample extract, the retention time of the two ions used for quantitation purposes must be within ±3 seconds of the isotopically labeled standard.

12.2.7 Method 8290, 23, 0023A, and TO-9A only - For 2,3,7,8-substituted isomers, which do not have an isotopically labeled internal standard present in the sample extract, the retention time must fall within 0.005 retention time units of the relative retention times measured in the routine calibration.

12.2.8 The retention time of peaks representing non-2,3,7,8-substituted PCDDs/PCDFs must be within the retention time windows established in section 10.2.4.

12.2.9 No peaks detected in the polychlorinated diphenyl-ether (PCDPE) mass channel in the same retention time region (± 2 sec for method 8290 & 0023A) as a PCDF peak.

12.3 Quantitation for PCDD's and PCDF's.

12.3.1 Calculate the Internal Standard and Cleanup Standard Recoveries (Ris) relative to the Recovery Standard according to the following equation:

$$\mathrm{Ris} = \frac{\mathrm{Ais} \times \mathrm{Qrs}}{\mathrm{Ars} \times \mathrm{RRFis} \times \mathrm{Qis}} \times 100\%$$

where:

Ais = sum of the areas of the quantitation ions of the appropriate internal standard (cleanup standard is single ion)
Ars = sum of the areas of the quantitation ions of the recovery standard
Qrs = ng of recovery standard added to extract
Qis = ng of internal standard added to sample
RRFis = mean relative response factor of internal standard obtained during initial calibration

Note: In some situations, such as high-volume water sampling or air train samples, the extract is split for multiple analyses. In this case, Qrs must be correctly calculated to account for the splitting of extracts before the recovery standard was added.

$$Qrs = \frac{Crs \times Vrs}{S}$$

Where:
Qrs = ng of recovery standard added to extract
Crs = concentration of recovery standard added to the split portion of the extract
Vrs = volume of recovery standard added to the split portion of the extract
S = split ratio of the extract (decimal fraction of the extract used)

12.3.2 The split ratio represents the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards. The split ratio is calculated as the product of all split ratios generated between these steps:

$$S = Spis \times Spcs \times Spfc$$

Where:
Spis = the decimal fraction of extract used from split taken once the internal standard has been added and the extraction is performed.
Spcs = the decimal fraction of extract used from split taken once the cleanup standard (if used) has been added.
Spfc = the decimal fraction of extract used from split taken once the cleanup fractionation column has been run.

12.3.3 When properly applied, isotope dilution techniques produce results that are independent of recovery. The recovery of each internal standard should be within the limits specified in Table 13 for method 1613B or 8290 or in Table 15 for method 23, 0023A, or TO-9A. If the recovery of any internal standard is not within the specified limits, calculate the S/N ratio of the internal standard. If the S/N is ≥ 10 and the method minimum levels are met, report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the minimum levels are not achieved, re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample may be re-extracted or additional clean-ups may be employed.

12.3.4 Calculate the concentration of target analytes according to the following equation:

$$C = \frac{Ata \times Qis}{Ais \times RRF \times Ws \times Ssl}$$

Where:

Ata = sum of the areas of the quantitation ions of the target analyte
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor from initial calibration.
Ws = amount of sample spiked and extracted (grams or liters)
Ssl = decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

Note: The percent solids calculation is performed by the laboratory LIMS system prior to final reporting.

12.3.5 The concentrations of non-2,3,7,8-isomers are calculated using the RRF for the corresponding 2,3,7,8-isomer. If more than one 2,3,7,8-isomer exist for a particular level of chlorination, the average of the individual 2,3,7,8-isomer RRF's is used in the calculation.

12.3.6 Calculate the total concentration of all isomers within each homologous series of PCDD's and PCDF's by summing the concentrations of the individual PCDD or PCDF isomers.

12.3.7 If no peaks are present in the region of the ion chromatogram where the compounds of interest are expected to elute, calculate the estimated detection limit (EDL) for that compound according to the following equation:

$$EDL = \frac{N \times 2.5 \times Qis}{His \times RRFs \times Ws \times Ssl}$$

Where:

N = average peak to peak noise of quantitation ion signals in the region of the ion chromatogram where the compound of interest is expected to elute
His = peak height of quantitation ions for appropriate internal standard
Qis = ng of internal standard added to sample
RRFs = mean relative response factor of compound for the shift opening and closing standards
W = amount of sample spiked and extracted (grams or liters)
Ssl = decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

Note: The percent solids calculation is performed by the laboratory LIMS system prior to final reporting.

12.3.8 If peaks are present in the region of the ion chromatogram which do not meet the qualitative criteria listed in section 12.2.3, calculate an Estimated Maximum Possible Concentration (EMPC). Two different calculation formulas may be used depending upon specific client requirements.

12.3.8.1 When performing method 8290 for EPA regulated analyses where the currently promulgated method is required by law (e.g. Trial Burns) and for all other analyses unless the client has

specified otherwise, use the equation in section 12.3.4, except that Ata should represent the sum of the area under the one peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The peak selected to calculate the theoretical area should be the one which gives the lower of the two possible results (i.e. the EMPC will always be lower than the result calculated from the uncorrected areas).

12.3.8.2 When the client has specifically requested, use the equation in section 12.3.4 without correcting the areas. This method will give an EMPC which is always higher than the method above and would be considered the worst case.

12.3.9 If peaks are present in the diphenyl ether mass channel at the same retention time as a PCDF peak, the peak cannot be identified as a PCDF. Calculate the concentration of the peak using the equation in section 12.3.4 but report the concentration as an Estimated Maximum Possible Concentration.

12.3.10 If the concentration in the final extract of any 2,3,7,8-substituted PCDD/PCDF isomer (except OCDD or OCDF) exceeds the upper method calibration limits, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. For the other congeners (including OCDD and OCDF), however, report the measured concentration and indicate that the value exceeds the calibration limit by flagging the results with "E". Dilutions of up to 1/10 may be performed on the extract. If the compounds that exceed the calibration range cannot be brought within the calibration range by a 1/10 dilution, extraction of a smaller aliquot of sample may be performed or the sample may be analyzed by a more appropriate analytical technique such as HRGC/LRMS. Consultation with the client should occur before any re-extraction is performed.

12.3.11 Evaluate the ion chromatograms of the PFK lock mass and calibration mass for each MID group. The PFK mass intensity should be consistent throughout the retention time of the target compounds. Negative excursions or variations in the PFK mass intensity indicate the elution of interferences from the GC column that are causing suppression in the ion source of the mass spectrometer. This ion suppression can reduce the instrument sensitivity and quantitative result of any peaks that elute at the same retention time. Either additional extract cleanup or dilutions can reduce ion suppression. The quantitative results should be carefully evaluated when there is evidence of ion suppression present in the PFK mass traces.

12.4 The DB-5 (RTX-5) column does not provide for isomer specificity of 2,3,7,8-TCDF using the operating condition required for this method. If a peak is determined to be present at the expected retention time of 2,3,7,8-TCDF and its calculated concentration is above the MinL, the sample extract must be analyzed on the DB-225 (RTX-225) column.

12.5 The Minimum Level (MinL) is defined as the level at which the instrument gives acceptable calibration assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. Deviation from the extraction amounts or final volumes listed Table 2 changes the MinL. The MinL is calculated as shown in the following equation:

$$\text{MinL} = \frac{C\min \times Vfe}{W\text{s}}$$

Where:

Cmin = the concentration the analyte in the lowest calibration standard
Ws = amount of sample spiked and extracted (grams or liters)
Vfe = the final volume of the extract, corrected for all splits and dilutions

$$\mathrm{V}fe = \frac{Vdel \times DFpr}{Spr \times S}$$

Where:

Vdel = the volume of extract delivered to the analysis
DFpr = the dilution factor for dilutions performed to the final extract
Spr = the split ratio for any post-recovery standard splits
S = the split ratio for any post-internal standard and post-cleanup standard splits

12.6 The Maximum Level (MaxL) is defined as the concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The MaxL is calculated as shown in the following equation:

$$\mathrm{M}axL = \frac{C\max \times Vfe}{W\mathrm{s}}$$

Where:

Cmax = the concentration the analyte in the highest calibration standard
Vfe and Ws are defined in Section 12.5.

12.7 Flag all compound results in the sample that were detected in the method blank with a “B” qualifier.

12.8 Flag all compound results in the sample that are below the minimum level with a “J” qualifier.

12.9 Flag all compound results in the sample that are above the upper calibration limit with an “E” qualifier.

12.10 Flag all compound results in the sample that are “Estimated Maximum Possible Concentrations” with a “Q” qualifier.

12.11 Flag compound results in the sample that exhibit chromatographic evidence of co-eluting compounds with a “C” qualifier.

12.12 Flag compound results in the sample that may be affected by ion suppression with a “S” qualifier.

12.13 Data review

12.13.1 The analyst who performs the initial data calculations must initial and date the front chromatogram of the raw data package to document that they have performed the qualitative and quantitative analysis on the sample data.

12.13.2 A second analyst must verify all qualitative peak identifications. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.13.3 A second analyst must check all hand calculation and data entry into calculation programs, databases, or spreadsheets at a frequency of 100 percent. If discrepancies are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.13.4 The reviewing analyst must initial and date the front chromatogram of the raw data package to document that they have performed the second level review on the sample data.

12.13.5 All items listed on the data review check list must be checked by both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review. An example data review check list is shown in Figure 4.

13. Method Performance

13.1 Method Detection Limit (MDL) - An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP S-Q-003, current revision, based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit. MDL summaries are stored on the local area network.

13.2 Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in STL Knoxville SOP KNOX-QA-0009.

13.3 Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009 current revision for further requirements for performing and documenting initial and on-going demonstrations of capability.

14. Pollution Prevention

14.1 All procedures shall be conducted in a manner to minimize, as far as practical, the use of solvents, reagents and other chemicals.

15. Waste Management

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 Waste Streams Produced by the Procedure: The following waste streams are produced when this method is carried out.

- Waste methylene chloride from quartz fiber filter preparation, PUF adsorbent preparation, XAD-2 resin preparation, PUF/XAD-2 cartridge preparation, glassware rinsing and sodium sulfate pre-rinsing. See SOP KNOX-HS-0017, "Waste Accumulation and Collection" for specific guidelines.
- Waste acetone and hexane from glassware and acid rinsing. See SOP KNOX-HS-0017, "Waste Accumulation and Collection" for specific guidelines.
- Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials that may or may not be contaminated/hazardous. See SOP KNOX-HS-0017, "Waste Accumulation and Collection" for specific guidelines.
- Extracted PUF filters, XAD-2 resin, paper funnel filters, glass wool, fish/crawfish and soil contaminated with methylene chloride. See SOP KNOX-HS-0017, "Waste Accumulation and Collection" for specific guidelines.
- Contaminated sulfuric acid used during extract cleanup. See SOP KNOX-HS-0017, "Waste Accumulation and Collection" for specific guidelines.
- Extracted aqueous samples, contaminated with methylene chloride.See SOP KNOX-HS-0017, "Waste Accumulation and Collection" for specific guidelines. S
- Silica gel, alumina, carbon and sodium sulfate, from column clean-ups, contaminated with various solvents and eluates. See SOP KNOX-HS-0017, "Waste Accumulation and Collection" for specific guidelines.

16. References

16.1 STL Quality Management Plan (QMP), current revision.

16.2 STL Knoxville Laboratory Quality Manual (LQM), current revision.

16.3 EPA Method 1613: Tetra- Through Octa- Chlorinated Dioxins And Furans by Isotope Dilutions HRGC/HRMS, Revision B, October 1994

16.4 USEPA SW-846 "Test Methods for Evaluating Solid Waste" Third Edition, Method 8290 and 0023A.

16.5 USEPA Method 23 – Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors. 40 CFR Part 60 Appendix A.

16.6 Method TO-9A: Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition EPA/625/R-96/010b.

16.7 STL SOP, KNOX-ID-0012, Method 0023A and Method 0010 Sampling Train Pre-Sampling Preparation and Sample Extraction Procedure (Includes TO-9A Sampling Components).

16.8 STL SOP, KNOX-QA-0002, Glassware Cleaning, current revision.

16.9 STL Policy, P-T-001, Selection of Calibration Points.

17. Miscellaneous

17.1 Deviations from reference method.

17.1.1 Spiking levels have been reduced to minimize the amount of dioxin contaminated waste generated by this procedure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.2 Method 1613B employs a gravimetric determination of sample size rather than a volumetric determination. This procedure employs a volumetric determination of sample size to allow reporting of sample concentration in the standard units of pg/L (ppq). This modification has no impact on the performance criteria of this method.

17.1.3 The solids determination has been modified from that specified by method 1613B. The modification reduces the sample prep turnaround time by eliminating the need to perform solids determinations on every aqueous sample with visible particles. This modification has no impact on the performance criteria of this method.

17.1.4 The determination of solids content procedure used for aqueous samples is the same as the 1613B procedure used for solid samples rather than the 1613B procedure for aqueous samples. The aqueous sample procedure in 1613B is subject to error if the sample density is not exactly 1.0 g/mL.

17.1.5 The amount of hexane used in the solvent exchange step has been reduced from that specified in the reference methods. The reduction in solvent used is a pollution prevention measure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.6 Method 1613B specifies that the sample bottle is rinsed twice with 5 mL of reagent water after the sample is transferred to the separatory funnel. This procedure specifies that the sample bottle is rinsed three times with methylene chloride after the sample is transferred to the separatory funnel. This modification improves the removal of target compounds from the sample bottle.

17.1.7 The separatory funnel is only rinsed once with methylene chloride after the sample is extracted instead of three times as specified in Method 1613B. The reduction in solvent used is a pollution prevention measure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.8 Toluene volumes and cycle rates for Soxhlet extractors have been optimized for the specific size of glassware used and may not be the same as those specified in the referenced method. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.9 Soxhlet extracts are not filtered before concentration and solvent exchange. The use of glass wool in the extraction thimbles eliminates the transfer of particles to the extraction solvent. The column cleanup procedures remove any particulate that may not be removed by the glass wool. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.10 Extraction amounts are based on wet weight as opposed to the adjusted amount based on percent moisture as specified in method 1613B. Particle size determination and reduction as specified in method 1613B is not performed on a routine basis. Silica and sand is not added to the Soxhlet extraction thimble as specified in method 1613B. Fish tissues are extracted with toluene rather than methylene chloride/hexane as specified in method 1613B. These procedures are considered to be outside the scope of the laboratories routine extraction procedures and are only performed on a client specific or project

specific basis. These procedures, if required, will be specified and documented in the appropriate QAPP's.

17.1.11 Benzene is used to aid in dissolving the samples and/or extracts in hexane. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.12 The absolute retention time requirements in Method 1613 section 15.4.1.1 is not required in this procedure. The routine maintenance required of GC columns when analyzing samples from hazardous waste sites makes this requirement virtually impossible to meet in a commercial laboratory environment. This requirement provides no additional quality assurance purpose beyond those already provided by the use of labeled internal standards and required relative retention time limits.

17.1.13 This procedure provides for additional calculation and reporting of sample specific detection limits and estimated maximum possible concentrations not required by Method 1613. These reporting conventions are similar to those required by EPA SW-846 Method 8290 and expected by data users familiar with EPA Office of Solid Waste program requirements.

17.1.14 The acid-base cleanup procedure is carried out in a VOA vial instead of a separatory funnel. Disposable glassware is used to decrease the risk of cross contamination. The volumes of the washes used have been adjusted for use in the VOA vials. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.15 The silica gel/alumina column cleanup used in this procedure has been optimized relative to amount and order of packings and may vary from the various columns and packings specified in the referenced methods. The solvent volumes and mixtures have been optimized based on evaluation of the elution of native and labeled standards. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.16 The carbon column used in this procedure is based on the column specified in method 8280. Silica gel is used as the carbon column support instead of Celite 545® as specified in methods 8290 and 1613B. It has been determined that silica gel is less likely to contain contaminants and interferences which are not removed by the precleaning procedures than Celite 545®, yet performs similarly. The solvents and elution schemes used are as specified in method 8280 rather than 8290 and 1613B. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.17 The calibration standards specified in method 23 are used for method 0023A and TO-9A.

17.1.18 Extracts are stored at room temperature rather than at <10 °C. The reference method requires that standards be stored at room temperature. Recovery studies performed by Cambridge Isotopes Laboratories (CIL) indicate freezing or refrigeration of standards causes problems with precipitation. CIL recommends the storage of standards and extracts at room temperature as long as they are protected from exposure to UV and evaporative losses.

17.2 Summary of modifications to SOP for revision 3.

17.2.1 Incorporated all PCDD/PCDF analysis methods including 8290, 23, 0023A, and TO-9A into this method.

17.2.2 Revised all Tables to reflect requirements for each analysis method.

17.2.3 Removed instruction to follow carbon cleanup with silica gel/alumina cleanup.

17.2.4 Modified the solids determination procedure in section 11.3.6.4 from that specified by method 1613B.

17.3 List of tables and figures referenced in the body of the SOP.

17.3.1 Table 1 – Polychlorinated Dibenzodioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography /High Resolution Mass Spectrometry (HRGC/HRMS)

17.3.2 Table 2 – Methods – All, Minimum Levels by Matrix

17.3.3 Table 3 – Methods – 1613B and 8290, Retention Time References, Quantitation References, and Relative Retention Times

17.3.4 Table 4 – Methods – 23, 0023A, and TO-9A, Retention Time References and Quantitation References.

17.3.5 Table 5 – Methods – 1613B and 8290, Initial Calibration Standard Concentrations and Acceptance Criteria.

17.3.6 Table 6 – Methods – 23, 0023A, and TO-9A, Initial Calibration Standard Concentrations and Acceptance Criteria.

17.3.7 Table 7 – Methods – 1613B and 8290, Daily Verification Standard (VER) Concentrations and Acceptance Criteria.

17.3.8 Table 8 – Methods – 23, 0023A, and TO-9A, Daily Verification Standard (VER) Concentrations and Acceptance Criteria.

17.3.9 Table 9 – Method – 1613B, Initial Precision and Recovery (IPR) Acceptance Criteria.

17.3.10 Table 10 – Methods – 8290, 23, 0023A, and TO-9A, Initial Precision and Recovery (IPR) Acceptance Criteria.

17.3.11 Table 11 – Laboratory Control Sample (LCS/OPR) Spiking Solution Component Concentrations and Acceptance Limits.

17.3.12 Table 12 – Method – 8290. Matrix Spike and Matrix Spike Duplicate Sample (MS/MSD) Spiking Solution Component Concentrations and Acceptance Limits.

17.3.13 Table 13- Methods – 1613B and 8290, Internal Standard Spiking Solution Component Concentrations and Acceptance Limits.

17.3.14 Table 14 – Method – 1613B, Cleanup Standard Spiking Solution Component Concentrations and Acceptance Limits.

17.3.15 Table 15 – Methods – 23, 0023A, and TO-9A, Internal Standard Spiking Solution Component Concentrations and Acceptance Limits.

17.3.16 Table 16 – Methods – 23, 0023A, and TO-9A, Surrogate Standard Spiking Solution Component Concentrations and Acceptance Limits.

17.3.17 Table 17 – Methods – All, Recovery Standard Spiking Solution Component Concentrations.

17.3.18 Table 18 – Rtx-5/DB-5 Column Window Defining Standard Mixture Components.

17.3.19 Table 19 – Rtx-5 (DB-5) Column Performance Standard Mixture Components.

17.3.20 Table 20 – DB-225 (Rtx-225) Column Performance Standard Mixture Components.

17.3.21 Table 21 – Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs.

17.3.22 Table 22 – Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs.

17.3.23 Figure 1 – Recommended GC Operating Conditions.

17.3.24 Figure 2 – Recommended MID Descriptors.

17.3.25 Figure 3 – Example Sample Prep Benchsheet

17.3.26 Figure 4 – Example Data Review Checklist.

17.3.27 Figure 5 – Aqueous sample Extraction Flowchart

17.3.28 Figure 6 – Solid Sample Extraction Flowchart

17.3.29 Figure 7 – Sample Cleanup Flowchart

17.3.30 Figure 8- Analysis of PCDD's and PCDF's by HRGC/HRMS Flowchart.

History of Revisions

HISTORY OF REVISION PAGE

REV NO.	DATE	PAGES AFFECTED	REASON FOR REVISION
0	02/26/97	All	Initial version of the SOP
1	08/31/99	All	Procedure review.
2	01/28/02	All	Procedure review.
3	04/26/03	All	Procedure review
4	11/12/03	56 of 83	Corrected the %D for $^{13}C_{12}$-1,2,3,6,7,8-HxCDD and –HxCDF for 23 and TO-9A. Updated sections 5 and 15 to meet corporate EH&S requirements.
5	6/18/04	All	Added information to sections 3.37, 8.1, 12.1, 13.1, Appendix I.

Table 1

Polychlorinated Dibenzodioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography /High Resolution Mass Spectrometry (HRGC/HRMS)

PCDD's/PCDF's [1] Isomer/Congener	CAS Registry	Labeled Analog	CAS Registry
2,3,7,8-TCDD	1746-01-6	$^{13}C_{12}$-2,3,7,8-TCDD	76523-40-5
		$^{37}Cl_4$-2,3,7,8-TCDD	85508-50-5
Total TCDD	41903-57-5		
2,3,7,8-TCDF	51207-31-9	$^{13}C_{12}$-2,3,7,8-TCDF	89059-46-1
Total TCDF	55722-27-5		
1,2,3,7,8-PeCDD	40321-76-4	$^{13}C_{12}$-1,2,3,7,8-PeCDD	109719-79-1
Total PeCDD	36088-22-9		
1,2,3,7,8-PeCDF	57117-41-6	$^{13}C_{12}$-1,2,3,7,8-PeCDF	109719-77-9
2,3,4,7,8-PeCDF	57117-31-4	$^{13}C_{12}$-2,3,4,7,8-PeCDF	116843-02-8
Total PeCDF	30402-15-4		
1,2,3,4,7,8-HxCDD	39227-28-6	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	109719-80-4
1,2,3,6,7,8-HxCDD	57653-85-7	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	109719-81-5
1,2,3,7,8,9-HxCDD	19408-74-3	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	109719-82-6
Total HxCDD	34465-46-8		
1,2,3,4,7,8-HxCDF	70648-26-9	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	114423-98-2
1,2,3,6,7,8-HxCDF	57117-44-9	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	116843-03-9
2,3,4,6,7,8-HxCDF	60851-34-5	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	116843-05-1
1,2,3,7,8,9-HxCDF	72918-21-9	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	116843-04-0
Total HxCDF	55684-94-1		
1,2,3,4,6,7,8-HpCDD	35822-46-9	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	109719-83-7
Total HpCDD	37871-00-4		
1,2,3,4,6,7,8-HpCDF	67562-39-4	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	109719-84-8
1,2,3,4,7,8,9-HpCDF	55673-89-7	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	109719-94-0
Total HpCDF	38998-75-3		
OCDD	3268-87-9	$^{13}C_{12}$-OCDD	114423-97-1
OCDF	39001-02-0	none	

Notes:

1. Polychlorinated dioxins and furans

TCDD =	Tetrachlorodibenzo-p-dioxin	TCDF =	Tetrachlorodibenzofuran
PeCDD =	Pentachlorodibenzo-p-dioxin	PeCDF =	Pentachlorodibenzofuran
HxCDD =	Hexachlorodibenzo-p-dioxin	HxCDF =	Hexachlorodibenzofuran
HpCDD =	Heptachlorodibenzo-p-dioxin	HpCDF =	Heptachlorodibenzofuran
OCDD =	Octachlorodibenzo-p-dioxin	OCDF =	Octachlorodibenzofuran

Table 2

Methods – All
Minimum Levels by Matrix

Analyte	Extract (ng/mL) [1]	Water (pg/L) [2]	Solid (pg/g) [3]	Waste (pg/g) [4]	Air/Wipe (pg) [5]
2,3,7,8-TCDD	0.5	10	1.0	10	10
2,3,7,8-TCDF	0.5	10	1.0	10	10
1,2,3,7,8-PeCDD	2.5	50	5.0	50	50
1,2,3,7,8-PeCDF	2.5	50	5.0	50	50
2,3,4,7,8-PeCDF	2.5	50	5.0	50	50
1,2,3,4,7,8-HxCDD	2.5	50	5.0	50	50
1,2,3,6,7,8-HxCDD	2.5	50	5.0	50	50
1,2,3,7,8,9-HxCDD	2.5	50	5.0	50	50
1,2,3,4,7,8-HxCDF	2.5	50	5.0	50	50
1,2,3,6,7,8-HxCDF	2.5	50	5.0	50	50
2,3,4,6,7,8-HxCDF	2.5	50	5.0	50	50
1,2,3,7,8,9-HxCDF	2.5	50	5.0	50	50
1,2,3,4,6,7,8-HpCDD	2.5	50	5.0	50	50
1,2,3,4,6,7,8-HpCDF	2.5	50	5.0	50	50
1,2,3,4,7,8,9-HpCDF	2.5	50	5.0	50	50
OCDD	5.0	100	10.0	100	100
OCDF	5.0	100	10.0	100	100

Notes:

1 Concentration in the extract assuming a 20 µL volume.
2 Based on a sample volume of 1.0 L.
3 Based on a sample volume of 10.0 g.
4 Based on a sample volume of 1.0g.
5 Based on extraction of the entire sample.

Table 3

Methods – 1613B and 8290
Retention Time References, Quantitation References, and Relative Retention Times

Analyte	Retention Time and Quantitation Reference	Relative Retention Time
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard		
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999-1.002
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999-1.003
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999-1.002
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999-1.002
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999-1.002
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976-1.043
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989-1.052
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923-1.103
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.567
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.425
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011-1.526
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard		
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999-1.001
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.998-1.004
1,2,3,7,8,9-HxCDD	--[1]	1.000-1.019
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999-1.001
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997-1.005
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0.999-1.001
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999-1.001
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999-1.001
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999-1.001
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999-1.001
OCDD	$^{13}C_{12}$-OCDD	0.999-1.001
OCDF	$^{13}C_{12}$-OCDD	0.999-1.008
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.000
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981-1.003
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944-0.970
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949-0.975
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959-1.021
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.047
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086-1.110
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043-1.085
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057-1.151
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032-1.311

Notes:

1 The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD. 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

Table 4

Methods – 23, 0023A, and TO-9A
Retention Time References and Quantitation References

Analyte	Retention Time and Quantitation Reference
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard	
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard	
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
OCDD	$^{13}C_{12}$-OCDD
OCDF	$^{13}C_{12}$-OCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

Table 5

Methods – 1613B and 8290
Initial Calibration Standard Concentrations and Acceptance Criteria

Analyte	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)	1613B %RSD	8290 %RSD
Native PCDD's and PCDF's							
2,3,7,8-TCDD	0.5	2.0	10	40	200	±20	±20
2,3,7,8-TCDF	0.5	2.0	10	40	200	±20	±20
1,2,3,7,8-PeCDD	2.5	10	50	200	1000	±20	±20
1,2,3,7,8-PeCDF	2.5	10	50	200	1000	±20	±20
2,3,4,7,8-PeCDF	2.5	10	50	200	1000	±20	±20
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000	±20	±20
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000	±20	±20
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000	±35	±20
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000	±20	±20
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000	±20	±20
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000	±20	±20
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000	±20	±20
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000	±20	±20
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000	±20	±20
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000	±20	±20
OCDD	5.0	20	100	400	2000	±20	±20
OCDF	5.0	20	100	400	2000	±35	±20
Labeled Internal Standards							
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	±35	±30
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-OCDD	200	200	200	200	200	±35	±30
Labeled Cleanup Standard							
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2.0	10	40	200	±35	±30
Labeled Recovery Standard							
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	-	-

Table 6

Methods – 23, 0023A, and TO-9A
Initial Calibration Standard Concentrations and Acceptance Criteria

Analyte	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)	23 / TO-9A %RSD	0023A %RSD
Native PCDD's and PCDF's							
2,3,7,8-TCDD	0.5	1.0	5	50	100	±25	±20
2,3,7,8-TCDF	0.5	1.0	5	50	100	±25	±20
1,2,3,7,8-PeCDD	2.5	5	25	250	500	±25	±20
1,2,3,7,8-PeCDF	2.5	5	25	250	500	±25	±20
2,3,4,7,8-PeCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500	±25	±20
2,3,4,6,7,8-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500	±25	±20
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500	±25	±20
OCDD	5.0	10	50	500	1000	±25	±20
OCDF	5.0	10	50	500	1000	±30	±20
Labeled Internal Standards							
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	±25	±30
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	±25	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-OCDD	200	200	200	200	200	±30	±30
Surrogate Standards							
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1.0	5	50	100	±25	±30
$^{13}C_{12}$-2,3,4,7,8-PeCDF	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500	±25	±30
Labeled Recovery Standard							
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	-	-

Table 7

Methods – 1613B and 8290
Daily Verification Standard (VER) Concentrations and Acceptance Criteria

Analyte	VER (ng/mL)	1613B All Isomers (ng/mL)	1613B Tetra only (ng/mL)	8290 Shift Open %D	8290 Shift Close[1] %D
Native PCDD's and PCDF's					
2,3,7,8-TCDD	10	7.8-12.9	8.2-12.3	±20	±25
2,3,7,8-TCDF	10	8.4-12.0	8.6-11.6	±20	±25
1,2,3,7,8-PeCDD	50	39-65	-	±20	±25
1,2,3,7,8-PeCDF	50	41-60	-	±20	±25
2,3,4,7,8-PeCDF	50	41-61	-	±20	±25
1,2,3,4,7,8-HxCDD	50	39-64	-	±20	±25
1,2,3,6,7,8-HxCDD	50	39-64	-	±20	±25
1,2,3,7,8,9-HxCDD	50	41-61	-	±20	±25
1,2,3,4,7,8-HxCDF	50	45-56	-	±20	±25
1,2,3,6,7,8-HxCDF	50	44-57	-	±20	±25
2,3,4,6,7,8-HxCDF	50	44-57	-	±20	±25
1,2,3,7,8,9-HxCDF	50	45-56	-	±20	±25
1,2,3,4,6,7,8-HpCDD	50	43-58	-	±20	±25
1,2,3,4,6,7,8-HpCDF	50	45-55	-	±20	±25
1,2,3,4,7,8,9-HpCDF	50	43-58	-	±20	±25
OCDD	100	79-126	-	±20	±25
OCDF	100	63-159	-	±20	±25
Labeled Internal Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	100	82-121	85-117	±30	±35
$^{13}C_{12}$-2,3,7,8-TCDF	100	71-140	76-131	±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	62-160	-	±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	76-130	-	±30	±35
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	77-130	-	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	85-117	-	±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	85-118	-	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	76-131	-	±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	70-143	-	±30	±35
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	73-137	-	±30	±35
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	74-135	-	±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	72-138	-	±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	78-129	-	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	77-129	-	±30	±35
$^{13}C_{12}$-OCDD	200	96-415	-	±30	±35
Labeled Cleanup Standard					
$^{37}Cl_4$-2,3,7,8-TCDD	10	7.9-12.7	8.3-12.1	±30	±35
Labeled Recovery Standard					
$^{13}C_{12}$-1,2,3,4-TCDD	100	-	-	-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	-	-	-	-

Notes:

1 If the closing standard %D exceeds the opening %D criteria, the average of the Opening and Closing RF is used instead of the Initial Calibration RF to calculate sample concentrations.

Table 8

Methods – 23, 0023A, and TO-9A
Daily Verification Standard (VER) Concentrations and Acceptance Criteria

Analyte	VER (ng/mL)	23 and TO-9A %D	0023A Shift Open %D	0023A Shift Close[1] %D
Native PCDD's and PCDF's				
2,3,7,8-TCDD	5	±25	±20	±25
2,3,7,8-TCDF	5	±25	±20	±25
1,2,3,7,8-PeCDD	25	±25	±20	±25
1,2,3,7,8-PeCDF	25	±25	±20	±25
2,3,4,7,8-PeCDF	25	±25	±20	±25
1,2,3,4,7,8-HxCDD	25	±25	±20	±25
1,2,3,6,7,8-HxCDD	25	±25	±20	±25
1,2,3,7,8,9-HxCDD	25	±25	±20	±25
1,2,3,4,7,8-HxCDF	25	±25	±20	±25
1,2,3,6,7,8-HxCDF	25	±25	±20	±25
2,3,4,6,7,8-HxCDF	25	±25	±20	±25
1,2,3,7,8,9-HxCDF	25	±25	±20	±25
1,2,3,4,6,7,8-HpCDD	25	±25	±20	±25
1,2,3,4,6,7,8-HpCDF	25	±25	±20	±25
1,2,3,4,7,8,9-HpCDF	25	±25	±20	±25
OCDD	50	±25	±20	±25
OCDF	50	±30	±20	±25
Labeled Internal Standards				
$^{13}C_{12}$-2,3,7,8-TCDD	100	±25	±30	±35
$^{13}C_{12}$-2,3,7,8-TCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	±25	±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	±30	±30	±35
$^{13}C_{12}$-OCDD	200	±30	±30	±35
Surrogate Standards				
$^{37}Cl_4$-2,3,7,8-TCDD	5	±25	±30	±35
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	±25	±30	±35
Labeled Recovery Standard				
$^{13}C_{12}$-1,2,3,4-TCDD	100	-	-	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	-	-	

Notes:

1 If the closing standard %D exceeds the opening %D criteria, the average of the Opening and Closing RF is used instead of the Initial Calibration RF to calculate sample concentrations.

Table 9

Method – 1613B
Initial Precision and Recovery (IPR) Acceptance Criteria

Analyte	Test Conc. (ng/mL) [1]	1613B s[2] (ng/mL) [1]	1613B X[3] (ng/ml) [1]	1613B Tetra Only s[2] (ng/mL) [1]	1613B Tetra Only X[3] (ng/ml) [1]
Native PCDD's and PCDF's					
2,3,7,8-TCDD	10	2.8	8.3-12.9	2.7	8.7-12.4
2,3,7,8-TCDF	10	2.0	8.7-13.7	2.0	9.1-13.1
1,2,3,7,8-PeCDD	50	7.5	38-66	-	-
1,2,3,7,8-PeCDF	50	7.5	43-62	-	-
2,3,4,7,8-PeCDF	50	8.6	36-75	-	-
1,2,3,4,7,8-HxCDD	50	9.4	39-76	-	-
1,2,3,6,7,8-HxCDD	50	7.7	42-62	-	-
1,2,3,7,8,9-HxCDD	50	11.1	37-71	-	-
1,2,3,4,7,8-HxCDF	50	8.7	41-59	-	-
1,2,3,6,7,8-HxCDF	50	6.7	46-60	-	-
2,3,4,6,7,8-HxCDF	50	7.4	37-74	-	-
1,2,3,7,8,9-HxCDF	50	6.4	42-61	-	-
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65	-	-
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56	-	-
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63	-	-
OCDD	100	19	89-127	-	-
OCDF	100	27	74-146	-	-
Labeled Internal Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	50	18.5	14-67	17.5	16-57.5
$^{13}C_{12}$-2,3,7,8-TCDF	50	17.5	15.5-56.5	17	17.5-49.5
$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	19.5	13.5-92	-	-
$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	17.0	13.5-78	-	-
$^{13}C_{12}$-2,3,4,7,8-PeCDF	50	19.0	8-139.5	-	-
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	50	20.5	14.5-73.5	-	-
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	50	19.0	17-61	-	-
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	50	21.5	13.5-76	-	-
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	50	17.5	15-61	-	-
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	50	18.5	14.5-68	-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	50	20.0	12-78.5	-	-
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	50	17.5	17-64.5	-	-
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	50	20.5	16-55	-	-
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	50	20.0	14-70.5	-	-
$^{13}C_{12}$-OCDD	100	47.5	20.5-138	-	-
Labeled Cleanup Standard					
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9-15.4	3.4	4.5-13.4

Notes:

1 All specifications are given as concentration in the final extract, assuming a 20-µL volume.

2 s = standard deviation of the concentration

3 X = average concentration The acceptance range for average recovery may be normalized (shifted to center on 100% recovery) to compensate for the bias in the collaborative study used to develop the acceptance criteria.

Table 10

Methods – 8290, 23, 0023A, and TO-9A
Initial Precision and Recovery (IPR) Acceptance Criteria

Analyte	Test Conc (ng/mL) [1]	s[2] (%Rec)	X[3] (%Rec)
Native PCDD's and PCDF's			
2,3,7,8-TCDD	10	15[4]	70-130[4]
2,3,7,8-TCDF	10	15[4]	70-130[4]
1,2,3,7,8-PeCDD	50	15[4]	70-130[4]
1,2,3,7,8-PeCDF	50	15[4]	70-130[4]
2,3,4,7,8-PeCDF	50	15[4]	70-130[4]
1,2,3,4,7,8-HxCDD	50	15[4]	70-130[4]
1,2,3,6,7,8-HxCDD	50	15[4]	70-130[4]
1,2,3,7,8,9-HxCDD	50	15[4]	70-130[4]
1,2,3,4,7,8-HxCDF	50	15[4]	70-130[4]
1,2,3,6,7,8-HxCDF	50	15[4]	70-130[4]
2,3,4,6,7,8-HxCDF	50	15[4]	70-130[4]
1,2,3,7,8,9-HxCDF	50	15[4]	70-130[4]
1,2,3,4,6,7,8-HpCDD	50	15[4]	70-130[4]
1,2,3,4,6,7,8-HpCDF	50	15[4]	70-130[4]
1,2,3,4,7,8,9-HpCDF	50	15[4]	70-130[4]
OCDD	100	15[4]	70-130[4]
OCDF	100	15[4]	70-130[4]

Notes:

1 All specifications are given as concentration in the final extract, assuming a 20-µL volume.
2 s = standard deviation of the percent recovery
3 X = average percent recovery
4 In-house generated historical control-limits may be used in place of the specified limit.

Table 11

Laboratory Control Sample (LCS/OPR) Spiking Solution Component Concentrations and Acceptance Limits

Analyte	LCS Solution Conc. (ng/mL)[1]	Final Extract Conc (ng/mL)[2]	1613B OPR Conc (ng/mL)[2]	8290, 23, 0023A, TO-9A Recovery (%Rec)
2,3,7,8-TCDD	0.2	10	6.7-15.8	70-130[4]
2,3,7,8-TCDF	0.2	10	7.5-15.8	70-130[4]
1,2,3,7,8-PeCDD	1.0	50	35-71	70-130[4]
1,2,3,7,8-PeCDF	1.0	50	40-67	70-130[4]
2,3,4,7,8-PeCDF	1.0	50	34-80	70-130[4]
1,2,3,4,7,8-HxCDD	1.0	50	35-82	70-130[4]
1,2,3,6,7,8-HxCDD	1.0	50	38-67	70-130[4]
1,2,3,7,8,9-HxCDD	1.0	50	32-81	70-130[4]
1,2,3,4,7,8-HxCDF	1.0	50	36-67	70-130[4]
1,2,3,6,7,8-HxCDF	1.0	50	42-65	70-130[4]
2,3,4,6,7,8-HxCDF	1.0	50	35-78	70-130[4]
1,2,3,7,8,9-HxCDF	1.0	50	39-65	70-130[4]
1,2,3,4,6,7,8-HpCDD	1.0	50	35-70	70-130[4]
1,2,3,4,6,7,8-HpCDF	1.0	50	41-61	70-130[4]
1,2,3,4,7,8,9-HpCDF	1.0	50	39-69	70-130[4]
OCDD	2.0	100	78-144	70-130[4]
OCDF	2.0	100	63-170	70-130[4]
Tetras Only				
2,3,7,8-TCDD	0.2	10	7.3-14.6	70-130[4]
2,3,7,8-TCDF	0.2	10	8.0-14.7	70-130[4]

Notes:

1 1.0 mL of this solution is added to the OPR sample before extraction (see section 7.11.1).

2 The final extract concentration is based on an extract volume of 20-µL.

3 Spike concentrations are based on a 1.0 L extraction for Water, 10.0g extraction for Solids, and entire sample extraction for Air/Wipe samples.

4 In-house generated historical control-limits may be used in place of the specified limit.

Table 12

Method - 8290
Matrix Spike and Matrix Spike Duplicate Sample (MS/MSD) Spiking Solution Component Concentrations and Acceptance Limits[1]

Analyte	LCS Solution Conc. (ng/mL)[2]	Final Extract Conc (ng/mL)[3]	8290 Recovery (%Rec)	8290 Precision (RPD)
2,3,7,8-TCDD	0.2	10	70-130[4]	±15[4]
2,3,7,8-TCDF	0.2	10	70-130[4]	±15[4]
1,2,3,7,8-PeCDD	1.0	50	70-130[4]	±15[4]
1,2,3,7,8-PeCDF	1.0	50	70-130[4]	±15[4]
2,3,4,7,8-PeCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,6,7,8-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,7,8,9-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,6,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
2,3,4,6,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,7,8,9-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,6,7,8-HpCDD	1.0	50	70-130[4]	±15[4]
1,2,3,4,6,7,8-HpCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8,9-HpCDF	1.0	50	70-130[4]	±15[4]
OCDD	2.0	100	70-130[4]	±15[4]
OCDF	2.0	100	70-130[4]	±15[4]

Notes:

1 If insufficient sample exists for MS/MSD analysis, these limits apply to LCS/LCSD samples.
2 mL of this solution is added to the OPR sample before extraction (see section 7.11.2).
3 The final extract concentration is based on an extract volume of 20-µL.
4 In-house generated historical control-limits may be used in place of the specified limit.

Table 13

Methods – 1613B and 8290
Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	1613B OPR Conc (ng/mL)[2]	1613B Sample Conc (ng/mL)[2]	8290 Recovery (%Rec)
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	10.0-87.5	12.5-82.0	40-135
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	11.0-76.0	12.0-84.5	40-135
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1.0	50	10.5-113.5	12.5-90.5	40-135
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1.0	50	10.5-96.0	12.0-92.5	40-135
$^{13}C_{12}$-2,3,4,7,8-PeCDF	1.0	50	6.5-164.0	10.5-89.0	40-135
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	1.0	50	10.5-96.5	16.0-70.5	40-135
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1.0	50	12.5-81.5	14.0-65.0	40-135
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1.0	50	9.5-101.0	13.0-76.0	40-135
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1.0	50	10.5-79.5	13.0-61.5	40-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	1.0	50	11.0-88.0	14.0-68.0	40-135
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	1.0	50	8.5-102.5	14.5-73.5	40-135
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1.0	50	13.0-83.0	11.5-70.0	40-135
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	50	10.5-79.0	14.0-71.5	40-135
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	1.0	50	10.0-93.0	13.0-69.0	40-135
$^{13}C_{12}$-OCDD	2.0	100	13.0-198.5	17.0-157	40-135
Tetras Only					
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	12.5-70.5	15.5-68.5	40-135
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	13.0-63.0	14.5-70.0	40-135

Notes:

1 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and LCS/OPR sample prior to extraction (see section 7.11.3).

2 Specifications given as concentration in the final extract, assuming a 20-µL volume

Table 14

Method – 1613B
Cleanup Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	1613B OPR Conc (ng/mL)[2]	1613B Sample Conc (ng/mL)[2]	1613B OPR Tetra Only Conc (ng/mL)[2]	1613B Sample Tetra Only Conc (ng/mL)[2]
$^{37}Cl_4$-2,3,7,8-TCDD	0.2	10	3.1-19.1	3.5-19.7	3.7-15.8	4.2-16.4

Notes:

1 1.0 mL of the Cleanup Standard Spiking Solution is added to each sample, method blank and LCS/OPR sample prior to cleanup (see section 7.11.4).

2 Specifications given as concentration in the final extract, assuming a 20-µL volume

Table 15

Methods – 23, 0023A, and TO-9A
Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	23 Recovery (%Rec)	0023A Recovery (%Rec)	TO-9A Recovery (%Rec)
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1.0	50	25-130	40-135	40-120
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	50	25-130	40-135	40-120
$^{13}C_{12}$-OCDD	2.0	100	25-130	40-135	40-120

Notes:

1 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and LCS/OPR sample prior to extraction (see section 7.11.3).

2 Specifications given as concentration in the final extract, assuming a 20-µL volume

Table 16

Methods – 23, 0023A, and TO-9A
Surrogate Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	23 Recovery (%Rec)	0023A Recovery (%Rec)	TO-9A Recovery (%Rec)
$^{37}Cl_4$-2,3,7,8-TCDD	20	100	70-130	70-130	50-120
$^{13}C_{12}$-2,3,4,7,8-PeCDF	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	20	100	70-130	70-130	40-120

Notes:

1 100 µL of the Surrogate Standard Spiking Solution is added to each sample train prior to sampling (see section 7.11.5).

2 Specifications given as concentration in the final extract, assuming a 20-µL volume

Table 17

Methods – All
Recovery Standard Spiking Solution Component Concentrations

Labeled Analyte	Solution Conc (µg/mL)[1]	Test Conc. (ng/mL)[2]
$^{13}C_{12}$-1,2,3,4-TCDD	0.1	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.1	100

Notes:
1 20 µL of the Recovery Standard Spiking Solution is added to each sample, method blank and LCS/OPR sample prior to analysis (see section 7.11.8).
2 Specifications given as concentration in the final extract, assuming a 20-µL volume

Table 18

Rtx-5/DB-5 Column Window Defining Standard Mixture Components

Congener	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,6,8-/ 1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-/ 1,2,4,6,8,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

Table 19

Rtx-5 (DB-5) Column Performance Standard Mixture Components

Isomer
1,2,3,7/1,2,3,8-TCDD
1,2,3,9-TCDD
2,3,7,8-TCDD

Table 20

DB-225 (Rtx-225) Column Performance Standard Mixture Components

Isomer
2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

Table 21

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass[1]	Ion ID	Elemental Composition	Analyte
1	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	342.9792	QC	C_8F_{13}	PFK
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
2	330.9792	LOCK	C_7F_{13}	PFK
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	380.9760	QC	C_8F_{15}	PFK
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	380.9760	LOCK	C_8F_{15}	PFK
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	404.9760	QC	$C_{10}F_{15}$	PFK
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE

Table 21 Continued

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass[1]	Ion ID	Elemental Composition	Analyte
4	404.9760	LOCK	$C_{10}F_{15}$	PFK
	407.7818	M+2	$C_{12}H\,^{35}Cl_6\,^{37}Cl\,0$	HpCDF
	409.7788	M+4	$C_{12}H\,^{35}Cl_5\,^{37}Cl_2\,0$	HpCDF
	417.8250	M	$^{13}C_{12}H\,^{35}Cl_7\,0$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H\,^{35}Cl_6\,^{37}Cl\,0$	HpCDF (S)
	423.7767	M+2	$C_{12}H\,^{35}Cl_6\,^{37}Cl\,0_2$	HpCDD
	425.7737	M+4	$C_{12}H\,^{35}Cl_5\,^{37}Cl_2\,0_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H\,^{35}Cl_6\,^{37}Cl\,0_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H\,^{35}Cl_5\,^{37}Cl_2\,0_2$	HpCDD (S)
	442.9728	QC	$C_{10}F_{17}$	PFK
	479.7165	M+4	$C_{12}H\,^{35}Cl_7\,^{37}Cl_2\,0$	NCDPE
5	430.9728	LOCK	C_9F_{17}	PFK
	441.7428	M+2	$C_{12}\,^{35}Cl_7\,^{37}Cl\,0$	OCDF
	443.7399	M+4	$C_{12}\,^{35}Cl_6\,^{37}Cl_2\,0$	OCDF
	457.7377	M+2	$C_{12}\,^{35}Cl_7\,^{37}Cl\,0_2$	OCDD
	459.7348	M+4	$C_{12}\,^{35}Cl_6\,^{37}Cl_2\,0_2$	OCDD
	469.7780	M+2	$^{13}C_{12}\,^{35}Cl_7\,^{37}Cl\,0_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}\,^{35}Cl_6\,^{37}Cl_2\,0_2$	OCDD (S)
	480.9696	QC	$C_{10}F_{19}$	PFK
	513.6775	M+4	$C_{12}\,^{35}Cl_8\,^{37}Cl_2\,0$	DCDPE

Notes:

1 Nuclidic masses used:

H = 1.007825 C = 12.00000 ^{13}C = 13.003355 F = 18.9984

O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903

Table 22

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

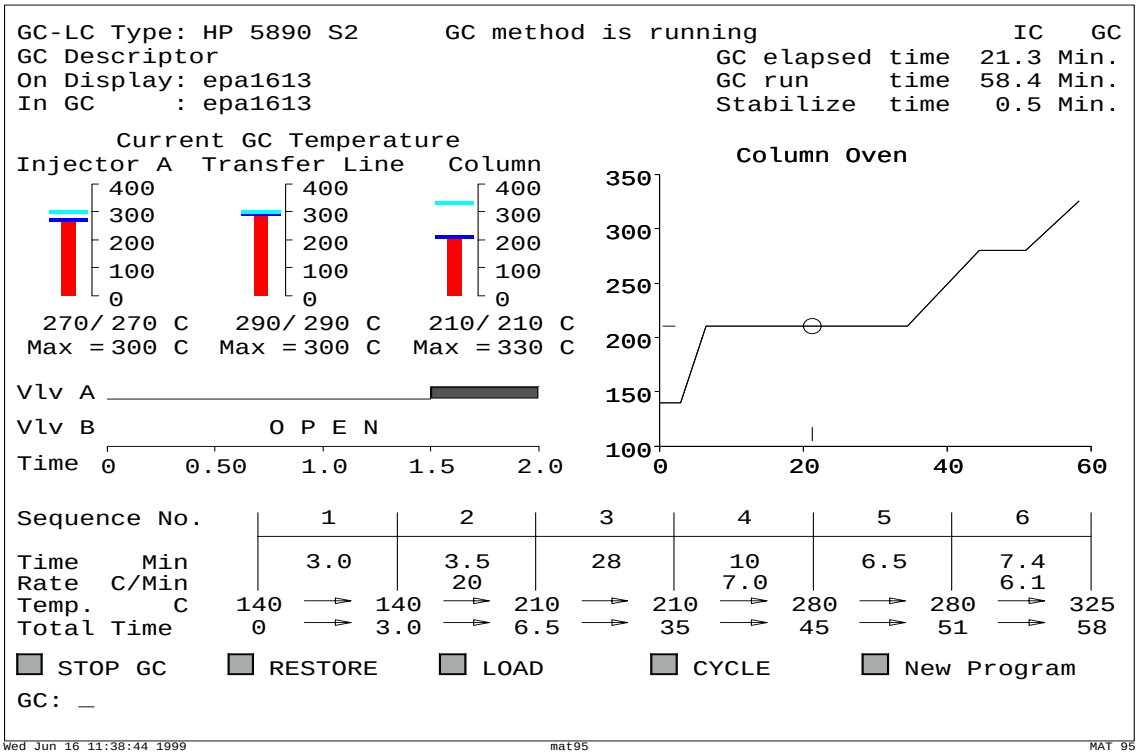
Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits Lower	Control Limits Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6 [1]	M/M+2	0.51	0.43	0.59
7	M+2/M+4	1.04/1.05[3]	0.88	1.20
7 [2]	M/M+2	0.44	0.37	0.51
8	M+2/M+4	0.89	0.76	1.02

Notes:

1 Used for ^{13}C-HxCDF (IS).
2 Used for ^{13}C-HpCDF (IS).
3 Method 1613B Theroretical Ratio

Figure 1

Rtx-5 Recommended GC Operating Conditions



DB-225 Recommended GC Operating Conditions

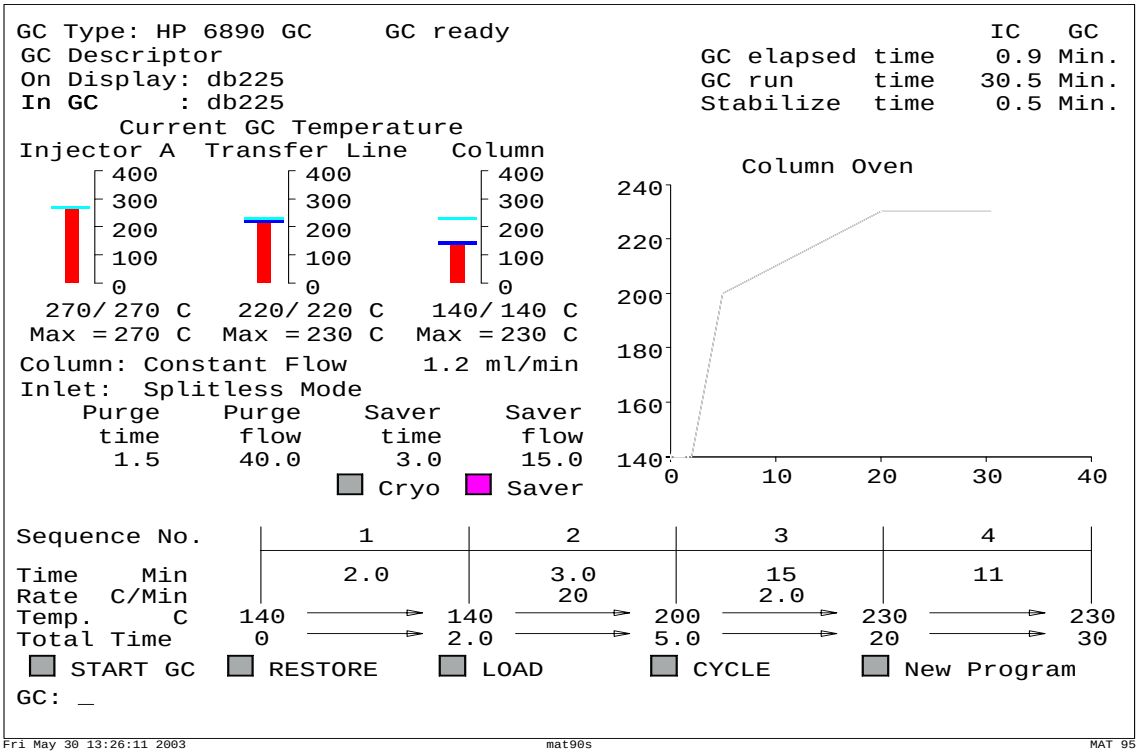


Figure 2

Rtx-5 Recommended MID Descriptors

```
MID Set Up Parameters
 MID File                      epa1613
 Measure/lock ratio (X)            1
 Set Damping relay  (T)        FALSE
 Width first lock   (A)         0.20 amu
 Electric jump time (E)           10 ms
 Magnetic jump time (D)           60 ms
 Offset             (O)          100 cts
 Electric range     (R)          300 %
 Sweep peak width   (W)         3.00
 Acq mode         (C|P)         Cent mode
 MID mode      (J|M|L|N)        Lock mode

MID  Time Windows
 #  Start  Measure  End      Cycletime
 1   8:00  28:12  36:12 min   1.00 sec
 2  36:12   7:28  43:40 min   1.00 sec
 3  43:40   5:49  49:30 min   1.00 sec
 4  49:30   5:00  54:30 min   1.00 sec
 5  54:30   3:50  58:20 min   1.00 sec
 6
 7
 8
 9

 Clear Menu      Clear Times      Clear Masses
 Stop MID        SAVE             Main

MID: _
```

```
MID Masses for Time Window   1
#      mass    F int  gr time(ms)
1    292.9825 l  10   1     8.19
2    303.9016     1   1    81.92
3    305.8987     1   1    81.92
4    315.9419     1   1    81.92
5    317.9389     1   1    81.92
6    319.8965     1   1    81.92
7    321.8936     1   1    81.92
8    327.8847     1   1    81.92
9    331.9368     1   1    81.92
10   333.9338     1   1    81.92
11   342.9792 c  10   1     8.19
12   375.8364     1   1    81.92
13
14
15
16
17
18
19
20
21
22
23
24

Lock Mass    Cali Mass
```

Wed Jun 16 11:39:22 1999 mat95 MAT 95

```
MID Set Up Parameters
 MID File                      epa1613
 Measure/lock ratio (X)            1
 Set Damping relay  (T)        FALSE
 Width first lock   (A)         0.20 amu
 Electric jump time (E)           10 ms
 Magnetic jump time (D)           60 ms
 Offset             (O)          100 cts
 Electric range     (R)          300 %
 Sweep peak width   (W)         3.00
 Acq mode         (C|P)         Cent mode
 MID mode      (J|M|L|N)        Lock mode

MID  Time Windows
 #  Start  Measure  End      Cycletime
 1   8:00  28:12  36:12 min   1.00 sec
 2  36:12   7:28  43:40 min   1.00 sec
 3  43:40   5:49  49:30 min   1.00 sec
 4  49:30   5:00  54:30 min   1.00 sec
 5  54:30   3:50  58:20 min   1.00 sec
 6
 7
 8
 9

 Clear Menu      Clear Times      Clear Masses
 Stop MID        SAVE             Main

MID: _
```

```
MID Masses for Time Window   2
#      mass    F int  gr time(ms)
1    330.9792 l  10   1     8.19
2    339.8597     1   1    91.48
3    341.8567     1   1    91.48
4    351.9000     1   1    91.48
5    353.8970     1   1    91.48
6    355.8546     1   1    91.48
7    357.8516     1   1    91.48
8    367.8949     1   1    91.48
9    369.8919     1   1    91.48
10   380.9760 c  10   1     8.19
11   409.7974     1   1    91.48
12
13
14
15
16
17
18
19
20
21
22
23
24

Lock Mass    Cali Mass
```

Wed Jun 16 11:39:27 1999 mat95 MAT 95

Figure 2 **Continued**

Rtx-5 Recommended MID Descriptors

```
MID Set Up Parameters
 MID File                    epa1613
 Measure/lock ratio (X)          1
 Set Damping relay  (T)      FALSE
 Width first lock   (A)       0.20 amu
 Electric jump time (E)         10 ms
 Magnetic jump time (D)         60 ms
 Offset             (O)        100 cts
 Electric range     (R)        300 %
 Sweep peak width   (W)       3.00
 Acq mode          (C|P)      Cent mode
 MID mode      (J|M|L|N)      Lock mode

MID  Time Windows
 #  Start  Measure  End      Cycletime
 1   8:00  28:12  36:12 min  1.00 sec
 2  36:12   7:28  43:40 min  1.00 sec
 3  43:40   5:49  49:30 min  1.00 sec
 4  49:30   5:00  54:30 min  1.00 sec
 5  54:30   3:50  58:20 min  1.00 sec
 6
 7
 8
 9

 Clear Menu      Clear Times      Clear Masses
 Stop MID        SAVE             Main
MID: _

MID Masses for Time Window  3
#      mass    F int  gr time(ms)
1    373.8208      1   1    91.48
2    375.8178      1   1    91.48
3    380.9760 l   10   1     8.19
4    383.8639      1   1    91.48
5    385.8610      1   1    91.48
6    389.8156      1   1    91.48
7    391.8127      1   1    91.48
8    401.8559      1   1    91.48
9    403.8529      1   1    91.48
10   404.9760 c   10   1     8.19
11   445.7555      1   1    91.48
12
13
14
15
16
17
18
19
20
21
22
23
24
 Lock Mass   Cali Mass

Wed Jun 16 11:39:32 1999          mat95          MAT 95
```

```
MID Set Up Parameters
 MID File                    epa1613
 Measure/lock ratio (X)          1
 Set Damping relay  (T)      FALSE
 Width first lock   (A)       0.20 amu
 Electric jump time (E)         10 ms
 Magnetic jump time (D)         60 ms
 Offset             (O)        100 cts
 Electric range     (R)        300 %
 Sweep peak width   (W)       3.00
 Acq mode          (C|P)      Cent mode
 MID mode      (J|M|L|N)      Lock mode

MID  Time Windows
 #  Start  Measure  End      Cycletime
 1   8:00  28:12  36:12 min  1.00 sec
 2  36:12   7:28  43:40 min  1.00 sec
 3  43:40   5:49  49:30 min  1.00 sec
 4  49:30   5:00  54:30 min  1.00 sec
 5  54:30   3:50  58:20 min  1.00 sec
 6
 7
 8
 9

 Clear Menu      Clear Times      Clear Masses
 Stop MID        SAVE             Main
MID: _

MID Masses for Time Window  4
#      mass    F int  gr time(ms)
1    404.9760 l   10   1     8.19
2    407.7818      1   1    91.48
3    409.7788      1   1    91.48
4    417.8250      1   1    91.48
5    419.8220      1   1    91.48
6    423.7767      1   1    91.48
7    425.7737      1   1    91.48
8    435.8169      1   1    91.48
9    437.8140      1   1    91.48
10   442.9728 c   10   1     8.19
11   479.7165      1   1    91.48
12
13
14
15
16
17
18
19
20
21
22
23
24
 Lock Mass   Cali Mass

Wed Jun 16 11:39:37 1999          mat95          MAT 95
```

Figure 2 Continued

Rtx-5 Recommended MID Descriptors

MID Set Up Parameters

MID File		epa1613
Measure/lock ratio	(X)	1
Set Damping relay	(T)	FALSE
Width first lock	(A)	0.20 amu
Electric jump time	(E)	10 ms
Magnetic jump time	(D)	60 ms
Offset	(O)	100 cts
Electric range	(R)	300 %
Sweep peak width	(W)	3.00
Acq mode	**(C|P)**	**Cent mode**
MID mode	**(J|M|L|N)**	**Lock mode**

MID Time Windows

#	Start	Measure	End	Cycletime
1	8:00	28:12	36:12 min	1.00 sec
2	36:12	7:28	43:40 min	1.00 sec
3	43:40	5:49	49:30 min	1.00 sec
4	49:30	5:00	54:30 min	1.00 sec
5	54:30	3:50	58:20 min	1.00 sec
6				
7				
8				
9				

Clear Menu | Clear Times | Clear Masses
Stop MID | SAVE | Main

MID: _

MID Masses for Time Window 5

#	mass	F	int	gr	time(ms)
1	430.9728	l	10	1	10.92
2	441.7428		1	1	120.15
3	443.7399		1	1	120.15
4	457.7377		1	1	120.15
5	459.7348		1	1	120.15
6	469.7780		1	1	120.15
7	471.7750		1	1	120.15
8	480.9696	c	10	1	10.92
9	513.6775		1	1	120.15
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					

Lock Mass | Cali Mass

Wed Jun 16 11:39:43 1999 mat95 MAT 95

DB-225 Recommended MID Descriptor

MID Set Up Parameters

MID File		db225
Measure/lock ratio	(X)	1
Set Damping relay	(T)	TRUE
Width first lock	(A)	0.20 amu
Electric jump time	(E)	10 ms
Magnetic jump time	(D)	60 ms
Offset	(O)	100 cts
Electric range	(R)	300 %
Sweep peak width	(W)	3.00
Acq mode	**(C|P)**	**Cent mode**
MID mode	**(J|M|L|N)**	**Lock mode**

MID Time Windows

#	Start	Measure	End	Cycletime
1	8:00	22:30	30:30 min	1.00 sec
2				
3				
4				
5				
6				
7				
8				
9				

Clear Menu | Clear Times | Clear Masses
Start MID | RESTORE | Main

MID: _

MID Masses for Time Window 1

#	mass	F	int	gr	time(ms)
1	292.9825	l	10	1	8.19
2	303.9016		1	1	81.92
3	305.8987		1	1	81.92
4	315.9419		1	1	81.92
5	317.9389		1	1	81.92
6	319.8965		1	1	81.92
7	321.8936		1	1	81.92
8	327.8847		1	1	81.92
9	331.9368		1	1	81.92
10	333.9338		1	1	81.92
11	342.9792	c	10	1	8.19
12	375.8364		1	1	81.92
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					

Lock Mass | Cali Mass

Fri May 30 13:22:09 2003 mat90s MAT 95

Figure 3

Example Sample Prep Benchsheets

STL Knoxville

Specialty Organics Group - Sample Tracking Sheet - GC/MS Analysis Group

QC Batch #: **1296110** Method: Q8 DX1668_L

Lot Number	Workorder	
H1J230000	EMKL21AA	B
	EMKL21AC	C
	EMKL21AD	L
H1J100175	ELWNN1AA	
	ELWNK1AA	
	ELWNQ1AA	
H1J100182	ELWQR1AA	
	ELWQ01AA	
	ELWQ11AA	
	ELWQ41AA	

Cleanup Standard Required (Methods F8, L1, Q8) ?: YES -- Add Method Required Cleanup Std

Figure 3 Continued

Example Sample Prep Benchsheets

STL Knoxville

Specialty Organics Group - Sample Tracking Sheet - GC/MS Analysis Group

QC Batch No **1296110** Relinquished to GC/MS By: _____ Date: _____

Received in GC/MS By: _____ Date: _____

Work Order Number		Column: DB-5 or RTX-5				Column: SPB-Octyl				Column: DB-225 or RTX-225			
		Date	Instrument	Analyst	Code	Date	Instrument	Analyst	Code	Date	Instrument	Analyst	Code
EMKL21AA	B												
EMKL21AC	C												
EMKL21AD	L												
ELWNN1AA													
ELWNK1AA													
ELWNQ1AA													
ELWQR1AA													
ELWQ01AA													
ELWQ11AA													
ELWQ41AA													

Comments: _____

ID0025R1 04/04/01

Figure 3 Continued

Example Sample Prep Benchsheets

STL Knoxville

Specialty Organics Group - Sample Tracking Sheet - Organic Preparation Group

QC Batch No: 1296110 **Cleanup Std. Spiked By:** _____ **Verified By:** _____

Work Order Number		Cleanup Spike (Book:Page)	Cleanup Spike Volume (uL)	SilicaGel Alumina Col (Initial/Date)	Acid/Base Wash (Initial/Date)	Carbon Column (Initial/Date)	Florisil Column (Initial/Date)	Mercury Cleanup (Initial/Date)	TBA Cleanup (Initial/Date)	Other Cleanup (Initial/Date)	Comments
EMKL21AA	B										
EMKL21AC	C										
EMKL21AD	L										
ELWNN1AA											
ELWNK1AA											
ELWNQ1AA											
ELWQR1AA											
ELWQ01AA											
ELWQ11AA											
ELWQ41AA											

Comments: _____

ID0035R1 4/04/01

Figure 3 Continued

Example Sample Prep Benchsheets

STL Knoxville

Specialty Organics Group - Sample Tracking Sheet - Organic Preparation Group

QC Batch No: 1296110 **Internal Std. Spiked By:** _____ **Verified By:** _____

Work Order Number		Filtered Y/N?	Vol of Sampling Surrogate (uL)	Soxhlet Started (Date/Time)	Soxhlet Finished (Date/Time	Blow Down (Initial/Date)	Recovery Standard (Book:Page)	Recovery Std Vol (uL)	Vol Delivered (uL)	Comments
EMKL21AA	B									
EMKL21AC	C									
EMKL21AD	L									
ELWNN1AA										
ELWNK1AA										
ELWNQ1AA										
ELWQR1AA										
ELWQ01AA										
ELWQ11AA										
ELWQ41AA										

Comments: _____

W.B. Temp _____

Volume of Alt Standard: _____

Split Ratios: Post I.S. _____
Post F.C. _____
Post C.S. _____
Post R.S. _____

ID0003JR1 04/04/01

Figure 4

Example Data Review Checklist

STL Knoxville **Specialty Organics Prep Batch Review/Checklist** **Batch #_____**

SOP: ❒ **KNOX-ID-0008, rev. 2** (water extraction) ❒ **KNOX-ID-0009, rev 2** (solid extraction) ❒ **KNOX-ID-0010, rev. 3** (cleanup) ❒ **KNOX-ID-0013, rev. 1** (PCB extraction)
❒ **KNOX-ID-0014, rev. 0** (Pesticide extraction) ❒ **KNOX-ID-0015, rev. 0** (PAH extraction) ❒ **KNOX-ID-0016, rev. 0** (LR PAH extraction) ❒ **KNOX-ID-0017, rev. 0** (filters & XAD-2)

Review Items	**N/A**	**Yes**	**No**	**If No, why is data reportable?**	**2nd Level**
1. Does the batch contain no more than 20 field samples? (Do not count MB, LCS, LCSD, MS, or MSD)					
2. Were the samples extracted by the proper method ?					
3. Were the samples extracted within the required holding times ?					
4. Were all project specific requirements met as noted on the Lot Checklists and Sample Worksheets ?					
5. Were all required QC samples prepared and extracted with the batch at the method required frequency ?					
6. Were MS Run# properly assigned and samples entered on QC tracking Sheet?					
7. Were samples requested properly and request form completed, signed, and dated?					
8. Were the correct weights and volumes entered in Quantims for all samples?					
9. Were the samples properly spiked and the spikes verified ? Were the spike solution ID and spike volumes entered correctly and verified?					
10. Were all cleanup steps properly documented by initials and date?					
11. Was the final volume checked and verified against the supplemental benchsheet and Quantims?					
12. Are the final extracts free of water, precipitates, multiple phases, and color?					
13. Were all appropriate notes and observations recorded on the prep benchsheet and in Quantims?					
14. Were all Quantims batch information completed including; • Batch reviewed • Correct volumes entered • Correct completion date entered • Samples released					
15. Does the prep batch paperwork package contain all required documentation which has been properly and completely filled out, including; • Prep Benchsheet • Supplemental Benchsheet • Standard concentration forms or copies of logbook pages, for all IS, RS, SS, CS, and Native standards. • Lot Checklists for all lots in the batch • Sample worksheets for all samples in the batch in proper order as recorded on tracking sheet					
16. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	**Date:**	**2nd Level Reviewer :**	**Date:**
Comments:		**Comments:**	

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Figure 4 Continued

Example Data Review Checklist

STL Knoxville Dioxin GC/MS Initial Calibration Data Review / Narrative Checklist
Method: 1613B - KNOX-ID-0004-R1

PFK Date/Time:		Inst:		Win Filename:		Col Perf Filename:	

CS1 Filename	CS2 Filename	CS3 Filename	CS4 Filename	CS5 Filename

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented before beginning the initial calibration?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 (at reduced voltage)?					
3. Was the measured exact mass of m/z 380.9760 (PFK) within 5 ppm at reduced accelerating voltage?					
4. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
5. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer?					
6. Were the five calibration standard solutions, at the concentrations specified in the SOP, analyzed?					
7. Was date/time of analysis verified between analysis header and logbook as correct?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound, quantitation ions, and formula.					
9. Are %RSD ≤20% for all unlabeled native analytes except 1,2,3,7,8,9-HxCDD and OCDF?					
10. Are %RSD ≤35% for 1,2,3,7,8,9-HxCDD and OCDF and all labeled internal standards ?					
11. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
12. Are the ion abundance ratios for all labeled and unlabeled analytes within the specified control limits?					
13. If manual integrations were performed, are they clearly identified, initialed and dated?					
14. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
15. Does the ICAL folder contain **complete** data in the following order? Data review checklist, a **complete** runlog, Avg. %RSD summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation, and Total RIC, EICP's and manual integration - for window and all standards, in order from low to high standard.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

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Figure 4 Continued

Example Data Review Checklist

STL Knoxville Dioxin GC/MS Continuing Calibration Review / Narrative Checklist
Method: 1613B - KNOX-ID-0004-R1

Start PFK:		VER Filename:		Win Filename:		Inst:	
End PFK:				Col Perf Filename:		ICAL Date:	

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented at both the beginning and end of the 12 hour shift?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 (at reduced voltage)?					
3. Was the measured exact mass of m/z 380.9760 (PFK) within 5 ppm at reduced accelerating voltage?					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
6. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer?					
7. Was the continuing calibration performed at the beginning of the 12 hour period after successful mass resolution and GC resolution performance check?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound, quantitation ions, and formula.					
9. Are the measured RRFs for each compound within the specified control limits in Table 9 for all PCDDs/PCDFs or Table 10 if only TCDD/TCDF are being determined?					
10. Are the relative retention times of all PCDDs/PCDFs and all labeled compounds within the limits specified in Table 8?					
11. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
12. Are the ion abundance ratios for all labeled and unlabeled analytes within the specified control limits?					
13. If manual integrations were performed, are they clearly identified, initialed and dated?					
14. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
15. Does the CCAL folder contain **complete** data in the following order? Data review checklist, a **complete** runlog, CCAL summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation, and Total RIC, EICP's and manual integration - for window and standard.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

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Figure 4 Continued

Example Data Review Checklist

STL Knoxville Dioxin GC/MS Data Review / Narrative Checklist **LOT #_____**
Method: 1613B - KNOX-ID-0004-R1 **Page 1 of 2**

Batch Number:	

Review Items **A. Initial Calibration**	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd Level**
1. Was the correct ICAL used for quantitation? (Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF.)					
B. Continuing Calibration					
1. Has a Continuing Calibration Checklist been completed for each analytical batch?					
C. Client Sample AND QC Sample Results					
1. Were all special project requirements met?					
2. Were the header information, prep factors, and dilution factors verified?					
3. Was date/time of analysis verified between analysis header and logbook as correct?					
4. Sample analyses done within preparation and analytical holding time (HT)? *If no, list samples:* _____ _____				• HT expired upon receipt. • * Client requested analysis after HT expired. • Re-extraction done after HT expired. • See Comment no. _____.	
5. Are internal standards within QC limits specified in Table 11 (TCDD/TCDF only Table12)? *If no, list samples and reason (e.g.,* **sur1***):* Sample Reason Sample Reason _____				• * **[sup]** Ion suppression due to matrix. • * **[low]** Low recovery. S/N >10 and EDL<ML. • **[sam]** Not enough sample to re-extract. • **[dil]** Dilution showed acceptable %R. • **[mtx]** Obvious matrix interference. Further cleanup not possible. • * **[unk]** At client's request, data was flagged as estimated and released without further investigation. • **[com]** See Comment no. _____.	
6. Were the following qualitative criteria met for all reported PCDD/Fs: • All 2378 isomers within the RRT limits specified in Table 8 and both ions maximized within ±2 seconds. • All non-2378 isomers within established RT windows and both ions maximized within ±2 seconds. • The ion abundance ratios for all labeled and unlabeled analytes within the specified control limits or within ±10% or the ratio in the CS3 or VER. • All peaks ≥2.5 S/N • No corresponding peak at PCDPE mass.					
7. Were peaks ≥2.5 S/N, which did not meet the above criteria, properly calculated and reported as EMPCs?					
8. Were all positive 2378-TCDF hits confirmed by analysis on DB-225?					
9. Are positive results within calibration range? *If no, list samples:* _____ _____				• OCDD/F or non-2378 exceeded calibration range • Sample extracted at lowest possible volume	
11. If manual integrations were performed, are they clearly identified, initialed and dated?					
12. Final report acceptable? (Results correct, DLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.)					
13. Was a narrative prepared and all deviations noted?					

* Such action must be taken in consultation with client.

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Figure 4 Continued

Example Data Review Checklist

STL Knoxville Dioxin GC/MS Data Review / Narrative Checklist **LOT #_____**
Method: 1613B - KNOX-ID-0004-R1 **Page 2 of 2**

D. Preparation/Matrix QC	N/A	Yes	No	Why is data reportable?	2nd Level
1. Have Initial Precision and Recovery (IPR) samples been analyzed? Was the data generated acceptable and all results within the control limits in Table 9 (TCDD/TCDF only Table 10)?					
2. LCS(OPR) done per prep batch and all analytes within the limits specified in Table 9 (TCDD/TCDF only Table 10)? *If no, list LCS(OPR) ID*: _____				• * Reanalysis not possible-insufficient sample. • LCS %R high and affected analyte(s) were <ML in associated samples. • See Comment no._____.	
2. Method blank done per prep batch and method blank or instrument blank analyzed with each sequence?					
3. Method blank internal standard recoveries within QC limits? *If no, list blank ID:* _____				• * Internal standards are high and blank demonstrates that analysis is free of contaminants. • * Sample internal standards OK and there is no analytes >ML in samples associated with blank.	
4. Are all analytes present in the method blank ≤ ML? *If no, list blank ID:* _____				• Sample results are > 20x higher than blank. • * There is no analyte > RL in the samples associated with method blank. • * Reanalysis not possible-insufficient sample	
E. Other					
1. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	Date:	Analyst:	Date:
Comments:		Comments:	

* Such action must be taken in consultation with client.

Figure 5

Aqueous Sample Extraction Flowchart

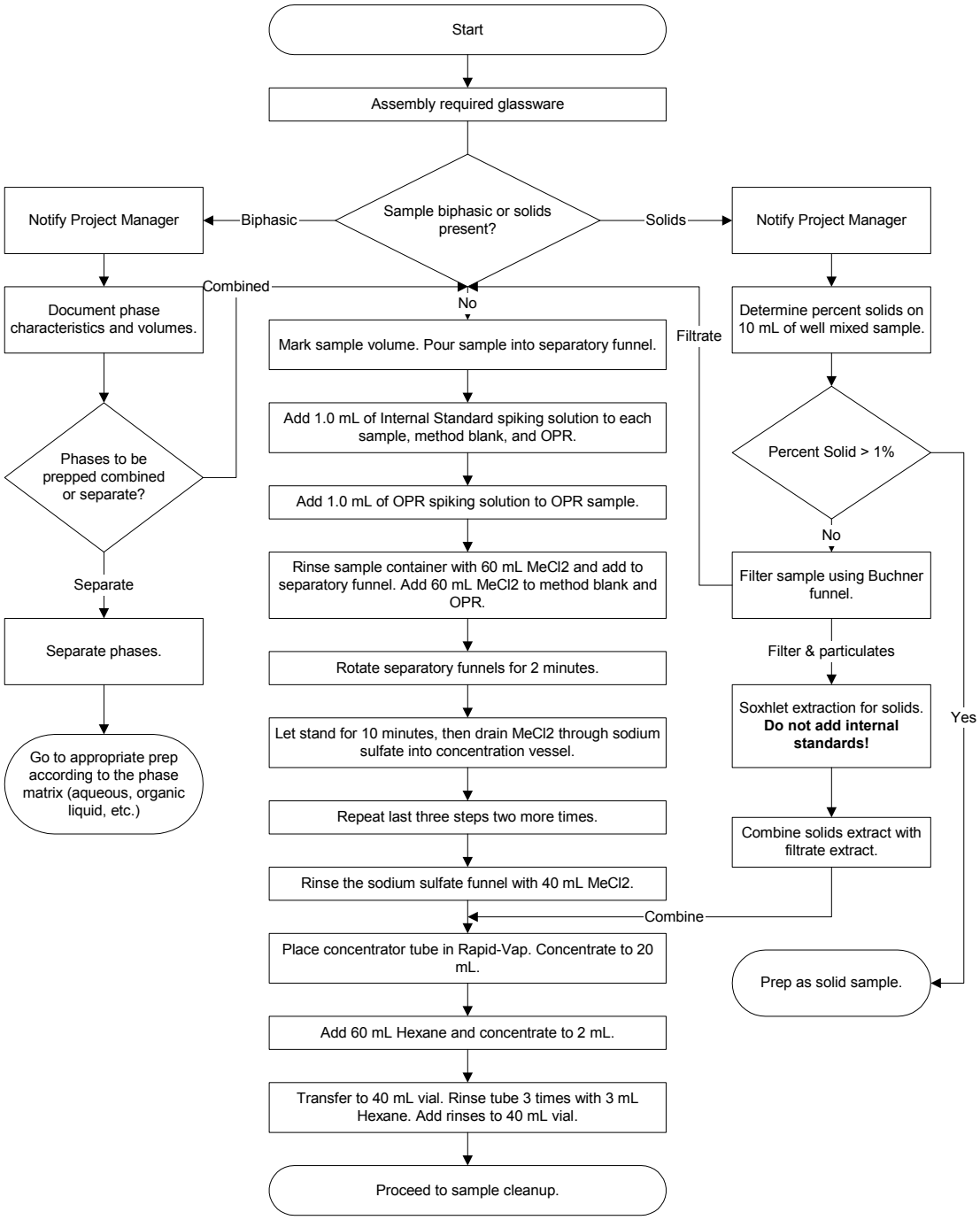


Figure 6

Solid Sample Extraction Flowchart

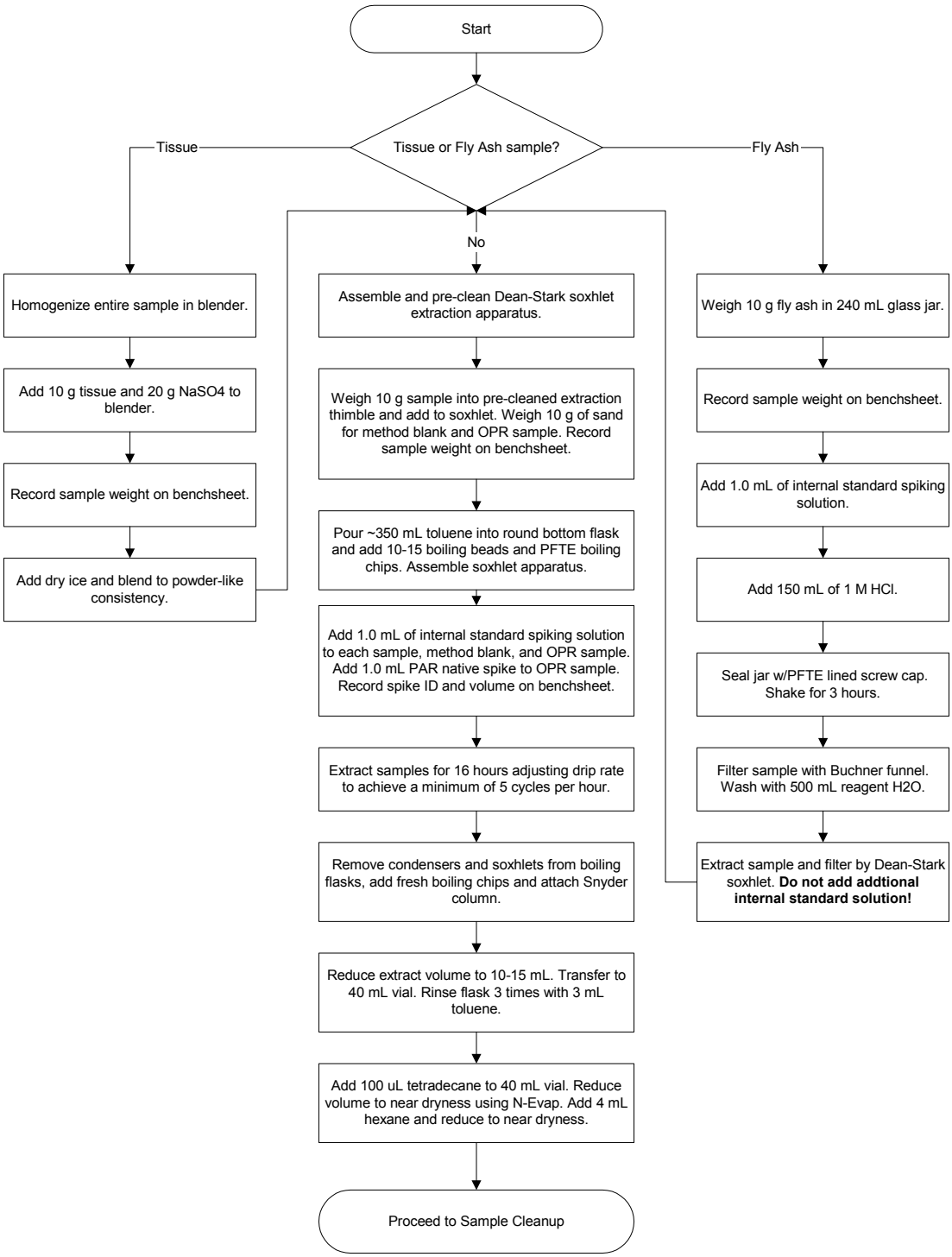


Figure 7

Sample Cleanup Flowchart

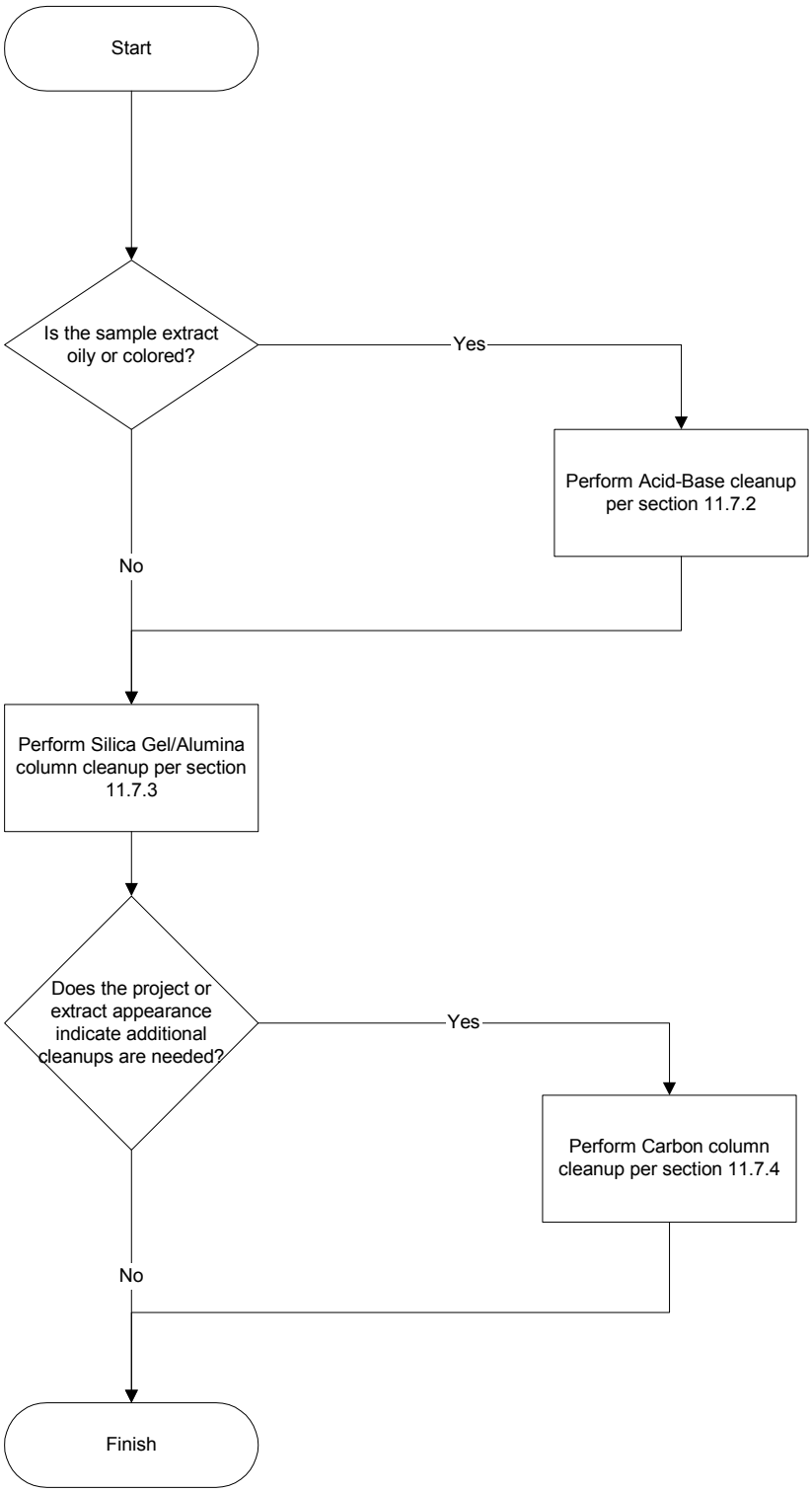
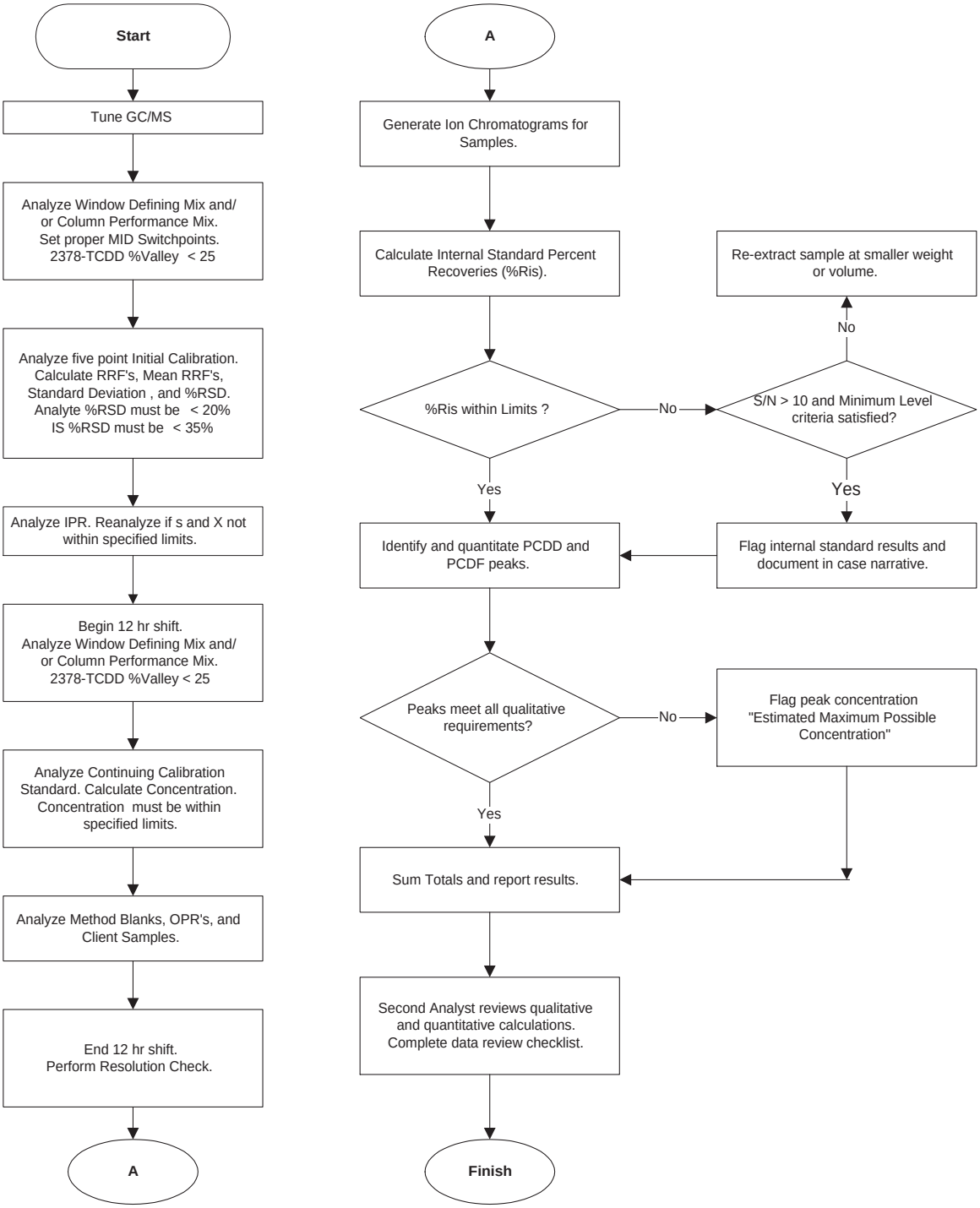


Figure 8

Analysis Of PCDD's and PCDF's by HRGC/HRMS



Appendix I

Evaluation of Method Blank Criteria for USACE Programs

18. Scope and Application

18.1 This modification to the standard procedure is designed to meet analytical program requirements for USACE Hazardous, Toxic and Radioactive Waste (HTRW) Projects. This procedure is based on the document entitled "Shell for Analytical Chemistry", US Army Corps of Engineers (USACE), EM200-1-3, Appendix I, 1 Feb 01.

18.2 This procedure modifies the evaluation and acceptance criteria for Method Blanks.

18.3 This procedures establishes Method Quantitation Levels (MQLs) based on Minimum Levels (MLs) and extract volumes that are specified in USEPA Method 8290.

19. Summary of Method

19.1 Same as the base procedure with the following exception.

19.2 Method blanks are evaluated based on the criteria specified in section 11.4.1 of the USACE "Shell".

20. Definitions

20.1 MDL Check Sample Concentration - The MDL Check sample concentration is one half of the Method Quantitation Level (MQL).

20.2 MQL - Method Quantitation Level - The MQL represents the value that the laboratory has demonstrated the ability to reliably quantitate target analytes. The MQLs for this method have been established based on the reference method calibration levels, required initial sample extraction weight/volume, and the recommended final extract volume.

20.3 Common Laboratory Contaminant - A target analyte which is present in the method blank due to environmental levels or reagent contamination which is beyond the control of the laboratory. For the purposes of this method, Octachlorodibenzodioxin is has been determined to be a common laboratory contaminant.

21. Procedure

21.1 The acceptance criteria in section 9.3 are replaced with the following;

The following criteria shall be used to evaluate the acceptability of the method blank data if project DQOs do not specify otherwise: The concentration of all target analytes shall be below the MDL check sample concentration for each target analyte, or less than 5 percent of the regulatory limit associated with that analyte, or less than 5 percent of the sample results for the same analyte, whichever is greater for the MB to be acceptable. When this criterion is exceeded, corrective action should be taken to find/reduce/eliminate the source of this contamination in the

method blank. However, sample corrective action may be limited to qualification for blank contamination (i.e, B-flag). When the concentration of any target analytes within the MB are above the MDL check sample for the majority of the target analytes or above the MQL for target analytes known to be common laboratory contaminants, assess the effect this may have on the samples. If an analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps shall be taken to find/reduce/eliminate the source of this contamination in the method blank. The case narrative should discuss this situation. If an analyte is found in the method blank and some, or all, of the other batch samples, additional corrective action is required to reanalyze the method blank, and any samples containing the same contaminant. If the contamination remains, the contaminated samples of the batch would be reprepared and reanalyzed with a new method blank and batch specific QC samples. Sporadic cases of contamination may be difficult to control, however, daily contamination would not be acceptable.

22. References

22.1 US Army Corps of Engineers (USACE), EM200-1-3, Appendix I, 1 Feb 01, Shell for Analytical Chemistry Requirements.

Table 23

Method Quantitation Levels[1] for USACE NTRW Projects

Native Analyte	Water (pg/L)	Solid (pg/g)	Tissue (pg/g)	Wipe (pg)	Air (pg)	Waste (pg/g)
2,3,7,8-TCDD	20	2.0	2.0	20	20	20
Total TCDD	20	2.0	2.0	20	20	20
2,3,7,8-TCDF	20	2.0	2.0	20	20	20
Total TCDF	20	2.0	2.0	20	20	20
1,2,3,7,8-PeCDD	50	5.0	5.0	50	50	50
Total PeCDD	50	5.0	5.0	50	50	50
1,2,3,7,8-PeCDF	50	5.0	5.0	50	50	50
2,3,4,7,8-PeCDF	50	5.0	5.0	50	50	50
Total PeCDF	50	5.0	5.0	50	50	50
1,2,3,4,7,8-HxCDD	50	5.0	5.0	50	50	50
1,2,3,6,7,8-HxCDD	50	5.0	5.0	50	50	50
1,2,3,7,8,9-HxCDD	50	5.0	5.0	50	50	50
Total HxCDD	50	5.0	5.0	50	50	50
1,2,3,4,7,8-HxCDF	50	5.0	5.0	50	50	50
1,2,3,6,7,8-HxCDF	50	5.0	5.0	50	50	50
2,3,4,6,7,8-HxCDF	50	5.0	5.0	50	50	50
1,2,3,7,8,9-HxCDF	50	5.0	5.0	50	50	50
Total HxCDF	50	5.0	5.0	50	50	50
1,2,3,4,6,7,8-HpCDD	50	5.0	5.0	50	50	50
Total HpCDD	50	5.0	5.0	50	50	50
1,2,3,4,6,7,8-HpCDF	50	5.0	5.0	50	50	50
1,2,3,4,7,8,9-HpCDF	50	5.0	5.0	50	50	50
Total HpCDF	50	5.0	5.0	50	50	50
OCDD	100	10.	10.	100	100	100
OCDF	100	10.	10.	100	100	100

(1) MQLs are based on the method calibration limits specified in Table 1 of USEPA Method 8290 assuming a 20µL final extract volume as specified in section 7.8.1 of that method.

Summary of SOP #BR-0068

Acid Digestion for Total Metals in Sediments, Soils, Coal, and Flyash

Brooks Rand LLC

5/23/2005

Acid Digestion for Total Metals in Sediments, Soils, Coal, and Flyash

1 SCOPE AND APPLICATION

1.1 This method describes an acid digestion of sediments, soils, coal, and flyash for analysis by inductively coupled plasma-mass spectrometry (ICP-MS) for total metals.

2 SUMMARY OF METHOD

2.1 Samples are digested in an oven overnight in Teflon® bombs using a solution of nitric acid (HNO_3), hydrochloric acid (HCl), and hydrofluoric acid (HF).

2.2 The samples are diluted with reagent water and stored in high-density polyethylene vials until analysis.

3 CONTAMINATION AND INTERFERENCES

3.1 Homogenized samples and small reproducible aliquots help minimize interferences.

3.2 The Cl^- ion from HCl can produce positive interferences on ^{51}V (^{35}ClO), ^{52}Cr ($^{35}ClOH$), ^{53}Cr (^{37}ClO), ^{63}Cu ($^{28}Si^{35}Cl$), ^{65}Cu ($^{28}Si^{37}Cl$), ^{75}As ($^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$) and ^{77}Se ($^{40}Ar^{37}Cl$).

3.3 The F^- ion from HF can produce polyatomic positive interferences like ^{35}Cl does with isobaric $^{16}O^{19}F$. Also CaF and ArF could produce a positive interference on ^{59}Co. Avoid using rare-earth elements as internal standards with fluoride matrices.

3.4 All de-ionized water (DIW), HF, HCl, and HNO_3 bottles are tested regularly to ensure there is no contamination. Method blanks are also prepared to monitor possible contamination and to correct for any trace contributions. Ultra-clean handling techniques should be used in preparing the samples.

3.5 HF in the digested sample forms precipitates with Al, Mn, Zr, Th, lanthanides, and alkaline earth metals. The evaporation sequence for HF is necessary for analysis of these metals.

3.6 HF is typically high in Cr and Al and it may be difficult to obtain low detection limits for these elements.

4 APPARATUS AND MATERIALS

4.1 <u>Teflon® digestion bombs.</u> Including screw caps and clamps for tightening. Require individual numbers etched on the side. Capacity of 60-mL and withstand 75 PSI.

4.2 Sample oven. Capable of heating at to 130˚C overnight and capable of fitting in a fume hood.

4.3 Concentrated HNO_3 (69-70% w/v). All reagents used for ICP-MS should be tested to be low for metals prior to their use. Low trace-metals grade nitric acid should be used. Often acids are still high in metals of interest and should always be tested prior to their use.

4.4 Concentrated HCl (36.5-38% w/w). Trace-metal grade should be used and is pre-tested for metals prior to use.

4.5 Hydrofluoric acid (48-51%). Trace-metal grade should be used and is pre-tested for metals prior to use.

5 PROCEDURE

5.1 Into a cleaned and dried Teflon® bomb, weigh out sample.

5.2 Add concentrated HCl. Add HNO_3 and HF and cap very tightly. Swirl.

5.3 Weigh the bomb pre-digestion and post-digestion to determine if any sample is lost in the process.

5.4 Heat the samples at 130˚C overnight in an oven in a fume hood.

5.5 Open the bombs and pour the contents into clean 50-mL HDPE tubes. The samples are then diluted to the 50-mL gradation of the tube with reagent water.

5.6 For metals where HF may be an interferant (4.5), an evaporation step may be completed.

6 QUALITY ASSURANCE

6.1 Four method blanks (minimum of 3) should be prepared for every set of 20 samples or less to assess the reagents, handling procedures, and apparatus used.

6.2 A matrix spike and a matrix spike duplicate should be analyzed for every set of 10 samples or less. A method duplicate is analyzed upon request of the client. If there is limited sample, a second sample can be spiked and another sample can be prepared in duplicate to measure duplicate precision.

6.3 For every set of samples of 20 or less that are digested, at least one relevant matrix CRM should be analyzed. Two are preferred.

6.4 A blank spike or preferably a matrix-matched spike can be prepared to demonstrate method recovery.

6.5 An MSA curve is also suggested during analysis.

Summary of SOP #BR-0060

Determination of Trace Elements by Inductively Coupled Plasma – Mass Spectrometry using a Perkin-Elmer ELAN DRC II

Brooks Rand LLC

Written 05/23/2005

Determination of Trace Elements by Inductively Coupled Plasma – Mass Spectrometry using a Perkin-Elmer ELAN DRC II

1. DESCRIPTION

1.1 This procedure describes a mode of analysis for the determination of dissolved and total recoverable trace elements in waters using inductively coupled plasma – mass spectrometry (ICP-MS).

1.2 This procedure is written specifically for use of a Perkin-Elmer ELAN DRC II ICP-MS. The instrument software is ELAN Version 3.0 for use on Windows XP®.

1.3 Matrices other than waters may be analyzed using this procedure. Sample preparations techniques can be utilized for the analysis of seawaters, municipal and industrial influents and effluents, and dilute digestates of sediments, soils, rocks, or tissues.

1.4 This procedure is a modification of Draft EPA Method 1638. The EPA method validation study (reference 11.5) reported that the "EPA intends to revise Method 1638 to recommend use of response factor or weighted linear regression calibrations, allowing unweighted linear regress as a acceptable calibration technique." As the lowest standards are more of an influence in weighted linear regressions than "fit-through-zero" calibrations, Brooks Rand intends to primarily use weighted linear regression calibrations. For samples that are measured at or near the highest standards, a "fit-through-zero" approach may be appropriate.

1.5 This procedure must be followed to assure complete accuracy and reproducibility of the samples results generated by all of the operating chemists. An analyst must first be fully trained in the use of ICP-MS, including the interpretation of spectral and matrix interferences and procedures for their correction, as well as ultra-clean sample handling.

1.6 This procedure can be utilized to analyze for a large list of analytes. However, at this time the method has been fully validated for Ag, Al, As, Ba, Be, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Sn, Th, Tl, and Zn. Following this method will aid in the analysis, method development, and validation of other analytes.

2. EQUIPMENT

2.1 Instrumentation: ICP-MS (Perkin-Elmer ELAN DRC II) with a free-running 40 MHz RF generator; controllers for nebulizer, plasma, auxiliary, DRC gas A, and DRC gas B flow control; and a getter is equipped for work with ammonia gas. The quadropole mass spectrometer has a mass range of 5 to 270 atomic mass units (amu). The turbo molecular vacuum system achieves 10^{-6} torr or better.

2.2 Cetac ASX-500 high-speed auto-sampler.

3. SUMMARY OF METHOD

3.1 An aliquot of homogenous sample is prepared for analysis. The determination of dissolved elements requires the sample be filtered through a 0.45-μm pre-cleaned filter unit as in BR-0104, and then preserved with acid. The determination of total and total recoverable elements in water samples requires the samples be digested with a combination of heat and acid, or the metals must be extracted from the sample matrix. Solid samples require matrix specific digestion steps before introduction into the instrument. All sample preparation procedures are detailed in depth in separate Brooks Rand SOPs.

3.2 A prepared, aqueous sample is pumped through a peristaltic pump and delivered to a nebulizer, where the liquid forms aerosol droplets as it enters a spray chamber. The aerosol separates into a fine aerosol mist and larger aerosol droplets. The larger droplets exit out the bottom of the spray chamber and are pumped off as waste. The finer droplets are transported out of the spray chamber and enter the ICP torch through an injector tube. Inside the ICP torch, the aerosol droplets are transported into a high-temperature plasma, where they become atomized and ionized as they are introduced through a radio frequency (RF) load coil. The ions are transported into the plasma through a differentially-pumped interface. The ion stream is then focused by a single ion lens, which focuses the ions through a cylinder with a carefully controlled electrical field. The focused ion stream is directed into the dynamic reaction cell (DRC) where, when operating in DRC mode with a pressurized cell, the ion beam will undergo chemical modifications to reduce elemental interferences. When not operating in DRC mode the ion stream will remain focused as it passes through the cell with no chemical modification taking place. The ion stream is then transported to the quadropole mass filter, where only ions having a specific mass-to-charge ratio (m/z) are passed through at any moment in time. The ions exiting the mass filter are detected by a solid-state detector and processed by the data handling system.

4. INTERFERENCES

4.1 Contamination

4.1.1 Contamination of the samples during sample collection is a great risk, and extreme care should be taken to avoid this. Potential sources of contamination during sampling include using metallic or metal-containing labware, containers, and sampling equipment.

4.1.2 Sample collection equipment such as tubing, pumps, filters, and homogenization equipment should be non-metallic (whenever possible) and tested for metals through the analysis of equipment blanks.

4.1.3 Contamination of samples by airborne particulate matter is a concern. Sample containers should remain closed as much as possible. Container lids should only be removed briefly and in a clean environment during sample preservation and processing, so that exposure to an uncontrolled environment is minimized.

4.1.4 Laboratory

4.1.4.1 All labware (including pipette tips, ICP-MS autosampler vials, sample and digestion bottles, extraction apparatus and reagent bottles) should be tested for the presence of trace-metals. If necessary, the labware should be acid-cleaned, rinsed with DIW, and dried in a clean hood.

4.1.4.2 All reagents and gases used for analysis and sample preparation should be tested for the presence of trace metals prior to use in the lab. Due to the ultra-low detection limits of this method, it is imperative that all the reagents and gasses be as low as possible. It is often required to test several different sources of reagents until an acceptable source has been found. Metals contamination can vary greatly from lot to lot. Once an acceptable reagent lot has been identified, several cases of the lot number should be sequestered from the supplier. A logbook should be maintained to better track the acids and is stored in the ICP-MS lab.

4.1.4.3 Metals concentrations in both reagent DIW and HNO_3 are monitored each day the instrument is used by adding the calibration blank to the ICP-MS Blank logbook. This logbook is stored in the ICP-MS lab. Although there are no established limits for the blanks, the data is useful for troubleshooting.

4.1.4.4 Great care should be taken to keep the facility free from all sources of metals contamination. Clean hood HEPA filters must be replaced with new filters on a regular basis to reduce the risk of airborne contaminants. Metal corrosion of any part of the facility should be

addressed and replaced. Every piece of apparatus that is directly or indirectly used in the collection, preservation, or processing of samples should be trace metals free.

4.2 Elemental interferences

4.2.1 Interference sources that may inhibit the accurate collection of ICP-MS data for trace elements are addressed below.

4.2.2 Isobaric elemental interferences are isotopes of different elements that form singly or doubly charged ions of the same mass-to-charge ratio (m/z) and cannot be resolved by the mass spectrometer.

4.2.3 Data obtained with isobaric overlap must be corrected for by:

4.2.3.1 Measuring the signal from another isotope of the interfering element and subtracting the contribution from the isotope of interest (based on the relative abundance of the alternate isotope and the isotope of interest). The correction equations can be entered into the corrections column on the equations page of the analysis method.

4.2.3.2 The data corrected will only be as accurate as the accuracy of the relative abundances used in the equation for the data correction. It is important to establish an abundance ratio that is relatively constant (i.e., using another isotope of the element that is free from overlap) before applying any correction. For example, the measurement of Cd at mass 114 (which has an isobaric overlap of Sn at mass 114) uses the abundance ratio of Sn 114 and Sn at mass 118 (which exhibits no overlap).

4.2.3.3 After the abundance ratio has been established, the correction equation can be entered into the corrections column using the formula:

Analyte of determination = Mass Intensity – (Relative Abundance of Original Interferant / Relative Abundance of alternate (overlap free) Interferant) * Interferant

4.2.3.4 The correction equation for the example above would look as follows:

Cd 114=mass 114- (0.65%/24.23%)*(Sn 118)
Where the relative abundance of Sn 114 is 0.65%
and Sn 118 is 24.23%

4.2.4 Abundance sensitivity occurs when part of an elemental peak overlaps an adjacent peak. This often occurs when measuring a small mass-to-charge ratio (m/z) peak next to a large m/z peak. The abundance sensitivity is

affected by ion energy and quadropole operating pressure. Proper optimization of the resolution during tuning will minimize the potential for abundance sensitivity interferences.

4.2.5 Isobaric Polyatomic Interferences are interferences caused by ions of more that one atom which have the same m/z as the isotope of interest, and which cannot be resolved by the mass spectrometer. These ions are commonly formed in the plasma or the interface system from the support gasses or sample components.

4.2.5.1 Most of the common isobaric polyatomic interferences have been identified. A list of these possible interferences is available in the equations page of the method window.

4.2.5.2 Appropriate corrections should be made to the data. When this is not possible, a different m/z should be used.

4.2.5.2.1 For Fe-57, a correction value may be applied for $CaOH^+$ for matrices high in Ca (>10 ppm). Running a clean Ca standard at 30 ppm, the ratio of $CaOH/^{43}Ca$ after blank correction was calculated to be 0.02986157. Therefore, the correction equation used is (-0.02986157*Ca43).

4.2.5.3 Polyatomic interferences are highly dependant on the sample matrix. Corrections should be considered at the time of analysis.

4.3 Physical Interferences occur when there are differences in the response of the instrument from the calibration standards and the samples. Physical interferences are associated with the physical processes that govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface.

4.3.1 Physical interferences can be associated with the transfer of solution to the nebulizer at the point of nebulization, transport of aerosol to the plasma, or during excitation and ionization processes in the plasma. High levels of TDS in a sample can result in physical interferences. Proper internal standardization (choosing standards that have analytical behavior similar to the associating elements) can compensate for many physical interferences.

4.4 Memory Interferences - Carryover of elements in a previous sample in the sample tubing, cones, torch, spray chamber, connections, and autosampler probe are minimized by rinsing the instrument with a reagent blank after samples high in metals concentrations are analyzed.

4.4.1 If carryover is suspected, the sample should be reanalyzed after a long rinse period or after the analysis of an acceptable blank (less than 10 times the MDL).

5. SAFETY

5.1 Refer to Draft EPA Method 1638, section 5.0, for safety issues associated with the use of the method.

5.2 Hydrofluoric acid (HF) is particularly dangerous and should be used with extreme caution. HF may not cause immediate pain but is still very harmful. If there is any contact, quickly rinse under water followed by an application an unopened tube of calcium gluconate gel. Then go directly to the hospital. There should always be at least one tube in the lab during any procedure involving the use HF. The MSDS should be consulted prior to the use of HF and prior training is required by an experienced staff member.

5.3 Nitric acid and hydrochloric acid are very caustic and adequate protective gear should be worn when working with these acids, including eye protection, gloves with the appropriate resistance, and a lab coat. An adequate fume hood should be used for all acids.

5.4 Many of the chemicals have toxicities that are not well established and should be handled with care. For all known chemicals used, the MSDS should be consulted in advance.

5.5 Reference 11.3 in Section 11 lists the local Washington state OSHA regulations. King County local sewer limits should be posted near the ICP-MS waste disposal sinks and no materials higher than the limits should be disposed of.

5.6 The ICP-MS emits UV light when the plasma is on. Goggles should be worn if working near the plasma.

5.7 The instrument generates high levels of radio frequency (RF) energy and is very hot when the plasma is on. In the case of an instrument failure, be aware of these potential dangers.

5.8 DRC gasses should be stored safely in a closed cabinet. Adequate caution should always be used with pressurized gasses. Prior training or experience is necessary to change any gas cylinders. Oxygen gas can be explosive with certain materials and ammonia has a very low odor threshold and is corrosive to tissue.

6. REAGENTS AND STANDARDS

6.1 Reagents may contain elemental impurities that could negatively affect high data quality. High-purity reagents should always be used. Each reagent lot should be tested and test low for the elements of interest before being used in the laboratory.

6.2 Deionized Water (DIW) (ASTM Type I) demonstrated to be free from the metals of interest and potentially interfering substances.

6.3 Nitric Acid (HNO_3), concentrated, tested low (limits are held on file with the QA department).

6.3.1 1% (v/v) HNO_3 - Stock standard preparation diluent and sample diluent.

6.3.2 2% (v/v) HNO_3 – Auto-sampler sample probe rinse solution and pipette cleaning solution.

6.4 Stock Standard Solutions - obtained from a reputable and professional commercial source.

6.4.1 Single element standards are obtained for each determined metal as well as for any metals used as internal standards and interference checks.

6.4.2 A second source is obtained for each determined metal.

6.5 Multi-element stock standard solution-elements must be compatible and stable in solutions together.

6.6 Internal Standard Solution - Dilute stock standard solutions. The solution is stable for six months after the date of preparation. Different internal standards can be chosen based on sample matrix, on-going research, and specific analytical requests. The internal standard solution is added to all standards and samples by passing through a mixing chamber prior to passing through the peristaltic pump device.

6.7 The date, standard information, and preparer's initials must be entered into the ICP-MS standard logbook at the time of preparation for all standards. The date, preparer's initials, expiration date, elements, and their concentrations must be recorded on all bottles of standards.

6.8 Calibration Standards - Fresh calibration standards should be prepared every two weeks or as needed. The standards and amounts used, date, and preparer's initials should be recorded in the ICP-MS calibration logbook each time a fresh calibration is prepared.

6.9 Initial calibration verification (ICV) - ICV solution is made up from secondary source standards in order to verify the validity of the calibration curve.

6.10 "Daily" optimization and tuning solution

6.11 Duel detector calibration solution

6.12 Certified reference material (CRM) - CRMs of various matrices (drinking water, seawater, sediment, soil, tissue, river water, etc).

7. SAMPLE COLLECTION, FILTRATION, PRESERVATION, AND STORAGE

7.1 Samples should be received as described in SOP BR-0300.

7.2 Samples for dissolved metals determination must be filtered (if not field-filtered) through a 0.45-μm or a 0.2-μm pre-cleaned disposable filter unit. Filtering procedures are described in SOP BR-0104.

7.3 Samples must be preserved to a pH less than or equal to 2. The following provides a list of common preservation schemes:

7.4 Store the preserved samples for a minimum of 48 hours before analysis to completely desorb the metals from the container walls. The sample pH should be verified to be less than pH 2 prior to sample preparation.

7.5 Preserved samples can be stored in a secure area of the laboratory at room temperature until analysis.

8. PROCEDURE

8.1 Sample Preparation

8.1.1 For the determination of dissolved analytes, samples should be preserved with HNO_3 to 1% (v/v) after filtration.

8.1.2 For the determination of total recoverable analytes, there are several digestion and preservation techniques that can be used. Evaluation of the sample matrix, detection limits, analytes of interest, and the client's needs is required before deciding on an appropriate preparation technique.

8.2 Startup the Instrument

8.3 Perform X-Y Adjustment

8.4 Tune the Instrument

8.5 Optimize the Nebulizer Gas Flow

8.6 Optimize the Autolens Voltage

8.7 Perform the Instrument Performance Check: "Daily"

8.8.Perform a Full Optimization

8.8.1. This is done only when "Daily" fails

8.8.1 Pulse Stage Voltage

8.8.2 Analog Stage Voltage

8.8.3 Repeat Pulse Stage Voltage

8.8.4 Performing Dead Time Correction

8.8.5 Dual Detector Cross Calibration

8.9 Optimize Cell Rod Offset for DRC

8.10 Optimize Cell Path Voltage for DRC

8.11 Sample Analysis

8.11.1 Create a Method

8.11.1 Calibrate the instrument

8.11.2 Starting an Automated Analysis

8.11.2.1 Immediately following the calibration, an Initial Calibration Verification (ICV) should be analyzed.

8.11.2.2 Immediately following the ICV, a blank should be analyzed. This is called the Initial Calibration Blank (ICB). This demonstrates that there is no carryover of the analytes of interest and that the analytical system is free from contamination.

8.11.2.3 A minimum of three reagent blanks should be analyzed following the ICV. These blanks are called Instrument Blank Waters (IBW).

8.11.2.4 Two certified reference materials (CRM) should be analyzed following the IBWs.

8.11.2.5 A continuing calibration verification (CCV) standard should be analyzed every ten samples. The CCV standard should be the mid-point calibration standard. A CCV should also be analyzed after all of the samples have been analyzed.

8.11.2.6 A blank should be analyzed after each CCV, this blank is called a continuing calibration blank (CCB). This demonstrates that there is not carryover and that the analytical system is free from contamination.

8.11.2.7 For every 10 client samples, prepare and analyze a matrix spike (MS) and a matrix spike duplicate (MSD). Matrix spikes should be spiked at a level two to five times the background concentration or at the practical quantitative limit (PQL), whichever is greater.

8.11.2.8 For every 10 client samples, prepare and analyze a matrix duplicate (MD) sample.

8.11.2.9 Method of Standard Additions (MSA) curves should also be performed when appropriate. In general, always prepare a four point MSA curve for solids digests.

8.11.2.10 The plasma can be extinguished at any time by clicking plasma "Stop" on the front panel of the instrument page or, if need be, manually by pressing the yellow "off" button on the front of the instrument.

9. PROCEDURE FOR ANALYSIS USING DYNAMIC REACTION CELL (DRC)

10 QUALITY CONTROL

10.1 The correlation coefficients of calibration curves for each element must be ≥ 0.995 to proceed with sample analysis. If the correlation coefficients for any element is < 0.995, the results for that element may not be reported from that run.

10.2 The percent recovery of the ICV standard must be 85-115% for each element being determined. If the percent recovery is not within the control limits of

85-115%, for any element, the results for that element may not be reported from that run, unless the laboratory manager approves it.

10.3 Instrument rinses should be performed after any samples suspected to be high in metals and before any method blanks.

10.4 Each analytical or digestion batch must have at least 3 preparation (or method) blanks associated with it. The blanks are treated the same as the samples, and must go through all of the preparative steps. All of the samples should be corrected for the mean concentrations of these blanks. Three times the standard deviation of these blanks is the estimated method detection limit (EMDL) for that batch.

10.5 For every 10 client samples, a matrix duplicate (MD) sample should be analyzed. The relative percent difference (RPD) for the replicate should be ≤ 25 for waters and ≤ 30 for solids if the sample concentrations are greater than 10 times the MDL. A duplicate matrix spike (MSD) may be substituted for the MD, with the same control limits unless client-specific data quality objectives require an MD sample.

10.6 For every 10 client samples, a matrix spike (MS) and a matrix spike duplicate (MSD) should be performed. The percent recovery of the spikes should be 75-125% with an RPD ≤ 25 for waters and 70-130% with an RPD ≤ 30. If the spike recovery is out of control limits, a MSA can be used to correct for the matrix effect. Samples may be corrected by the slope of the MSA curve if the correlation coefficient of the MSA curve is ≥ 0.995. If the sample concentration levels are sufficiently high, the sample may be diluted to reduce the matrix effect. Spike sets should be performed at the same dilution factor as the native sample.

10.7 The percent recoveries of the CRMs should be 75-125%. If the results are not within control limits for each analyte, the sample results may not be reportable.

10.8 The percent recoveries of the CCV standards should be within 75-125%. If the CCV results are not within the control limits for any analyte, the sample results may not be reportable for that element.

10.9 CCBs should be monitored for the effects of carry-over and for possible system contamination. If carry-over of the analyte at levels greater than 10 times the MDL is observed, the sample results may not be reportable.

10.10 Reductive precipitation (RP) and APDC results can be corrected by an efficiency factor that is calculated quarterly based on the previous year's data.

10.11 The absolute response of any one internal standard should not vary from the original response in the calibration blank by more than 60-125%. Some analytical samples, such as those containing concentrations of the internal standard and tissue digestates, can have a serious effect on the internal standard intensities, but this does not necessarily mean that the analytical system is out of control. In some situations, it is appropriate to reprocess the samples using a different internal standard monitored in the analysis. Careful evaluation of the data and notification to the project manager should be given before doing this.

KLM
3-20-03

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF TOTAL ORGANIC CARBON IN SOILS AND SEDIMENT

Applicable Matrices: Soils, Sediments, Solids

Approvals and Signatures

Laboratory Director:	Michael F. Wheeler, Ph.D.	Date: 10/24/02
QA Manager:	Kirstin L. McCracken	Date: 10/25/02
Inorganic Technical Director:	Kristine A. Dusablon	Date: 10/25/02
Inorganic Supervisor:	William S. Cicero	Date: 10/25/02

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of total organic carbon (TOC) in soils, sediments and other solids.

1.2 The reporting limit (RL) and the accuracy and precision criteria are given in Section 9.0 of this SOP. Method Detection Limit (MDL) information is located in Section 14.0 (method performance).

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LLM 3-26-03

2.0 SUMMARY OF METHOD

2.1 A small aliquot of sample, usually 5.0 mg, is transferred to a tin capsule and treated with phosphoric acid to separate the inorganic carbon from carbonates and bicarbonates. The sample is placed in an oven and dried at 105°C for approximately 30 minutes to one hour. The sample is then transferred to an instrument where the sample is pyrolyzed in an inductive type furnace, where the carbon is converted to carbon dioxide. The carbon dioxide is measured by a differential thermal conductivity detector.

2.2 This procedure is based on the EPA Region II document "Determination of Total Organic Carbon in Sediment", July 27, 1998 that was authored by Lloyd Kahn, Quality Assurance Specialist.

3.0 DEFINITIONS

Accuracy: the degree of agreement between a measurement and the true or expected value, or between the average of a number of measurements and the true or expected value.

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of a similar matrix, meeting the above mentioned criteria.

Calibration: the establishment of an analytical curve based on the absorbance, emission intensity or other measured characteristic of known standard.

Calibration Blank (ICB/CCB): a volume of reagent water acidified with the same acid matrix as in the calibration standards.

Calibration Standards: a series of known standard solutions used to calibrate the instrument response with respect to analyte concentration. A standard containing the analyte in question (sulphanilimide) is prepared at varying weights and analyzed. This standard is a separate source from the LCS. The sulphanilimide is used to calibrate the instrument response with respect to analyte concentration.

Continuing Calibration Verification (CCV): a prepared standard solution used to verify the stability of the instrument calibration and instrument performance during the analysis of samples.

Corrective Action: action taken to eliminate the causes of an existing non-conformance, defect or other undesirable situation in order to prevent recurrence.

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Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Initial Calibration Verification (ICV): A prepared standard solution from a source separate from that of the calibration standards used to verify the concentration of the calibration standards and the adequacy of instrument calibration.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as samples, through all steps of the analytical procedure.

Matrix: the substrate of a test sample.

Matrix Duplicate (DP): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate; Laboratory Duplicate.

Matrix Spike (MS): field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a replicate matrix spike.

Method Blank: a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which the relative uncertainty is +100%. The MDL represents a range where qualitative detection occurs using a specific method. Quantitative results are not produced in this range.

Percent Solids (%S): the proportion of solid in a soil sample.

Quality Control Sample: a control sample, generated at the laboratory or in the field, or obtained from an independent source, used to monitor a specific element in the sampling

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and/or testing process.

4.0 INTERFERENCES

4.1 Volatile organics in the sediments may be lost in the decarbonation step resulting in a low bias. Maintaining the sample at 4°C, analyzing the sample within the specified holding time, and analyzing the wet sample, may minimize bacterial decomposition and volatilization of the organic compounds.

5.0 SAFETY

5.1 The toxicity or carcinogenity of each chemical used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be minimized as reasonably possible. A reference file of Material Safety Data Sheets (MSDS) for this test method is available to all personnel and must be read prior to performing this procedure. All laboratory personnel must be familiar with the laboratory environmental health and safety plan described in the STL Corporate Safety Manual (CSM).

5.2 Concentrated sulfuric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. These reagents should be used in a fume hood, whenever possible and if eye or skin contact occurs, immediately flush with large volumes of water. Protective clothing and eye shields should always be worn when working with these reagents.

6.0 EQUIPMENT AND SUPPLIES

6.1 Oven maintained at temperatures of 103°C-105°C.

6.2 Carlo Erba Elemental Analyzer Model EA1108 and Model NA 1500.

6.3 Analytical balance capable of weight determinations to 0.001mg.

6.4 Metal Trays capable of withstanding 105°C

6.5 Tweezers

7.0 REAGENTS AND STANDARDS

7.1 Acetanilide Crystals: purchased commercially.

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7.2 Sulfanilamide Crystals: purchased commercially.

7.3 Phosphoric Acid Solution
Tare a 2000 mL bottle (reserved for this solution) on a scale. In the 2000 mL bottle, add 183.4 g of H_3PO_4. Bring the total volume to 1700 mL with nanopure water.

7.4 Standards

Standard reference materials are purchased from commercial vendors and used as the laboratory control sample and matrix spike/matrix spike duplicate.

The Calibration Standard is purchased commercially. Analyst prepares a calibration curve when a new combustion column is to be used.

Calibration Standard Sulfanimide	Weight (mg)	% Carbon
Calibration Level 1	0.100	41.84
Calibration Level 2	0.500	41.84
Calibration Level 3	1.00	41.84
Calibration Level 4	1.75	41.84
Calibration Level 5	2.50	41.84

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT & STORAGE

8.1 Samples should be collected in sediments in amber glass jars. Immediately following collection, the samples should be cooled to 4°C (±2) and maintained at that temperature until time of analysis.

8.2 The holding time is 14 days from date of collection.

8.3 Samples are stored from the time of receipt in the laboratory until 60 days after delivery of the reconciled data package report. Unless otherwise specified by a federal, state or client-specific protocol, samples are disposed of after 60 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

Method Blank
For each analytical batch of 20 or fewer samples, a method blank is analyzed to assess

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potential contamination from the laboratory environment. The analyte values in the MB must be less than the reporting limit. When values in the MB exceed the reporting limit, contamination should be suspected. The source of contamination should be identified and corrected and the associated samples should be re-prepared and reanalyzed.

Laboratory Control Standard (LCS)
For each analytical batch of 20 or fewer samples, a laboratory control sample (LCS) is analyzed. The percent recovery of the LCS should be within the established accuracy limits. If client has not requested a MS/DP, then an LCSD will be analyzed. If the criteria are not met, associated samples and QC items should be re-prepared and reanalyzed.

Column Verification Standard (ICV/CCV)
An acetanilide standard is analyzed in duplicate after the initial calibration curve, after every 10 drops, and at the end of the analysis. The recovery of this standard is used to determine if degradation of the column is evident and the recovery of the standard should be within ±10% of the true value. If this criterion is not met for one of the duplicate analyses, assess the data, and continue analysis. If the recovery for both of the duplicate analyses is not within the limit, stop analysis, correct the problem and reanalyze until acceptable performance is demonstrated. Samples not bracketed by passing acetanilide standards must be reanalyzed.

Column Blank (ICB/CCB)
Instrument blanks are analyzed in duplicate immediately following the acetanilide standards, every 10 drops and at the end of the analytical sequence to verify that the system is free of contamination. The concentration of the instrument blank must be less than the established reporting limit. If this criterion is not met for one of the duplicate analyses, assess the data, and continue analysis. If the recovery for both of the duplicate analyses is not within the limit, stop analysis, correct the problem and reanalyze until acceptable performance is demonstrated. Samples not bracketed by passing instrument blanks must be reanalyzed.

Precision
All samples are analyzed in triplicate. The relative standard deviation between replicate results should be ≤ 20. If this criterion is not met, review the data for error and reanalyze the sample, when necessary.

Matrix Spike (MS) / Sample Duplicate (DP)
Matrix spikes are analyzed at a frequency of one per 20 samples per site-specific matrix. The MS is used to provide information to the client about the effect of a site-specific matrix on the analytical procedure. The percent recovery for each sample replicate should be within the established accuracy and precision limits.

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10.0 CALIBRATION AND STANDARDIZATION

Prepare a calibration curve when there is a new combustion column, by plotting peak area against mg of Carbon using five different weights of a constant percent Carbon standards that cover the range of the instrument. Using linear regression analysis, calculate a correlation coefficient (r). The (r) values must be ≥0.995 for the curve to be considered acceptable. If this criterion is not met, the calibration procedure must be repeated prior to further analysis.

11.0 PROCEDURE

11.1 Instrument Standards

Calibration Curve
Prepare the calibration standards by weighing the appropriate amount of sulfanimide into a tin capsule for each calibration level. Place the tin capsules in the metal tray.

Instrument Check Standards
Prepare the column verification standard by weighing approximately 0.400mg to 0.700mg of acetanilide into tin capsules. Prepare as many as needed to bracket the samples. Place the tin capsules in the metal tray.

Prepare a bypass by putting approximately .300-.600mg of acetanilide. The bypass is the first rep that is dropped into the combustion column and analyzed by the instrument. It is used to confirm that the column is working correctly.

Prepare the column blanks by crushing empty tin capsules and placing them in the metal tray. Prepare as many as needed to bracket the samples.

Method Blank
Prepare the method blank by placing 2 drops of into three tin capsules 1:19 H_3PO_4 into three tin capsules. Place in metal tray, and let dry in the 103-105° oven until dry.

LCS
Prepare the LCS by weighing approximately 9 mg of the LCS standard into four tin capsules in the metal tray. Add two drops of into each tin1:19 H_3PO_4 into each tin. Place in oven and dry.

11.2 Samples
Weigh approximately 4-8mg of the sample into a tin capsule. Record the weight to the nearest 0.001 mg. Place the tin capsule in the metal tray and record the location in the

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analysis run log. Repeat for each sample.

Add 1-2 drops of 1:19 H_3PO_4 to each tin capsule and check for effervescence. Add additional H_3PO_4 until effervescence does not occur.

Place the metal tray(s) into an oven maintained at approximately 103-105 °C for 15-20 minutes, or until samples appear dry.

11.3 Analysis
Transfer all the tin capsules from the metal tray to the plexiglass analysis tray.

Turn on the analyzer and allow the instrument to equilibrate according to manufacturer instructions. Follow the manufacturer instructions for analysis.

Analyze the calibration standards, QC samples and field samples according to the following sequence:

Initial Calibration Blank
Initial Calibration (Level 1-5)
Column Verification Standard
Column Verification Standard
Column Blank
Column Blank
Method Blank
LCS
3 "Drops"
Column Verification Standard
Column Verification Standard
Column Blank
Column Blank
10 "Drops"
Column Verification Standard (Closing)
Column Blank (Closing)

11.4 Reporting Results
Convert the percent carbon into mg/kg carbon using the equation provided in Section 12.0. Quantitative results should be reported in appropriate units and significant figures. Data must be corrected for percent solids.

12.0 CALCULATIONS

12.1 % Carbon to Weight Conversion

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KLM 3-26-03

X% Carbon × 10,000 mg/kg Carbon

Value to be recorded = X mg/kg carbon × dry/wet ratio = mg/kg.

12.2 % Recovery

LCS: $\frac{\text{LCS found in sample}}{\text{TV of LCS (8800mg/Kg)}} \times 100 = \%\text{Recovery}$

Matrix Spike:

$\frac{\text{(A)mg/Kg wet carbon}}{\text{\%solid}} \times 100 = \text{(B)mg/Kg dry carbon}$

$\frac{\text{(spike TV)(SA)}}{\text{wt. of spiked sample}} \times \frac{1\text{million}}{} = \frac{\text{mg/Kg wet S.A.}}{\text{\% solid}} \times 100 = \text{mg/kg dry SA wt. of sample}$

$\frac{\text{mg/Kg dry carbon-mg/Kg dry carbon from parent sample}}{\text{mg/Kg dry S.A.}} \times 100 = \%\text{ Recovery}$

Where: A= mg/Kg wet carbon of parent sample
B= mg/Kg dry carbon of parent sample
SA= spike added (mg/Kg)
Spike TV= 0.8011mg/Kg

12.3 %RPD: The Relative Percent Difference between the sample and duplicate analysis is calculated with the following equation:

$$\%RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

Where:

RPD = Relative Percent Difference

D_1 = First Sample Value

D_2 = Second Sample Value (duplicate)

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13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 Review the samples, standards and QC samples against the performance criteria given in section 9.0 for Quality Control. If the results do not fall within the established limits or criteria, corrective action is required. A QC Summary is provided in Section 17.0, Table 1 along with recommended corrective actions for each test method. If corrective action is not taken or unsuccessful, the situation should be documented and reported in the project narrative. All data that does not meet established criteria must be flagged with the appropriate data qualifier and noted in the project narrative.

14.0 METHOD PERFORMANCE

14.1 An Initial Demonstration of Capability is required for each analyst before unsupervised performance of this method.

14.2 An Initial Method Detection Limit (MDL) determination for each test method referenced in this SOP is performed following the procedure described in the reference method, 40CFR, Part 136, Appendix B and laboratory SOP LP-LB-009. The MDL is verified or repeated when a significant change to the method occurs. Significant changes include the use of alternate reagents or standard reference materials, new instrumentation or the use of alternate sample preparation procedures.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 The laboratory optimizes technology to minimize pollution and reduce the production of hazardous waste whenever possible.

15.2 The laboratory procedures for waste management comply with applicable federal, state and local regulations and are described in SOP LP-LB-001HAZWD.

16.0 REFERENCES

16.1 Determination of Total Organic Carbon in Sediment, July 27, 1988. Lloyd Kahn, Quality Assurance Specialist, U.S. Environmental Protection Agency, Region II,

17.0 TABLES, DIAGRAMS, FLOWCHARTS

17.1 Table 1: *QC Summary & Recommended Corrective Action*
17.2 Appendix C: *Operating Instructions for the Carlo Erba Elemental Analyzer*
17.3 Appendix B: *TOC Procedure for High Concentration Marine Sediments*

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KLM 3/26/03

Table 1: QC Summary & Recommended Corrective Action

QC Item	Frequency	Acceptance	Recommended Corrective Action*
ICAL 5 standards	As Required	Correlation Coefficient <0.995	System Check, Reanalyze
IPCS – ICV	Following ICAL	%R ± 10% of true value	System Check, Reanalyze, Prepare new standard solutions, Recalibrate, Reanalyze any samples not bracketed by one acceptable ICV.
IPCS - CCV	After every 10 analytical samples	%R ± 10% of true value	System Check, Recalibrate. Reanalyze any samples not bracketed by one acceptable CCV.
ICB/CCB	Following each ICV/CCV	Target < RL	System Check, Recalibrate
Method Blank	With each sample batch of 20 samples or less	Target < RL	Reanalyze with associated samples
Lab Control Sample	With each sample batch of 20 samples or less	%R within control limits	System Check, Reanalyze, Recalibrate, Reprep
Matrix Spike	With every 20 field samples or as needed	%R (75-125)	Note in project narrative
Sample Duplicate	With every 20 field samples or as needed	%RPD ± 20% of original sample determination	Note in project narrative

**The recommended corrective action may include some or all of the items listed in this column. The analyst must use professional judgment to investigate and correct problems before proceeding with analysis. Suspect data must be qualified and reported in the project narrative.*

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Appendix B
Marine Sediments High in Inorganic Carbon

1.0 SAMPLE PREPARATION

Transfer approximately 10grams of a thoroughly mixed sample to an aluminum weigh dish, and dry in the 105°C oven. Once dry, grind sample with pink mortar and pestle to a fine powder (the pink mortar and pestle have a much smoother surface than most other mortars, thus reducing contamination). Record the weight of a 250mL Teflon beaker. Transfer approximately 5grams of ground sample to this beaker.

If the sample is to be spiked, weigh the beaker to the nearest 0.1mg. Record the weight. Likewise, determine and record the weight of the added sample. Now add 0.1grams of NIST 1632b Trace Elements in Coal (80.11% Carbon) to the sample. Record this weight as well. Evenly distribute the spike over the sample when adding, rather than make one big pile, and use a glass stirring rod to mix the spike in the sample. Make sure not to use that stirring rod with any other sample.

Talc-free latex gloves should be worn from this point on to minimize the risk of acid burns. Add several drops of 1:1 HCL to each sample and stir each with its own glass stirring rod. Samples containing large concentrations of inorganic carbon may effervesce to the point of overflowing the beaker, so take care to add the acid in small aliquots and stir vigorously. Should the sample "boil over" it must be re-prepared from step 1.

Continue to add 1:1 HCL in small aliquots until there is no further reaction, taking sample to dryness after each addition of acid with the hot plate provided.

Very carefully rinse the stirring rod and beaker walls with DIH_2O. Use a fine-tipped squirt bottle and use only what is needed to bring the entire sample to the bottom of the beaker. Remember, you are "adding water to acid" so take all necessary precautions to avoid splashing!

Dry the treated samples on the hot plate in the hood, after each acid/water addition. In no case shall more than 200mL of 1:1 HCL total be added to any sample.

Weigh beaker with residue and record.
***NOTE**: Samples are hydroscopic and will absorb water if they are exposed to air for too long.*

Once thoroughly dried, scrape the sample residue from the beaker and grind it to a powder using the pink mortar and pestle. Transfer the ground sample to a clean, dry 40-

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mL vial reserved for this analysis.

NOTE: *Depending on the nature of the sample, it may be quite difficult to completely remove the dried residue from the beaker or to grind it to a homogenous powder. Where difficulties are encountered, make a note on the preparation worksheet. Also, it is comparatively more important to remove and grind all of a spiked sample otherwise percent recoveries may be affected.*

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LLM 3-26-03

Appendix C
Operating Instructions for the Carlo Erba Elemental Analyzer

1.0 INSTRUMENT SET-UP

The power switch a white handle located on the right side of the machine.

The furnace temperature dial is located on the left and the dial should be set to 102, (instrument dial can only be set to three places, but it can be seen from instrument temperature that it is actually 1020°, not 102°). Pull the "FURN STBY" button to the out position to turn "ON".

Turn UHP Oxygen to "ON" and adjust the carrier gas knob from "stby" to flow. Turn the purge knob from "OFF" to "ON". Check the pressure gauges. The output should read from left to right: 95, 60, 90, 350 kPa.

When the LED temperature readout is 1020___, pull the "FIL OFF" button to the "ON" position.

Turn the autosampler tray until the number 1 position is behind the post, in front of the autosampler.

Turn on the computer monitor. The main menu of the EAGER200 program should be available. If it is not, select the EAGER200 icon to open the program.

The Carlo Erba is calibrated with each new combustion column (Refer to Section 2: Changing the Column and Section 3: Calibration), and that calibration is used until quality control or the column fails. Typically the column holds for approximately 200 drops or one typical run. The instrument is left in stand-by between analytical batches.

2.0 Changing the Column

A typical column will last for approximately 200 drops; however; a column may fail at any time. Samples high in sulfur will especially shorten a column's useful life. The surest sign that a column needs replacing is failing blanks. Also, many small "noise peaks" may be observed in the last third of a run. To change the column:

Turn off the gases to the instrument.

Depress the "FURN STBY" and "FIL OFF" buttons to the "in" position. (Out is on, In is off).
Turn the dials in the upper left corner of the instrument panel for the left furnace

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temperature to 052. Wait until the temperature readout is approximately 500-600°C. Gloves are provided to protect analysts hands while changing the column.

Remove the panel covering the furnace and unscrew the autosampler from the top of the column.

Unscrew the bottom of the column. Wiggle the nut and O-ring until they come off the column bottom.

Lift the column out of the furnace by the upper O-ring.

CAUTION: DO NOT TOUCH THE COLUMN!!!!! IT WILL BE HOT!!!!!

Pack a new column using a new quartz column, and following "Figure A". Do not pack the quartz wool too tightly; it is there to keep the tungsten oxide on alumna and copper wire separated and retained in the column. Packing too tightly will only serve to restrict the flow of gas through the system and may result in retention time shifts and missed peak identification. Set temperature back to 102 and press "FURN STBY" to the out position.

Set used column to the side of the instrument and let cool overnight. Place column into box provided to be disposed of by hazardous waste personnel.

Once temperature of 1020°C is reached calibrate the new column. Refer to Sec.3.

3.0 Calibration

To calibrate the Carlo Erba for carbon, click on the correct channel. Channel A is for instrument EA 1108 and channel B is for NA 1500. At main menu follow these steps:

1. "Load Method"
2. "OK"
3. "Template.MTH"
4. OK
5. "Save Method."

Type CHNS (for Channel A), or N-C (for Channel B) *MMDD* (current date), then click OK and OK. Now you should be back at the main menu. Click on the sample table. Under file name column (screen should like a spreadsheet), click on Row #17 and follow these steps:

1. "Edit"
2. Fill sample table"
3. Chr. filename: highlight box and type C (if using Channel B use N), and the month and day

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LLK 3-26-03

4. No. of samples: 180
5. Sample name index: 17
6. File name index: 17

(Steps 4 through 6 tell the computer where to start filling the chromatogram name and where to end it).

7. "Replace"

Then go back to position #1 under filename and enter C (*MMDD*) 01 through 17 for the first seventeen positions. On line #4 begin entering the Sulfanilamide weights. Sulfanilamide is used for the curve, and should weigh approximately: <0.100, 0.500, 1.000, 1.750, and 2.500 milligrams. Blank weights should be entered as 30mg. Line #9 will be the first set of check standards for the analysis. #9 and #10 should be Acetanilides and #11 and #12 will be blanks. These standards will be every ten drops.

To make instrument stop after running "X" number of samples, click after the line that you want to stop at in the sample table. Then choose "Edit," "Insert sample line," and hit "OK." This is always good to do just after the curve, just in case the curve does not pass, your prepped samples are not wasted on a failing curve.

To Start Instrument: in sample table click in space next to sample you wish to begin acquiring, and the computer will ask "Acquiring Sample #*XX*," and click "OK." Don't forget to enter a sample line at the end of your run log. This instructs the instrument to stop acquiring. Finally, go back to the main menu. At the tool bar located at the top of the screen, choose "RUN," and "Start Analysis."

After curve has run and at main menu follow these steps:

1. View;
2. View Calibration Curve;
3. Component, click on Carbon;
4. OK;
5. Print;
6. Graph Title: enter date of calibration.
7. Print:
8. Print single component curve;
9. File;
10. Exit.

After the curve runs and produces a ≥0.995 correlation, go back to sample table at Main Menu, delete the blank sample line after the curve, and choose "Edit," "Delete Sample Line," and "OK." Always remember to return to the main menu and save whenever entering information.

4.0 Analysis

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Place a tin capsule on the balance and tare. Remove the capsule and add a few crystals of acetanilide. Replace the capsule on the balance and record the weight of the acetanilide. This weight should be between 0.4 and 0.7mg.

Enter data for the acetanilide in position accordingly, selecting "unknown" for sample type. Other options are only used to setup the template. Pay attention to the filename; the date must be correct and the sample position must match the number at the far left of the row.

Crush the sample by pinching the top closed, then folding it over. Press into a small cube using the forceps and place in the corresponding position.

Note: It is helpful to fold the blanks into rectangular shapes to help differentiate between blanks and samples.
Repeat this procedure for all remaining positions.

Load prepared samples into autosampler tray, making sure sample ID's, filenames and sample weights are in the sample table. Remember that every 10 drops a series of two acetanilides and two blanks must be analyzed. (Remember to enter a blank line at the end of the run to stop instrument from acquiring.)

Note: When crushing the tin capsules of prepared samples, be aware that the phosphoric acid/heat (used in Organic Carbon analysis only) can make the tin brittle and easy to tear. Rather than use excessive force or pressure to produce the smallest package possible, concentrate on making a smooth, intact cube with nothing "sticking out" which might hang up the capsule in the sample tray or catch as the capsule drops into the combustion column. Should a capsule tear while compacting it, immediately place it into a new capsule and continue. Of course, should any sample be lost as the result of a tear or any other circumstance that sample must be discarded and a new one prepared.

When all is loaded correctly, the sample table is typed and the correct position for the sample to be acquired corresponds with the autosampler tray. Analysis can then begin. At main menu, using tool bar, select "Run," and "Start Analysis."

5.0 Reporting Results:

When run has been completed according to the sample table set up, using tool bar at the main menu, click on "Recalculation," and "Summarize Results," (results can also be looked at as instrument is acquiring).

Place a "1" next to each of four lines next to LCS (this allows for the LCS to be calculated on a separate page), and "0" in all others (so that only the LCS will print). Under "print" choose "single group."

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STANDARD OPERATING PROCEDURE
PARTICLE-SIZE ANALYSIS OF SOILS
ASTM D422-63

Applicable Matrix: Soil

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1.0 SCOPE AND APPLICATION

1.1. This SOP describes the laboratory procedure for the determination of particle size distribution in soil samples that contain sand, silt, clay and gravel.

2.0 SUMMARY OF METHOD

2.1. A soil sample submitted for particle size analysis is prepared according to laboratory SOP LM-SL-D421 *Dry Preparation of Soil for Particle Size Analysis* or LM-SL-D2217 *Wet Preparation of Soil Samples for Particle Size Analysis*. Particles greater than 75um (gravels to fine sands) are determined by sieve analysis while particles less than 75um (silts and clays) are determined by sedimentation using a hydrometer followed by sieve analysis.

After wet or dry sample preparation, the sample is passed through No.10 sieve. The particles retained on the No.10 sieve (greater than 2.00mm) are further separated by sieve analysis. A portion of the sample that passed through the No.10 sieve is transferred to a glass sedimentation cylinder to which distilled water has been added. Seven hydrometer readings are taken over 24 hours. After the final hydrometer reading, the suspension is rinsed over a No. 200 (75 um) sieve, dried, and further separated by sieve analysis.

Particle size determinations for each sieve measurement and hydrometer reading are calculated and corrected for hygroscopic moisture and specific gravity. Unless a separate analysis for specific gravity is requested, the specific gravity is s assumed to be 2.65.

2.2. This procedure is based on ASTM D422-63.

3.0 DEFINITIONS

Not Applicable

4.0 INTERFERENCES

Not Applicable

5.0 SAFETY

5.1. Care should be taken to avoid exposure to the sample matrix since all environmental samples are potentially hazardous. Protective clothing, eye protection and disposable gloves should be worn when handling samples. All laboratory personnel must be familiar with the environmental health and safety plan described in the STL Chemical Safety Manual.

6.0 EQUIPMENT AND SUPPLIES

6.1. Top-Loading Balance sensitive to 0.01 g

6.2. Mechanical Stirring Apparatus and Dispersion Cup

6.3. Sedimentation Cylinder(s) 1000 mL

6.4. Hydrometer: ASTM 151H in specification E 100.

6.5. Thermometer: Accurate to 0.5°C

6.6. Mortar and Rubber Tipped Pestle

6.7. Sieves of the following size(s):

3.0 in (75.00mm)	No. 20 (850.0um)
2.0 in (50.00mm)	No. 40 (425um)
1.5 in (37.50mm)	No. 60 (250.0um)
1.0 in (25.00mm)	No. 80 (180.0um)
3/4 in (19.00mm)	No. 100 (150.0um)
3/8 in (9.50mm)	No. 200 (75.0um)
No. 4 (4.75mm)	
No. 10 (2.00mm)	

6.8. Oven with temperature range of 60° C to 110° C

6.9. Timing Device with second hand and capable of counting up to 25 hours

6.10. Stainless steel spatulas, spoons, metal and bristle brushes

6.11. Ro-tap machine

7.0 REAGENTS AND STANDARDS

7.1. Reagents

Deionized (DI) Water: Milli-Q System

Sodium Hexametaphosphate Solution: Combine 2940 g of DI water with 120 g of sodium hexametaphosphate in an appropriate container. Mix until the solution is homogeneous. Assign an expiration date of 30 days from date of preparation.

8.0 SAMPLE HANDLING AND PRESERVATION

8.1. At least 500 grams of soil sample should be collected in glass or polyethylene jars. Immediately following collection the sample should be sealed and cooled to 4°C in order to preserve the moisture content of the sample.

8.2. Samples are stored from the time of receipt in the laboratory until 30 days after delivery of the reconciled data package report. Unless otherwise specified by a federal, state or

client-specific protocol, samples are disposed of after 30 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

Not Applicable

10.0 CALIBRATION AND STANDARDIZATION

10.1. Calibrate the balance on each day of use, prior to use.

10.2 Calibrate the hydrometers every two years following the procedure given in LM-SL-001.

11.0 PROCEDURE

11.1 Sample Preparation

Prepare the sample following either laboratory SOP LM-SL-D421 (Dry Preparation) or LM-SL-D2217 (Wet Preparation).

11.2 Sample Analysis

11.2.1 Hydrometer Test

Transfer the sample/sodium hexametaphosphate mixture into a dispersion cup ensuring a quantitative transfer using DI water. Fill the dispersion cup ~half full with DI water. Mix the sample for one minute using the immersion blender.

Pour the contents of the dispersion cup through a #10 sieve into a 1000 mL sedimentation cylinder (1000 mL graduated cylinder). Rinse the cup with DI water, to ensure that the entire sample is transferred to the sedimentation cylinder.

Add DI water to the sedimentation cylinder until the volume is 1000 mL then cover the cylinder with a sheet of parafilm. Allow the sample to stabilize to ambient temperature.

Transfer the material retained on the No. 10 sieve to a labeled medium-size aluminum dish, and place the aluminum dish into an oven maintained at a temperature of 105ºC for a minimum of 16 hours.

After up to 12 sedimentation cylinders have been prepared, ensure that each cylinder is filled to the reference line with DI water, covered with parafilm, and that there is sufficient clean DI water available to rinse the hydrometer.

Record the ID of the hydrometer that you intend to use. Record the start time and set the timer for elapsed time.

Use the hydrometer reading table used to perform the activities as indicated (shake, place or read) for each 1000 mL cylinder.

To shake, rotate the flask up and down for one minute approximating at least 60 turns (one turn upside down and then right side up constitutes two turns).

To take a reading, gently insert the hydrometer into the cylinder then wait ~ 20 seconds. Read the hydrometer at the top of the meniscus to the nearest 0.0005. Enter the hydrometer reading into the appropriate cell on the benchsheet. Clean the hydrometer by twisting and dropping into a clean DI water bath.

Insert a temperature sensor into the cylinder to the depth the hydrometer reached. Read the temperature to the nearest 0.5°C. Enter the temperature reading into the appropriate cell on the benchsheet. After reading, rinse the sensor in a DI water bath.

Take readings every 2, 5, 15, 30, 60, 240 and 1440 minutes. Record each reading on the benchsheet, then transfer this information into the appropriate cell of the EXCEL worksheet.

11.2.2 Large Sieves

Tare the balance and weigh an aluminum dish. Enter the weight measurement in the non-material section of the EXCEL worksheet in the cell labeled "Pan, g".

Carefully transfer the non-soil material (e.g.- sticks, grass, wood, plastic) from the drying dish to the pre-weighed dish and enter the weight measurement in the non-soil material section of the EXCEL worksheet in the cell labeled "Pan/Dry Sample, g".

Enter a brief description of the type of non-soil material (e.g.- sticks, grass, wood, plastic) in the non-soil material section of the EXCEL worksheet in the cell labeled "Description".

Tare the balance and weigh each of the 3/4", 3/8", #4 and #10 sieves. Record the weight measurements in the EXCEL worksheet in the cells labeled "Sieves (Tares)". Also weigh any larger sieves if necessary.

Stack the sieves then transfer the soil material retained on the #10 sieve into the sieve stack. Shake for 2 minutes. If there is greater than ~30 g of material, place the sieve stack into the Ro-tap machine and shake for 10 minutes.

Weigh each sieve along with the material retained on it. Enter these weight measurements in the "Sieve + Sample Weights" section of the Excel worksheet.

Determine the average hardness of the particles retained on the #10 sieve by dropping a hammer on the particle from a height of approximately one foot. Hardness qualifiers are hard, soft or brittle. Record the hardness qualifier in the "Description of >#10 Particles" section of the Excel worksheet.

Observe and record the shape of the particles in the "Description of >#10 Particles" section of the Excel worksheet. Shape qualifiers are well rounded, rounded, subrounded, subangular, and angular.

11.2.3 Small Sieves

When the hydrometer test is complete, transfer the soil from the sedimentation cylinder to a #200 wet wash sieve.

Wash the soil through the #200 sieve until the water from the bottom of the sieve runs clear. Carefully transfer the material retained on the sieve to a labeled 250 mL glass beaker.

Place the beaker into the oven. Dry at a temperature of 105ºC for at least 16 hours. After 16 hours, remove the beaker from the oven and allow it to cool.

Gently mix the dried contents of the beaker with a rubber-tipped pestle to break any soil aggregates that may have formed during the drying stage.

Tare the balance and weigh each of the sieves between #20 and #200. Record the weight measurements in the EXCEL worksheet in the cells labeled "Sieves (Tares)".

Transfer the dry sample into the sieve stack, ensuring that all material is transferred. Use hair or wire brushes to clean the beaker.

Place the sieve stack on the Rotap machine and shake for ten minutes.

Weigh each sieve along with the material retained on it. Enter these weight measurements in the "Sieve + Sample Weights" section of the Excel worksheet.

Determine particle size using the following formula.

12.0 CALCULATIONS

12.1. Sample Used (SU)

<u>Wet Method</u>

$$SU = (pan + wet\ sample - pan) \otimes PS$$

Where:

PS = Percent solids

Note: for hydrometer SU, subtract the dry weight of any material retained on the No. 10 sieve.

Dry Method

$$SU = (pan + dry\ sample - pan) - (pan + non - soil\ material - pan) \otimes HMCF$$

Where:

HMCF = Hygroscopic moisture correction factor

12.2 Sieve Analysis (Percent Finer = PF)

Large Sieves:

3 inch: PF = 100-100 (Sieve and Sample (3 inch) - Sieve (3 inch))/SU*

2 inch: PF = PF (3 inch) - 100(Sieve and Sample (2 inch) - Sieve (2 inch))/SU and so on through the #10 Sieve.*

Small Sieves:

#20: PF = PF(#10) - 100(mass passing #10/sample mass (Hyd))*(sieve and sample (#20) - sieve(#20))/sample used*

#40: PF = PF (#20) - 100(mass passing #10/sample mass (Hyd))*(sieve and sample (#40) - sieve (#40))/sample used and so on up through #10 sieve.*

12.5 Hydrometer Analysis

Particle size, Micron

1000*sqrt [930*viscosity/980*(SG-1))*(effective depth/time)]

Viscosity at sample temperature, poises
Effective Depth, cm = 16.29-264.5*(actual Hydrometer reading - 1) above equation for effective depth based on equation found with table 2 in method, in which 16.29 = 0.5*(14.0-67.0/27.8)+10.5 and 264.5 = (10.5-2.3)/0.031
Time, minutes = Time of hydrometer reading from beginning of sedimentation
Sqrt - square root
SG - Specific Gravity of soil
Viscosity - is the resistance of a liquid to flow

12.6 Percent Finer (PF):

PF = Constant*(actual hydrometer reading - hydrometer correction factor - 1)

Where:

Constant = (100,00/W)*SG/(SG-1)
W = (Total sample used *sample used for hydrometer analysis*HMCF)/Amount of total sample passing #10 sieve
Hydrometer Correction = slope*sample temperature + Intercept
Slope = ((low temp. reading -1)-(high temp. reading -1)/(low temp. - high temp.))
Intercept = (low temp. reading -1) - (low temp. * slope)

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.0. Complete the sample preparation benchsheet and EXCEL spreadsheet. Document any problems encountered during sample analysis so they may be properly addressed in the project narrative. Perform primary and secondary data review following the guidance given in laboratory SOP LP-LB-003 *Data Review*.

14.0 METHOD PERFORMANCE

Not Applicable

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1. The laboratory optimizes technology to minimize pollution and reduce the production of hazardous waste whenever possible.

15.2. The laboratory procedures for waste management comply with applicable federal, state and local regulations and are described in SOP LP-LB-001HAZWD.

16.0 REFERENCES

16.1. Standard Test Method for Particle-Size Analysis of Soils, ASTM D422-63, Volume 04.08 Soil and Rock, American Society for Testing and Materials, Philadelphia, Pa., 1998.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

17.1 Table 1: Hydrometer Reading Table

Table 2: Hydrometer Reading Table (For up to 12 Sedimentation Cylinders)

Elapsed Time (hr:min)	Task	Cyl. No.	Actual Time (min)	Elapsed Time (hr:min)	Task	Cyl. No.	Actual Time (min)
0:00	Shake	1		1:01	Read	10	5
0:01	**Place**	**1**		**1:02**	Shake	11	
0:01	**Shake**	**2**		**1:03**	Place	11	
0:02	Place	2		1:04	Read	9	15
0:03	Read	1	2	1:05	Read	11	2
0:04	Read	2	2	1:06	Read	7	31
0:06	Read	1	5	1:07	Read	3	58
0:07	Read	2	5	1:08	Read	11	5
0:08	Shake	3		**1:09**	Shake	12	
0:09	**Place**	**3**		**1:10**	Place	12	
0:09	**Shake**	**4**		1:11	Read	10	15
0:10	Place	4		1:12	Read	12	2
0:11	Read	3	2	1:13	Read	4	63
0:12	Read	4	2	1:14	Read	8	32
0:14	Read	3	5	1:15	Read	12	5
0:15	Read	4	5	1:18	Read	11	15
0:16	Read	1	15	1:19	Read	9	30
0:17	Read	2	15	1:21	Read	5	60
0:20	Shake	5		1:25	Read	12	15
0:21	Place	5		1:26	Read	10	30
0:23	Read	5	2	1:27	Read	6	59
0:24	Read	3	15	1:33	Read	11	30
0:25	Read	4	15	1:34	Read	7	59
0:26	Read	5	5	1:41	Read	12	31
0:27	Shake	6		1:42	Read	8	60
0:28	Place	6		1:52	Read	9	63
0:30	Read	6	2	1:53	Read	10	57
0:31	Read	1	30	2:06	Read	11	63
0:32	Read	2	30	2:07	Read	12	57
0:33	Read	6	5	4:17	Read	1	256
0:34	Shake	7		4:18	Read	2	256
0:35	Place	7		4:19	Read	3	250
0:36	Read	5	15	4:20	Read	4	250
0:37	Read	7	2	4:21	Read	5	240
0:38	Read	3	29	4:22	Read	6	234
0:39	Read	4	29	5:00	Read	7	265
0:40	Read	7	5	5:01	Read	8	259
0:41	Shake	8		5:02	Read	9	253
0:42	Place	8		5:03	Read	10	247
0:43	Read	6	15	5:04	Read	11	241
0:44	Read	8	2	5:05	Read	12	235
0:47	Read	8	5	24:01	Read	1	1440
0:48	Shake	9		24:02	Read	2	1440
0:49	Place	9		24:03	Read	3	1434
0:50	Read	7	15	24:04	Read	4	1434
0:51	Read	9	2	24:05	Read	5	1424
0:52	Read	5	31	24:06	Read	6	1418
0:54	Read	9	5	24:07	Read	7	1412
0:55	Shake	10		24:08	Read	8	1406
0:56	Place	10		24:09	Read	9	1400
0:57	Read	8	15	24:10	Read	10	1394
0:58	Read	10	2	24:11	Read	11	1388
0:59	Read	6	31	24:12	Read	12	1382
1:00	**Read**	**1**	**59**				
1:00	**Read**	**2**	**58**				

Source: Laboratory Prepared Reference Document

SEVERN TRENT STL

STANDARD OPERATING PROCEDURE
DETERMINATION OF TRACE ELEMENTS BY ICP-MS

Applicable Matrices: Water/Soil
Standard Compound List and Reporting Limit: See Table 1

APPROVAL SIGNATURES

Laboratory Director: Michael F. Wheeler, Ph.D. Date: 4/27/04

QA Manager: Kirstin L. McCracken Date: 4/27/04

Department Manager: William S. Cicero Date: 4/27/04

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1.0 SCOPE AND APPLICATION

1.1. This SOP describes the laboratory procedure for the determination of total/dissolved metals in groundwater, surface water, drinking water, wastewater, sludge and soil samples using inductively coupled-mass spectrometry (ICP-MS).

1.2. The elements for which this procedure is applicable are given in Table 1 along with the routine reporting limit (RL). Elements and matrices other than those listed in Table 1 may be analyzed by this procedure upon client request if performance at the concentration levels of interest is demonstrated.

2.0 SUMMARY OF METHOD

2.1. A sample submitted for analysis is acid digested, nebulized and transported by argon gas to a plasma torch. The ions produced are introduced via direct interface into a mass spectrometer. Characteristic emission spectra are produced and sorted according to their mass-to-charge ratios, quantified using an electron multiplier and processed by a data handling system.

2.2. This procedure is based on EPA Method 200.8 and SW-846 Method 6020

3.0 DEFINITIONS

3.1. Dissolved Metals: The concentration of metals determined in a sample after the sample is filtered through a 0.45µm filter (Method 3005).

3.2. Total Metals: The concentration of metals determined in a sample following digestion by Methods 3010 or 3050.

3.3. Definitions for general laboratory terms are included in Appendix B.

4.0 INTERFERENCES

4.1. Isobaric Elemental Interferences

Isobaric Elemental Interferences are caused by isotopes of different elements that form singly or doubly charged ions of the same nominal mass-to-charge ratio and cannot be resolved by the mass spectrometer. Correction for this interference is handled by the data system and is accomplished by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest.

4.2. Abundance Sensitivity

Abundance sensitivity is a property that defines the degree to which the wings of a mass peak contribute to adjacent mass. The abundance sensitivity is affected by ion energy and mass filter operating pressure. Wing overlap interferences may result when a small

ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize occurrence.

4.3. Isobaric Polyatomic Ion Interference

Isobaric Polyatomic Ion Interference is caused by ions consisting of more than one atom, which have the same mass-to-charge ratio as the isotope of interest and cannot be resolved by the mass spectrometer. These interferences should be recognized, and when they cannot be avoided by the selection of alternative isotopes, appropriate corrections should be made to the data. Instrument operating parameters should be set to conditions that will minimize this phenomenon.

4.4. Physical Interference

Physical interferences such as a change in viscosity, surface tension and dissolved solids are known to affect instrument responses to certain samples. These physical effects can be reduced by dilution, matrix matching, as well as not allowing dissolved solids within the samples to exceed 0.2% (w/v).

4.5. Memory Interferences

Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. An active rinse monitoring cycle is employed by the software and will not allow the analysis of the next sample until levels drop below those of the determined baseline. The analytes chosen for this are B, Al, Ag, and Sb at masses 11, 27, 107, and 123, respectively. The minimum rinse time is set at 120 seconds. Memory interference can also be identified by monitoring the three replicate integrations that are used for data acquisition.

4.6. Polyatomic Interference

Nitric acid is preferred for ICP-MS in order to minimize polyatomic interferences known in the presence of the chloride ion. Hydrochloric acid is required to maintain stability in solutions containing antimony and silver. Corrections for chloride polyatomic interferences are applied to data regardless of whether hydrochloric acid is used in digestion, as the chloride ion is common in environmental samples.

5.0 SAFETY

5.1. The toxicity or carcinogenity of each chemical used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be minimized as reasonably possible. A reference file of Material Safety Data Sheets (MSDS) for this test method is available to all personnel and must be read prior to performing this procedure. All laboratory personnel must be familiar with the laboratory environmental health and safety plan described inthe STL Corporate Safety Manual (CSM).

5.2. Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. These reagents should be used in a fume hood, whenever possible and if eye or skin contact occurs, immediately flush with large volumes of water. Protective clothing and eye shields should always be worn when working with these reagents.

5.3. The analytical plasma sources emit radiofrequency radiation and intense UV radiation. ICP plasma should only be viewed with proper eye protection from UV emissions.

5.4. Metal salts are extremely toxic if inhaled or swallowed. Hands must be washed thoroughly after handling.

6.0 EQUIPMENT AND SUPPLIES

6.1. Inductively Coupled Plasma Mass Spectrometer: Capable of scanning a mass range of 5-240 amu with a minimum resolution capability of 0.9 amu peak width at 10% peak height.

6.2. Radio frequency generator compliant with FCC regulations.

6.3. Argon Gas Supply: High purity grade (99.99%)

6.4. Variable Speed Peristaltic Pump

6.5. Mass Flow Controller for the Nebulizer Gas Supply

6.6. Water Cooled Spray Chamber

6.7. Class A, Volumetric Flasks.

6.8. Volumetric pipettes: Calibrated daily at volumes bracketing the points of use.

6.9. Analytical balance with capability to measure 0.1 mg

7.0 REAGENTS AND STANDARDS

7.1. Reagents

Due to the sensitivity of the ICP/MS, all reagents must be high-purity, whenever possible. All acids used for this procedure must be ultra high-purity grade suitable for trace metal analysis.

Nitric Acid, concentrated (HNO_3)

Nitric Acid. 1:1 Solution (HNO_3 1:1)

Reagent Water

7.2. Standards

Certified standard stock standard solutions are purchased from commercial vendors and used to prepare the tune standard, mixed calibration, ICS and internal standard solutions. "Recipes" for prepared intermediate and working standard solutions are given in Appendix A.

Unless otherwise specified in Appendix A, the prepared standards are stored at room temperature protected from light and assigned an expiration date of 6 months from date of preparation unless the expiration date of the parent standard is earlier in which case the expiration date of the parent material is assigned.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Samples may be collected in either glass or plastic containers. The sample volumes required depend on the digestion procedure but the laboratory recommends that a minimum sample collection volume of 500mL for aqueous samples and 5 grams for soil samples. Immediately following collection, aqueous samples must be preserved with nitric acid to a pH less than 2. If dissolved metals are to be determined, the aqueous sample must be filtered (on-site) prior to preservation.

8.2. The holding time is 6 months from date of collection.

8.3. Unless otherwise specified by client or regulatory program, after analysis, samples are held for 30 days and then disposed of in accordance with applicable regulations.

9.0 QUALITY CONTROL

9.1. QC Requirements

The following QC samples are analyzed with each batch: Method Blank (MB), Laboratory Control Sample (LCS), Matrix Spike (MS) and a Serial Dilution (5X). Sample Duplicates (DP) are performed per client request. Internal standards are added to every sample. The internal standards used are given in Appendix A. Sample results that exceed the linear range (high calibration standard) are diluted and reanalyzed.

The instrument is calibrated daily with a minimum of three standards and a blank. Prior to calibration, a tune standard is analyzed. Instrument calibration is checked with the following QC samples, Second Source Calibration Verification (ICV), Low Level Standard (CRI), Continuing Calibration Verification (CCV), Calibration Blank (CCB) and Interference Check Solutions (ICSA, ICSAB).

The upper linear range for each element is established every 3 months by the analysis of the high-level calibration standard (CAL Level 3). The concentration of this standard for each element is given in Appendix A. The high-level calibration check standard is analyzed as part of the sample sequence and is used to verify the accuracy of data up to the high-level concentration. The percent recovery of this standard should be within ±5% of the expected value.

The minimum frequency requirements, acceptance criteria and recommended corrective action for QC samples are summarized in Table 2, Section 17.0.

10.0 CALIBRATION AND STANDARDIZATION

10.1. Instrument Operating Conditions & Precalibration Routine

Initiate and set-up the operating parameters of the instrument following the instructions provided by the instrument manufacturer. The plasma, sample uptake parameters and the power levels are fixed and set to the recommended level for optimal sensitivity and to minimize interferents. Allow the instrument to equilibrate (warm-up) for at least 30 minutes prior to analysis. Check the sample flow through the pump tubing to ensure that flow to the nebulizer and drain flow is smooth. If the flow is erratic, check the tubing placement on the pump rollers and replace, as necessary.

Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. Verify the operating conditions by analyzing a tune solution.

Use a rinse cycle time of 120 seconds (rinse blank) between each acquisition to remove traces of the previous sample. Detector-mass calibration and cross calibration are re-determined as needed or whenever a major change (i.e. installation of new detector) in instrumentation is implemented.

10.2. ICP-MS Tune Standard

Analyze the tune standard solution five times consecutively following the procedure that begins in Section 11.1. The recommended components and concentration of the tune standard solution is given in Appendix A. The percent standard deviation of the absolute signals for all analytes in the tune standard solution must be less than or equal to 5%.

Perform initial mass calibration and resolution checks in the mass regions of interest. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10 percent peak height.

10.3. Initial Calibration

Immediately following the tune standard, calibrate the instrument with a blank and three standards. The recommended components and concentration of the calibration standards are given in Appendix A. Prepare and analyze the standards following the procedure that begins in Section 11.1. Perform three replicate integrations and use the average of the three integrations for instrument calibration and quanitification. The correlation coefficient for the curve must be >0.995 for each analyte of interest.

Immediately following daily calibration, analyze an ICV, calibration blank (ICB) and a continuing calibration verification (CCV) following the procedure that begins in Section 11.1. Repeat the CCV and calibration blank after every tenth sample and at the end of

the sequence. Analyze the ICSA and ICSAB and the low level standard (CRI) solutions after the first ICB. The criteria for the instrument check standards are provided in Table 2, Section 17.0 along with recommended corrective actions.

11.0 PROCEDURE

11.1. Standard & Sample Preparation

Transfer ~40mL of each calibration standard [CAL #1,2,3, ICV, ICSA, ICSAB, CRI] into individual, labeled autosampler tubes. Use 40mL of nitric acid solution (2%HNO3) for each calibration blank. The CCV standard is the Level 2 calibration standard; after every ten samples, the autosampler returns to the position that holds the Level 2 standard and injects another aliquot of the standard as the CCV.

Analyze the Level 3 calibration standard every 3 months in order to establish the linear range of the calibration. To prepare the high-level calibration check standard, transfer 40mL of the Level 3 working calibration standard into a clean autosampler tube and enter the standard into the analytical sequence as an "unknown" sample.

Transfer approximately 10mL of each digestate to individual autosampler tubes. Prepare a serial dilution and post digestion spike using an aliquot of the un-spiked sample that was used for the matrix spike. To prepare the serial dilution, transfer 2.0mL of parent sample to an autosampler tube and add 8.0mL of nitric acid solution (2%HNO3). To prepare the post digestion spike, transfer 0.1mL of the ICP-MS post spike solution and 9.9mL of parent sample to an autosampler tube.

11.2. Analysis

Allow the instrument to become thermally stable prior to analysis. Create a new autosampler template on the instrument PC and enter the sample Ids in the order of analysis. Place the samples, serial dilution, post-digestion spike, calibration blanks, mixed calibration standards, and performance check standards in the position on the autosampler rack that corresponds to their assigned position in the autosampler template. Place the autosampler rack in the autosampler tray and initiate the software macro to begin analysis.

An example analytical sequence is given below:

Tune Standard
Calibration Blank
Calibration Standard #1
Calibration Standard #2
Calibration Standard #3
ICV
ICB
CRI
ICSA
ICSAB

CCV
CCB
10 Samples*
CCV
CCB
10 samples*
CCV
CCB

***The number of samples between each CCB/CCV (10) includes the method blank, laboratory control sample, matrix spike, sample duplicate, serial dilution and the post digestion spike.*

After analysis is complete, review the results against the criteria given in Table 2. Perform corrective action, as needed and dilute and reanalyze any sample whose result exceeds the linear range.

Report results in the appropriate units and significant figures corrected for dilutions and percent solids. The calculations performed by the data acquisition system include interference correction and internal standard normalization. The equations used to generate concentrations by the data handling system are given in section 12.0.

12.0 CALCULATIONS

12.1. Sample Concentration / Aqueous

$$C_{(\mu g/L)} = \mu g/L_{DIG} * (V_{DIG}/V_{SAMP})$$

Where:
μ/L_{DIG} = Sample Result*
V_{DIG} = Digestate volume
V_{SAMP} = Sample volume

**adjustment for dilution factor performed by instrument software*

Sample Concentration / Soil, Sediment

$$C_{(mg/kg)} = (\mu g/L_{DIG} * (V_{DIG}/G_{SAMP})) * 100/\%solids$$

Where:
μ/L_{DIG} = Sample Result*
V_{DIG} = Digestate volume
G_{SAMP} = Sample weight

**adjustment for dilution factor performed by instrument software*

12.2. Percent Recovery (%R) LCS and CCVs

$$\%R = \frac{SR}{SA} * 100\%$$

Where:
SR= Sample Result
SA=Concentration of Spike Added

12.3. Percent Recovery (%R) MS

$$MSRecovery(\%) = \frac{SSR - SR}{SA} * 100\%$$

Where:
SSR=Matrix Spike Result
SR=Sample Result
SA=Concentration of Spike Added

12.4. Relative Percent Difference (%RPD)

$$\%RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

Where:
D1 = Sample result
D2 = Duplicate Result

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1. Review the samples, standards and QC samples against the performance criteria given in Table 3. If the results do not fall within the established limits or criteria, corrective action. If corrective action is not taken or unsuccessful, the situation should be documented and reported in the project narrative. All data that does not meet established criteria must be flagged and noted in the project narrative.

14.0 METHOD PERFORMANCE

14.1. A demonstration of analyst capability (IDOC) is required prior to use of this SOP and any time there is a significant change in instrument type, personnel or test method. IDOC procedures are further described in laboratory SOP LP-QA-011, *Employee Training.*

14.1. A Method Detection Limit (MDL) Study is performed at initial method set-up and subsequently once per 12 month period. A Instrument Detection Limit (IDL) study is performed at initial set up and subsequently every 3 months. The procedure and acceptance criteria for MDL studies are given in laboratory SOP LP-LB-009, *Method Detection Limits & Instrument Detection Limits.* MDL and IDL studies are kept on file by the QA Department.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1. Waste is disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention." The laboratory procedures for waste management are described in SOP LP-LB-001HAZWD.

15.2. Chemists and technicians accumulate hazardous waste in satellite containers located in the work area. Each satellite container is labeled "Hazardous Waste" along with the name of the waste category. The Hazardous Waste Coordinator or designee routinely empties the satellite containers and transfers the waste to the hazardous waste storage room.

16.0 REFERENCES

16.1. *Determination of Trace Elements in Waters and Waters by Inductively Coupled Plasma-Mass Spectrometry (Method 6020),* Revision 0; September 1994. USEPA SW-846 Methods for Evaluating Solid Waste, Update III.

16.2. *EPA Method 200.8, Revision 5.4, 1994.* US EPA Office of Research and Development, Cincinnati, Ohio.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

17.1 Table 1: *Analyte List and Reporting Limits*
17.2 Table 2: *QC Summary, Acceptance Criteria and Corrective Action*

Table 1: Target List and Reporting Limit (ICP-MS)

Element		CAS Number	Isotope (amu)	Reporting Limit	
				Aqueous ug/L	Soil/Sediment mg/Kg
Al	Aluminum	7429-90-5	27	40	4.0
Sb	Antimony	7440-36-0	123	20	2.0
As	Arsenic	7440-38-2	75	2.0	0.20
Ba	Barium	7440-39-3	135	100	10
Be	Beryllium	7440-41-7	9	2.0	0.20
B	Boron	7440-42-8	11	20	2.0
Cd	Cadmium	7440-43-9	111	2.0	0.20
Ca	Calcium	7440-70-2	44	1000	100
Cr	Chromium	7440-47-3	52	4.0	0.40
Co	Cobalt	7440-48-4	59	10	1.0
Cu	Copper	7440-50-8	65	20	2.0
Fe	Iron	7439-89-6	54	200	20
Pb	Lead	7439-92-1	208	2.0	0.20
Mg	Magnesium	7439-96-5	25	1000	100
Mn	Manganese	7439-96-5	55	4.0	0.40
Mo	Molybdenum	7439-98-7	98	20	2.0
Ni	Nickel	7440-02-0	60	20	2.0
K	Potassium	7440-09-7	39	1000	100
Se	Selenium	7782-49-2	82	2.0	0.20
Ag	Silver	7440-22-4	107	2.0	0.20
Na	Sodium	7440-23-5	23	1000	100
Tl	Thallium	7440-28-0	205	2.0	0.20
V	Vanadium	7440-62-2	51	4.0	0.40
Zn	Zinc	7440-66-6	66	20	2.0

Table 2: QC Frequency, Criteria and Recommended Corrective Action (ICP-MS)

QC Check	Acronym	Minimum Frequency	Acceptance Criteria	Corrective Action
Tune Standard		Prior to Initial Calibration	> 5% RSD for all measured analytes	Correct problem and reanalyze tune standard
Initial Calibration	ICAL	Daily	r ≥ 0.995	Correct problem and repeat calibration
Second-Source Calibration Verification	ICV	After each calibration	±10% of expected value	Correct problem, verify second source standard. If that fails, repeat calibration.
Initial Calibration Blank	ICB	Beginning of analytical sequence after ICV	No analytes ≥ RL DoD: No analytes ≥ ½ RL	Correct problem and reanalyze
Continuing Calibration Verification	CCV	After every 10 samples and at the end of the analytical sequence	±10% of expected value	Correct problem, reanalyze CCV. If that fails, repeat calibration and reanalyze all samples since last successful calibration.
Calibration Blank	CCB	Beginning of sample run, after every 10 samples and at end of the sequence (i.e. after each CCV)	No analytes ≥ RL DoD: No analytes ≥ ½ RL	Correct problem and reanalyze the calibration blank and previous 10 samples.
Interference Check Solutions	ICSA ICSAB	At the beginning of the analytical run	ICSA: Non-Spiked <RL ICSAB: ±20% of expected value	Stop analysis, locate and correct problem, reanalyze ICS and all associated QC and samples.
Low Level Standard	CRI	Daily, after ICSA and ICSAB	±50% of expected value DoD: ±30% of expected value	Correct problem, then reanalyze
Method Blank	MB	One per digestion batch	No analytes ≥RL DoD: No analytes > ½ RL	Correct problem, redigest and reanalyze MB and associated samples.
Laboratory Control Sample	LCS	One per digestion batch *A duplicate LCS (LCSD) should be performed only per client request.*	6020: %R= 80-120% 200.8: %R=85-115%	Correct problem, redigest and reanalyze LCS, MB and associated samples for failed analytes if sufficient sample volume is available.
Matrix Spike	MS	One per every 20 project samples per matrix	%R= 75-125% DoD: 80-120%	Examine project DQO's with Project Manager. Evaluate data to determine if outage is related to analytical error or matrix effect.
Sample Duplicate	SD	One per every 20 project samples, per matrix, per client request	RPD ≤ 20%	Examine project DQO's with Project Manager. Evaluate data to determine source of difference between results
Serial Dilution		Each digestion batch	5X dilution within ±10% of original sample result	Perform Post Digestion Spike Flag Data
Post Digestion Spike		When dilution test fails or analyte concentration in all samples <25 x MDL	%R within 75-125%	Flag data or perform method of standard addition (MSA)
Internal Standards	IS	Every Sample	IS intensity within 30-120% of intensity of the IS in the initial calibration	Dilute the sample five-fold and reanalyze with the addition of appropriate amounts of internal standard. Repeat this procedure until the internal standards are within the criteria window.

Appendix A: Standard Preparation Tables

Unless otherwise specified all are diluted to the final volume using 2% nitric acid solution.

Intermediate Tune Standard Solution

Element	Stock Standard Concentration (mg/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (mg/L)
Li	10000	0.02	200	1.0
Be	1000	0.20		1.0
Mg	10000	0.02		1.0
Al	10000	0.02		1.0
Sc	1000	0.20		1.0
V	1000	0.20		1.0
Co	1000	0.20		1.0
Y	10000	0.02		1.0
In	1000	0.20		1.0
Ba	1000	0.20		1.0
Ce	1000	0.20		1.0
Tb	1000	0.20		1.0
Pb	1000	0.20		1.0
Th	1000	0.20		1.0
U	1000	0.20		1.0
Bi	1000	0.20		1.0

Solution: *2% nitric acid*

Working Tune Standard Solution

Element	Stock Standard Concentration mg/L	Volume Used mL	Final Volume mL	Final Concentration ug/L
Li	1.0	0.5	50	10
Be	1.0			10
Mg	1.0			10
Al	1.0			10
Sc	1.0			10
V	1.0			10
Co	1.0			10
Y	1.0			10
In	1.0			10
Ba	1.0			10
Ce	1.0			10
Tb	1.0			10
Pb	1.0			10
Th	1.0			10
U	1.0			10
Bi	1.0			10

Solution: 2% nitric acid

Intermediate Calibration Standard Solution

Element	Stock Standard Concentration mg/L	Volume Used mL	Final Volume mL	Final Concentration mg/L
Al	10,000	2.0	500	40
Sb	1000	10		20
As	1000	1.0		2.0
Ba	1000	50		100
Be	1000	1.0		2.0
B	1000	10		20
Cd	1000	1.0		2.0
Ca	10,000	50		1000
Cr	1000	2.0		4.0
Co	1000	5.0		10
Cu	1000	10		20
Fe	10,000	10		200
Pb	1000	1.0		2.0
Mg	10,000	50		1000
Mn	1000	2.0		4.0
Mo	1000	10		20
Ni	1000	10		20
K	10,000	50		1000
Se	1000	1.0		2.0
Ag	1000	1.0		2.0
Na	10,000	50		1000
Tl	1000	1.0		2.0
V	1000	2.0		4.0
Zn	1000	10		20
U	1000	1.0		2.0

Solution: *2% nitric acid*

Working Calibration Standards

Element	Intermediate Calibration Standard (mg/L)	Calibration Level 3			Calibration Level 2 (made from Cal 3)			Calibration Level 1 (made from Cal 3)		
		Volume Used mL	Final Volume mL	Final Concentration mg/L	Volume Used mL	Final Volume mL	Final Concentration mg/L	Volume Used mL	Final Volume mL	Final Concentration mg/L
Al	40	25	1000	1000	100	500	200	20	500	40
Sb	20			500			100			20
As	2.0			50			10			2.0
Ba	100			2500			500			100
Be	2.0			50			10			2.0
B	20			500			100			20
Cd	2.0			50			10			2.0
Ca	1000			25000			5000			1000
Cr	4.0			100			20			4.0
Co	10			250			50			10
Cu	20			500			100			20
Fe	200			5000			1000			200
Pb	2.0			50			10			2.0
Mg	1000			25000			5000			1000
Mn	4.0			100			20			4.0
Mo	20			500			100			20
Ni	20			500			100			20
K	1000			25000			5000			1000
Se	2.0			50			10			2.0
Ag	2.0			50			10			2.0
Na	1000			25000			5000			1000
Tl	2.0			50			10			2.0
V	4.0			100			20			4.0
Zn	20			500			100			20

Solution: *2% nitric acid*

Intermediate Second Source Calibration Verification (ICV) Standard

Element	Stock Standard Concentration mg/L	Volume Used mL	Final Volume mL	Final Concentration mg/L
Al	10,000	1.0	200	50
Sb	1000	5.0		25
As	1000	0.5		2.5
Ba	1000	25		125
Be	1000	0.5		2.5
B	1000	5.0		2.5
Cd	1000	0.5		2.5
Ca	10,000	25		1250
Cr	1000	1.0		5.0
Co	1000	2.5		12.5
Cu	1000	5.0		25
Fe	10,000	5.0		250
Pb	1000	0.5		2.5
Mg	10,000	25		1250
Mn	1000	1.0		5.0
Mo	1000	5.0		25
Ni	1000	5.0		25
K	10,000	25		1250
Se	1000	0.5		2.5
Ag	1000	0.5		2.5
Na	10,000	25		1250
Tl	1000	0.5		2.5
V	1000	1.0		5.0
Zn	1000	5.0		25
U	1000	0.5		2.5

Solution: 2% nitric acid

ICV Working Standard Solution

Element	ICV Intermediate Standard Concentration mg/L	Volume Used mL	Final Volume mL	Final Concentration ug/L
Al	50	5	500	500
Sb	25			250
As	2.5			25
Ba	125			1250
Be	2.5			25
B	2.5			250
Cd	2.5			25
Ca	1250			1250
Cr	5.0			50
Co	12.5			125
Cu	25			250
Fe	250			2500
Pb	2.5			25
Mg	1250			1250
Mn	5.0			50
Mo	25			250
Ni	25			250
K	1250			12500
Se	2.5			25
Ag	2.5			25
Na	1250			12500
Tl	2.5			25
V	5.0			50
Zn	25			250

Solution: 2% nitric acid

ICSA Working Standard

Multi-Element Stock Standard	Volume Used mL	Final Volume mL	Final Concentration mg/L
10000ppm Cl	6020ICS-0A* 20mL	200	1000
1000ppm Ca			100
1000ppm Fe			100
1000ppm S			100
1000ppm Na			100
2000ppm C			200
1000ppm Al			100
20ppm Mo			2.0
1000ppm Mg			100
1000ppm P			100
1000ppm K			100
20ppm Ti			2.0

Solution: 2% nitric acid

**Mixed Element Stock standard Solution purchased from Inorganic Ventures*

ICSAB Intermediate Standard Solution

Element	Stock Standard Concentration mg/L	Volume Used mL	Final Volume mL	Final Concentration mg/L
Sb	1000	5.0	100	50
Ba	1000	25		250
Be	1000	1.0		10
B	1000	5.0		50
Cr	1000	1.0		10
Co	1000	1.5		15
Cu	1000	4.0		40
Pb	1000	1.0		10
Mn	1000	1.0		10
Ni	1000	4.0		40
Se	1000	1.0		10
Tl	1000	1.0		10
V	1000	2.0		20
Zn	1000	4.0		40

Solution: 2% nitric acid

ICSAB Working Standard Solution

Multi-Element Stock Standard	Volume Used mL	Final Volume mL	Final Concentration[1] mg/L
10000ppm Cl	6020ICS-0A* 50mL	500	1000
1000ppm Ca			100
1000ppm Fe			100
1000ppm S			100
1000ppm Na			100
2000ppm C			200
1000ppm Al			100
20ppm Mo			2.0
1000ppm Mg			100
1000ppm P			100
1000ppm K			100
20ppm Ti			2.0
2ppm As	6020ICS-0B* 5.0mL		0.02
2ppm Cd			0.02
2ppm Cr[1]			0.02
2ppm Co[1]			0.02
2ppm Cu[1]			0.02
2ppm Mn[1]			0.02
2ppm Ni[1]			0.02
2ppm Ag			0.02
2ppm Zn			0.02
50ppm Sb	ICSAB Intermediate Standard 1.0mL		0.10
250ppm Ba			0.50
10ppm Be			0.02
50ppm B			0.10
10ppm Cr[1]			0.02
15ppm Co[1]			0.03
40ppm Cu[1]			0.08
10ppm Pb			0.02
10ppm Mn[1]			0.02
40ppm Ni[1]			0.08
10ppm Se			0.02
10ppm Tl			0.02
20ppm V			0.04
40ppm Zn			0.08

Solution: 2% nitric acid

**Mixed Element Stock standard Solution purchased from Inorganic Ventures*

[1]Final Concentration in Prepared Standard

Chromium: 0.04 mg/L Cobalt: 0.05 mg/L
Copper: 0.10 mg/L Manganese: 0.04 mg/L
Nickel: 0.10 mg/L

Intermediate Internal Standard Solution

Element/Mass	Stock Standard Concentration mg/L	Volume Used mL	Final Volume mL	Final Concentration mg/L
Y 89	10000	0.25	50	50
In 115	1000	2.5		50
Li 6 & 7	10000	16.7		3333
Sc 45	1000	5.0		100
Tb 159	1000	1.25		25
Bi 209	1000	2.8		56.7

Solution: 2% nitric acid

Working Internal Standard Solution

Parent Standard	Stock Standard Concentration mg/L	Volume Used mL	Final Volume mL	Final Concentration mg/L
Y/ 89	50	Intermediate Internal Standard Solution 2.0mL	2000mL	0.05
In/115	50			0.05
Li/6&7	3333			3.3
Sc/45	100			0.10
Tb/159	25			0.025
Bi/209	56.7			0.057
Li/6&7	10000	2.0mL		10

Solution: 2% nitric acid

Final Concentration:
Lithium:13.3mg/L

Appendix A: Terms & Definitions

Accuracy: the degree of agreement between a measurement and the true or expected value, or between the average of a number of measurements and the true or expected value.

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Calibration: the establishment of an analytical curve based on the absorbance, emission intensity or other measured characteristic of known standard.

Calibration Blank (ICB/CCB): a volume of reagent water acidified with the same acid matrix as in the calibration standards.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Calibration Standards: a series of known standard solutions used to calibrate the instrument response with respect to analyte concenteration.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: action taken to eliminate the causes of an existing non-conformance, defect or other undesirable situation in order to prevent recurrence.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

ICP-MS: A technique for the multi-element determination of elements in solution. The basis of the technique is the detection of atomic ions produced by an ICP and sorted by mass/charge ratio.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Initial Calibration Verification (ICV): solution prepared from a separate source from that which is used to prepare the calibration curve.

Inteference Check Solution (ICS): a solution of known concentrations of intefering elements that will demonstrate the magnitude of inteference and provide an adequate test for any corrections.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Linear Dynamic Range: The concentration range over which the instrument response remains linear.

Matrix: the substrate of a test sample.

Matrix Duplicate (MD): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Percent Solids (%S): the proportion of solid in a soil sample.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample. The RL must be minimally at or above the MDL.

Serial Dilution: the dilution of a sample by a factor of five.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Tune: the analysis of a solution containing a range of isotope masses to establish ICP-MS accuracy, resolution and precision prior to calibration.

STANDARD OPERATING PROCEDURE
DETERMINATION OF MERCURY IN SOLID OR SEMISOLID WASTE
SEMI-AUTOMATED COLD VAPOR TECHNIQUE

Applicable Matrices: Soils, Sediments, Sludge
Standard Compound List and Reporting Limits: See Section 1.1-1.2.

APPROVAL SIGNATURES

Laboratory Director: Michael F. Wheeler, Ph.D. Date: 7/16/04

QA Manager: Kirstin L. McCracken Date: 7-16-04

Department Manager: William S. Cicero Date: 7/16/04

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1.0 SCOPE AND APPLICATION

1.1. This SOP describes the laboratory procedure for the determination of total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials.

1.2. The routine RL for solid samples is 0.04mg/Kg based on a routine sample digestion weight of 0.6 grams an a final volume of 100mL.

2.0 SUMMARY OF METHOD

2.1. A weighed portion of solid sample is acid digested for 2 minutes at a temperature of 95°C then digested with potassium permanganate and potassium persulfate for 30 minutes at a temperature of 95°C. Hydroxylamine hydrochloride is added to each digestate in order to reduce excess permanganate. The digestate is placed on a closed-system mercury autoanalyzer and stannous chloride is added to each sample. The elemental mercury released is measured spectrophotometrically at a wavelength of 253.7 nm. The concentration is calculated from the response of the sample absorbance applied against the calibration curve.

2.2. This procedure is based on Method 7470A. Test methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition September 1986.

3.0 DEFINITIONS

3.1. A list of general terms and definitions used by the laboratory is given in Appendix A.

4.0 INTERFERENCES

4.1. Potassium permanganate is added to the samples to eliminate possible interference from sulfide. Copper has also been noted as an interferent but per reference method SW-846 7471 concentrations as high as 10mg/Kg had no effect on recovery of mercury from spiked samples.

4.2. Samples high in chlorides may require additional permanganate because during the oxidation step, chlorides are converted to free chlorine which also absorbs radiation of 253nm. Care must be taken to ensure free chlorine is not present and this is accomplished by the addition of hydroxylamine hydrochloride and stannous chloride.

5.0 SAFETY

5.1. Employees must be trained on and adhere to the policies and procedures for safety in the Corporate Safety Manual and this document.

5.2. Safety Concerns or Requirements

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added. Protective clothing

such as a lab coat, safety glasses and latex gloves must be worn while performing this procedure.

5.3. Primary Materials Used

Table 1, Section 17.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. The table does not include all materials used in the procedure. A complete list of materials used can be found in section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

6.1. Mercury Auto-Analyzer; Leeman Labs PS 200 and Leeman Labs Hydra AA with autosampler or equivalent.

6.2. Water Bath capable of maintaining temperature at 90-95°C.

6.3. Polyethylene Digestion Vessels with Volumetric Indicators; Environmental Express brand or equivalent, 100mL volume.

6.4. Volumetric Autopipettes; Finpipette brand or equivalent. Range of use 0.2-1.0mL & 1.0-5.0mL.

6.5. Top Loading Balance capable of measurements to 0.1mg.

6.6. Graduated Cylinders, 100mL Class A; Fisher brand or equivalent.

7.0 REAGENTS AND STANDARDS

7.1. Reagents

Reagent Water

Aqua Regia: Prepare each day of use by carefully adding 3 volumes of concentrate HCl to one volume of concentrated nitric acid.

Reagent Water

Nitric Acid (HNO_3) concentrated - Reagent grade; JT Baker or equivalent

Hydrocloric Acid (HCl), concentrated-Reagent Grade; JT Baker or equivalent

HCl (10%): Add 100mL of concentrated HCl to a 1L volumetric flask and adjust to 1000mL with distilled water.

Stannous Chloride Solution: Add 100g of $SnCl_2 \cdot H_2O$ (JT Baker or equivalent) to 1L of 10% hydrochloric acid.

Hydroxylamine Hydrochlorid(JT Baker or equivalent): Dissolve 240grams of Hydroxylamine Hydrochloride in 2L of reagent water.

Potassium Permanganate ($KMNO_4$) (JT Baker or equivalent): 5% solution w/v: Dissolve 100g of $KMNO_4$ in 2L of reagent water.

Potassium Persulfate ($K_2S_2O_8$) (JT Baker or equivalent) 5% solution w/v: Dissolve 100g of $K_2S_2O_8$ in 2L of reagent water.

7.2. Standards

Hg Stock Standard Solution (1000mg/L), purchase commercially from Spex.

Mercury Intermediate Standard (10,000ug/L): Add 1mL of 1000mg/L Hg Stock Standard Solution and 0.15mL of concentrated HNO_3 to a 100mL volumetric flask that contains approximately 800mL reagent water. Adjust to volume with reagent water.

Mercury Working Standard (100ug/L): Add 10mL of the Hg Intermediate Standard Solution and 1.5mL of concentrated HNO_3 to a 1000mL volumetric flask that contains approximately 800mL reagent water. Adjust to volume with reagent water. Use this standard to prepare the calibration standards (ICAL & CCV)

ICV Stock Standard Solution (1000mg/L): purchase commercially from Inorganic Ventures.

ICV Intermediate Standard Solution (10,000ug/L): Add 1mL of the 1000mg/L ICV Stock Standard Solution and 0.15mL of concentrated HNO_3 to a 100mL volumetric flask that contains approximately 800mL reagent water. Adjust to volume with reagent water.

ICV Working Standard Solution (60ug/L): Add 3mL of the ICV Intermediate Standard Solution and 0.75mL of concentrated HNO_3 into a 500mL volumetric flask that contains approximately 300mL reagent water. Adjust to volume with reagent water.

8.0 SAMPLE HANDLING AND PRESERVATION

8.1. Samples should be collected in glass or polyethylene containers. Immediately following collection the samples should be cooled to a temperature of (±2°C) and maintained at that temperature until digestion.

8.2. The holding time is 28 days from collection of the sample.

8.3. Unless otherwise specified by client or regulatory program, after digestion and analysis, samples are retained for 30 days and then disposed of in accordance with applicable regulations.

9.0 QUALITY CONTROL

9.1. QC Requirements

The following QC samples are analyzed: Method Blank (MB) Laboratory Control Sample (LCS), and a Matrix Spike (MS). Sample Duplicates (DP) are performed per client request. Sample results that exceed the range of calibration are diluted and reanalyzed such that the diluted sample result in near the midpoint or in the upper half of the calibration range.

In addition to calibration (ICAL), instrument standardization is checked with the following QC samples, Initial Calibration Verification (ICV), Continuing Calibration Verification (CCV), and Calibration Blanks (ICB/CCB). A low level standard (CRI) is analyzed per client request.

The minimum frequency requirements, acceptance criteria and recommended corrective action for QC samples are summarized in Table 2.

10.0 CALIBRATION AND STANDARDIZATION

10.1. Calibration

Calibrate the autoanalyzers daily with five calibration standards and a blank using the instrument operating conditions established by the instrument manufacturer. Prepare the calibration standards daily by making successive dilutions of the Hg Working Standard Solution (100ug/L) in100mL of reagent water. The final concentration of the prepared calibration standards is as follows:

Calibration Standards

Level	Hg Standard 100ug/L (mL)	Final Volume (mL)	Final Concentration (ug/L)
Blank	0	100	0
Level 1	0.2	100	0.2
Level 2	0.5	100	0.5
Level 3	1	100	1
Level 4	5	100	5
Level 5	10	100	10

Note: If a reduced sample volume is used, reduce the final volume of the standards and adjust the final concentration accordingly.

Process the calibration standards following the procedures given in Section 11.1.The instrument data system constructs a standard curve by plotting the instrument response

from each standard solution against the final concentration and using linear regression, the data system calculates the correlation coefficient. The correlation coefficient must be greater than or equal to 0.995.

10.2. Initial Calibration Verification (ICV)

Following calibration, analyze the ICV. The ICV is a second source standard whose concentration (3ppb) is near the midpoint of the calibration range but at a different concentration than the CCV (5ppb). Process the ICV following the procedure given in Section 11.1. The percent recovery of the ICV must be within 90-110%.

10.3. Continuing Calibration Verification (CCV).

Analyze a CCV initiall after every 10th sample and at the end of the sample run. The CCV standard is at a concentration of 5ppb and is prepared from the same source of standard used for the calibration standards. Process the CCV following the procedure given in Section 11.1. The percent recovery of the CCV must be 80-120%.

10.4. Calibration Blanks (ICB/CCB)

Analyze a calibration blank after each CCV. The results of each calibration blank must be less than the RL.

10.5. Support Equipment Calibration

Check the calibration of the auto-pipettes and the top-loading balance on the day of use prior to use and record the calibration check in the logbook designated for this purpose.

11.0 PROCEDURE

11.1. Sample Preparation

Weigh triplicate 0.2g portions of sample into a Polyethylene digestion vessel. Add 10mL of reagent water. Use reagent water for the method blank the laboratory control sample, and each calibration blank. Add 1mL of the Hg working standard solution (100ug/L) to the LCS and the matrix spike.

11.2. Digestion

To each sample, standard and blank add 5mL of aqua regia Heat for 2 minutes in a water bath at 95°C. Allow the samples to cool then add 40mL of reagent water, 15mL of potassium permanganate, and swirl to mix. Return to the hot water bath for 30 minutes. Cool and add 6mL of hydroxylamine hydrochloride to reduce the excess permanganate. Swirl each vessel to ensure that any soluble residue dissolves back into solution. If the color of any sample is still purple, add hydroxylamine hydrochloride in 6mL increments until the purple color disappears. Add 50mL of reagent water to each vessel and transfer the digestate to individual autoanalyzer tubes for analysis.

11.2. Instrument Set Up & Analysis

Turn the instrument lamp, gas and pump on and allow 15 minutes for the instrument to warm up. Fill the rinse bath with 10% hydrochloric acid solution. Check all tubing connections and reset the calibration curve. Check the stannous chloride reductant reservoir and fill if necessary.

Select the autosampler template and enter the sample Ids in the order of analysis. Place the samples, calibration blanks, calibration standards, and performance check standards in the position on the autosampler rack that corresponds to their assigned position in the autosampler template. Place the autosampler rack in the autosampler tray and initiate the software macro to begin analysis. An example analytical sequence is given below:

Example Analytical Sequence:
Calibration Blank
0.2 Calibration Standard
0.5 Calibration Standard
1.0 Calibration Standard
5.0 Calibration Standard
10.0 Calibration Standard
ICV
ICB
CRI
CCV
CCB
10 Samples*
CCV
CCB
9 Samples*
CCV
CCB

**The number of samples between each CCB/CCV (10) includes the method blank, laboratory control sample, matrix spikes, and sample duplicates.*

Select the autosampler template and enter the sample Ids into the template. Place the autosampler rack in the autosampler tray and initiate the software macro to begin the analytical sequence. During analysis, the data processing system constructs a calibration curve by plotting the absorbances of standards versus units of mercury and sample concentrations are determined from the calibration curve (See Section 12.0).

After analysis is complete, review the data against the criteria given in Section 9.0 for Quality Control and Section 10.0 for Calibration and Standardization. Perform corrective action, as needed. Dilute and reanalyze any samples that exceed the linear range.

Transfer the data from the network server into the MARRS data processing software program. Route preparation log, analysis run log and associated raw data to the Inorganic Data Review department for secondary data assessment and report generation.

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12.0 CALCULATIONS

12.1. Concentration

$$C_{(mg/Kg\ drywt.)} = \frac{\mu g}{L_{dig}} * \frac{V_{dig}}{g_{samp}} * \frac{100}{\%\ solids}$$

Where:
$\mu g/L_{dig}$ = Instrument result adjusted for dilution factors
V_{dig} = Final digestate volume
g_{samp} = Sample weight in grams
% Solids = Percent solids to nearest 0.1%

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1. Review the samples, standards and QC samples against the performance criteria given in section 9.0 for Quality Control and in section 10.0 for Calibration and Standardization. If the results do not fall within the established limits or criteria, corrective action is required as contained in Table 1. If corrective action is not taken or unsuccessful, the situation should be documented and reported in the project narrative. All data that does not meet established criteria must be noted in the project narrative.

14.0 METHOD PERFORMANCE

14.1. A demonstration of analyst capability (IDOC) is required prior to use of this SOP and any time there is a significant change in instrument type, personnel or test method. IDOC procedures are further described in laboratory SOP LP-QA-011, *Employee Training*.

14.2. A Method Detection Limit (MDL) Study is performed at initial method set-up and subsequently once per 12 month period. The procedure and acceptance criteria for MDL studies are given in laboratory SOP LP-LB-009, *Method Detection Limits & Instrument Detection Limits.*

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1. Where reasonably feasible, technological changes have been implemented to minimize the production of hazardous waste and minimize potential source of pollution to the environment.

15.2. Hazardous waste is accumulated in satellite containers located in the work area. The satellite containers are labeled "Hazardous Waste" along with the type of waste category generated. Authorized personnel routinely transfer the contents of the satellite containers to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations. The procedures for waste management are further given in laboratory SOP LP-LB-001 *Hazardous Waste*.

16.0 REFERENCES

16.1. Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

17.1 Table 1: *Primary Material Used*
17.2 Table 2: *QC Summary, Acceptance Criteria, Recommended Corrective Action*

Table 1: Primary Materials Used (Mercury / CVAA)

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 PPM in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 2: QC Frequency, Criteria and Recommended Corrective Action (SW-846 7471A)

QC Check	Acronym	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	ICAL	Daily	r ≥ 0.995	Correct problem and repeat calibration
Initial Calibration Verification	ICV	After each calibration, prior to sample analysis.	±10% of expected value	Correct problem, verify second source standard. If that fails, repeat calibration.
Initial Calibration Blank	ICB	Beginning of analytical sequence after ICV	No analytes ≥ RL	Correct problem and reanalyze
Low Level Standard	CRI	Per Client Request	±50% of expected value	Correct problem, then reanalyze
Continuing Calibration Verfication	CCV	Beginning of sequence, after every 10 samples and at the end of the analytical sequence	±20% of expected value	Correct problem, reanalyze CCV. If that fails, repeat calibration and reanalyze all samples since last successful calibration.
Calibration Blank	CCB	After every 10 samples and at end of the sequence (i.e. after each IPC)	No analytes ≥RL DoD: ≥MDL	Correct problem and reanalyze the calibration blank and previous 10 samples.
Method Blank	MB	One per digestion batch	No analytes ≥RL DoD: ½ ≥RL	Correct problem, redigest and reanalyze MB and associated samples.
Laboratory Control Sample	LCS	One per digestion batch	%R= 85-115%	Correct problem, redigest and reanalyze LCS, MB and associated samples for failed analytes if sufficient sample volume is available.
Matrix Spike	MS	One per every 20 project samples per matrix	%R= 70-130%	Examine project DQO's with Project Manager. Evaluate data to determine if outage is related to analytical error or matrix effect.
Sample Duplicate	SD	One per every 20 project samples, per matrix, per client request	RPD ≤ 20%	Examine project DQO's with Project Manager. Evaluate data to determine source of difference between results

Appendix A: Terms & Definitions

Analyte: The element or ion an analysis seeks to determine; the element of interest.

Analytical Sequence: The actual instrumental analysis of the samples from the time of instrument calibration through the analysis of the final CCV or CCB.

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Calibration: The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards.

Calibration Blank: A blank solution containing all of the reagents and in the same concentration as those used in the analytical sample preparation.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Duplicate: A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Initial Calibration Verification (ICV): solution prepared from a separate source from that which is used to prepare the calibration curve.

Interferents: Substances which affect the analysis for the element of interest.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Linear Range, Linear Dynamic Range: The concentration range over which the instrument response remains linear.

Matrix Duplicate (MD): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample. The RL must be minimally at or above the MDL.

Relative Percent Difference (RPD): As used in the SOW and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

Sample: A portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Shaker Table Extraction

1.0 Identification of Test Method

This standard operating procedure (SOP) is a performance-based method. This SOP describes the procedure as developed by Woods Hole Group.

2.0 Applicable Matrix or Matrices

2.1 This method is applicable to the extraction of non-volatile and semivolatile organic compounds in solid samples (including soils, sediments, sludges, tissue and wastes).

2.2 This procedure may be used for the extraction of all types of organic compounds. Because this procedure is performance based, it should only be used for compounds where studies have assessed the precision, accuracy, and sensitivity of the technique relative to the project specific goals.

	Approval Signatures	
Laboratory Director	Peter J. Thorne	Date: 2/20/02
Section Head	Don [illegible]	Date: 2/20/02
Quality Assurance Manager	Gabe Porta	Date: 2/20/02

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A signed original is available in the files of Woods Hole Group Environmental Laboratories.

3.0 Detection and Quantitation Limits

3.1 The Method Detection Limit (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 indicative of the accuracy, precision, and sensitivity of the analytical method. It is essential that all analytical processing steps be included in the determination of the MDL. The MDLs are performed annually or if there is a major change in instrumentation or method procedure. The procedures described in 40CFR Part 136 must be followed to determine the MDLs. The MDLs are performed by extracting and analyzing seven to ten replicates of a low-level spike containing the organic compounds of interest (at 3-5x the expected MDL) in sodium sulfate. The MDLs are calculated by multiplying the standard deviation of the replicates by the corresponding Student T test value (*i.e.*, 3.143 for seven replicates). MDL results are kept on file in the laboratory QA department.

3.1.1 Prepare a blank of purified sodium sulfate (see Section 10.4) that is free of the organic compounds of interest and interfering compounds.

3.1.2 Prepare a standard that is equivalent to, or at least in, the same concentration range of, the estimated method detection limits (between 1-5 times the estimated MDL). If after analysis the measured level is less than the estimated detection limit, prepare a standard at a higher concentration, to bring the concentration level to 1-5 times the estimated MDL. If the measured level is greater than the estimated detection limit, prepare a standard at a lower concentration. Alternatively, the standard may be used as is if the concentration of the standard does not exceed 10X the determined MDLs [*i.e.,* If the standard concentration is 0.5 μg/L and the determined MDL is 0.04 μg/L, multiply 0.04 x 10 = 0.4 μg/L. Since 0.4 (10X the MDL) is less than 0.5 (the standard spike concentration), the spike level, or standard concentration, *does* exceed 10X the MDL. In this case the MDL must be repeated at a lower standard spike concentration].

3.1.3 A minimum of seven replicates are taken through the entire extraction and analytical procedures. Calculate the results in the appropriate units. Calculate any concentration found in the method blank. If any organic compounds of interest are detected in the associated method blank at concentrations greater than 2X the MDL, the MDL must be repeated for the exceeded compound(s).

3.1.4 Calculate the standard deviation of the seven replicate measurements. Multiply the standard deviation by the correct Students' T-Value, depending on the number of replicates. For seven replicates, use 3.143 as the Student's T-Value constant.

3.1.5 To report the MDLs, use the pre-prepared Excel spreadsheets on the Woods Hole Group (WHG) server. The following information must be supplied: Method name or number; Analyst; Analysis date; Units; Matrix; Instrument used; Concentration analyzed (true value spiked) and *all* of the actual values determined from the seven replicates and their file IDs; Mean concentration; Standard Deviation; Reporting Limit and the Calculated MDL. All supporting raw data and the MDL spreadsheets must be forwarded to the Quality Assurance Manager for review, acceptance and storage of the MDL data.

3.1.6 For information regarding the laboratory solid MDLs see the appropriate WHG analytical SOPs:

- Total Petroleum Hydrocarbons by Gas Chromatography / Flame Ionization Detector (O-003),
- Extractable Petroleum Hydrocarbons - EPH (O-001),
- Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (O-006),
- Polynuclear Aromatic Hydrocarbons by Gas Chromatography / Mass Spectrometry with Selected Ion Monitoring (O-007),
- Organochlorine Pesticides by Gas Chromatography / Electron Capture Detection (O-011)
- Polychlorinated Biphenyls as Aroclors or Congeners by Gas Chromatography / Electron Capture Detection (O-012),
- Analysis of Parent and Alkylated Polynuclear Aromatic Hydrocarbons and Selected Heterocyclic Compounds by Gas Chromatography / Mass Spectrometry with Selected ion Monitoring (O-008),
- Determination of PCB Homologs and Individual Congeners by Gas Chromatography / Mass Spectrometry with Selected ion Monitoring (O-010).

3.2 The Practical Quantitation Limit (PQL) or Reporting Limit (RL) is the level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. For information regarding the solid PQLs, see the appropriate WHG analytical SOPs in Section 3.1.6, above. These values are generally equivalent to approximately 3-5X the calculated MDL and can also be equivalent to the lowest standard concentration, which is analyzed with, and included in the initial calibration curve for the determinative analytical method.

4.0 Scope and Application

4.1 Shaker Table extraction is the process of isolating organic compounds of interest from the

solid sample matrix. Sample cleanup is highly recommended, since the compounds cannot be analyzed directly without removal of some interferences in the sample matrix. See Section 7.2 for a listing of WHG sample cleanup SOPs.

4.2 This procedure uses a Shaker Table set at 1.5 to 2.0 x 100 rotations per minute for agitation of the mixture. Groups of organic compounds such as semivolatiles, pesticides, polychlorinated biphenyls (PCBs), and petroleum hydrocarbons are separated on the basis of their common solubility in solvents and then analyzed in accordance with the appropriate WHG analytical SOP (see Section 3.1.6).

5.0 Summary of Method

5.1 A 20-50 gram aliquot of solid sample is weighed, then dried by mixing with sodium sulfate, to form a free-flowing powder. If tissue samples are going to be analyzed using this technique, they must be dissected and/or homogenized prior to drying with sodium sulfate. See the WHG SOP *Tissue Preparation* (OP-014) for additional details.

5.2 This mixture is then solvent extracted three times using the Shaker Table extractor.

5.3 The extract is allowed to settle and the solvent is separated from the sample mixture by decanting through a filter funnel packed with sodium sulfate and glass wool.

5.4 Finally, the extract is concentrated and if necessary, cleanup procedures are performed prior to analysis in accordance with the appropriate WHG analytical SOP. See Section 7.2 for the list of WHG cleanup SOPs and Section 3.1.6 for analytical SOPs.

6.0 Definitions

Accuracy
A determination of how close a measured value is to a known true value, usually measured as the percent recovery of a spike analysis.

Aliquot
A measured portion of a sample taken for analysis.

Analyte
The chemical element or compound an analyst seeks to determine; the chemical element of interest.

Analytical Batch
The basic unit for analytical quality control, defined as samples that are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g., groundwater, sludge, and ash).

Analytical Sample
Any solution or media introduced into an instrument, on which an analysis is performed, excluding instrument calibration, initial calibration verification, initial calibration blank, continuing calibration verification, and continuing calibration blank. The following are all analytical samples: undiluted and diluted samples, pre-digestion spike samples, duplicate samples, post-digestion spike samples, laboratory control sample, and method blank sample.

Assessment
The evaluation process used to measure the performance or effectiveness of a system and its elements. Assessment is used as an all-inclusive term to denote any of the following: performance, systems, data and compliance audits, management systems reviews, peer reviews, inspections, or spot assessments.

Bias
A systematic (consistent) error in test results. Bias is expressed as the difference between the population mean and the true or reference value, or as estimated from sample statistics, the difference between the sample average and the reference value.

Blank
An artificial sample designed to monitor the introduction of artifacts into the measurement process. For aqueous samples, reagent water is used as a blank matrix. A universal matrix does not exist for solid samples; therefore, no matrix is routinely used. There are several types of blanks, which monitor a variety of processes: 1) A *method blank* is taken through sample preparation and analysis only. It is a test for contamination in the laboratory procedure. 2) An *instrument blank* monitors any instrument drift during analysis. 3) A *field blank* is opened in the field and tests for contamination from the atmosphere as well as provides a test for contamination from sample preservation, site conditions, and transport as well as sample storage, preparation, and analysis.

Calibration
The systematic determination of the relationship of the response of the measurement system to the concentration of the analyte of interest. Instrument calibration performed before any samples are analyzed is called the initial calibration. Subsequent checks on the instrument calibration performed throughout analysis are called continuing calibration. Calibration is also the act of

making a scheduled comparison of instrument performance against national standards for instruments which measure physical parameters such as mass, time, and temperature.

Certified Reference Material
A reference material accompanied by a certificate issued by an organization certifying the contents and concentration(s) of the material. (See also Standard Reference Material.)

Code of Federal Regulations (CFR)
A collection of the federal regulations established by law and published by the Government Printing Office. Environmental regulations are codified in Title 40 of the CFR.

Concentration
The amount of chemical (analyte) present per amount of sample. For trace analyses, usually expressed as ppm, ppb, or ppt.

Contract Laboratory Program (CLP)
A program ordinated through the EPA to provide a wide range of analytical services by commercial laboratories in support of investigation, remediation, and enforcement actions at Superfund sites. Laboratories participating in this program are under contract to the EPA and must follow very specific analytical protocols during analyses and data delivery, as specified in the Statement of Work associated with the contract.

Control Chart
A graphical representation of analytical accuracy. Displays the arithmetic mean of a data set, the upper and lower warning limits and the upper and lower control limits.

Corrective Action
A measure taken to rectify conditions adverse to quality and, where necessary, to preclude their recurrence.

Dry Weight
The weight of a sample based on percent solids. Also, the weight of a sample after drying in an oven at a specified temperature.

Error
The difference between an observed or measured value and its true value.

Extractables
Organic chemicals which generally contain six to thirty carbon atoms and are amenable to GC, GC/MS, or HPLC analysis. (Also called Semi-Volatile Organics).

Extraction
The process of isolating chemicals of interest from a sample matrix (e.g., water, soil) when the sample cannot be analyzed directly.

False Negative Result
A term used to describe a result that was incorrectly reported as "not detected". False negatives can be monitored by analysis of instrument blanks.

False Positive Result
A term used to describe a result that was incorrectly reported as present. False positives can be monitored by analysis of method and instrument blanks.

Field Blank
A blank that is prepared and handled in the field and analyzed in the same manner as its corresponding field samples.

Hazardous Waste
Waste regulated under RCRA that can pose a substantial or potential hazard to human health or the environment when improperly managed. Such wastes possess at least one of four characteristics (ignitability, corrosivity, reactivity, or toxicity) or appear on special hazardous waste lists. The term is not interchangeable with hazardous substance or material.

Holding Time
The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

Hydrocarbons
Chemical compounds that consist entirely of carbon and hydrogen.

Inorganic Chemicals
Chemical substances of mineral origin, unlike organic chemicals whose structure relies on carbon atoms.

Material Safety Data Sheet (MSDS)
A compilation of information required under the OSHA Communication Standard on the identity of hazardous chemicals and their associated health and physical hazards, exposure limits and precautions.

Matrix
The component or substrate which contains the analyte(s) of interest. Examples of matrices are water, soil, sediment, and air. Matrix is not synonymous with phase (liquid or solid).

Matrix Effect
An interference in the measurement of analyte(s) in a sample that is caused by materials in the sample. Matrix effects may cause elevated reporting limits or may prevent the acquisition of acceptable results.

Matrix Spike (MS)
An aliquot of a matrix fortified sample spiked with known quantities of specific compounds and subjected to an entire analytical procedure. The percent recovery for the respective compound(s) is a measure of accuracy.

Matrix Spike Duplicate (MSD)
A second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

Method Blank
An analytical control consisting of all reagents, that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background contamination. Examples of method blanks are a volume of deionized or distilled laboratory water for water samples, a purified solid matrix for soil/sediment samples, or a generated zero air.

Method Detection Limit (MDL)
The minimum concentration of an analyte that, in a given matrix and with a specific method, can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Narrative
In an analytical report, a descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution.

Organics
Chemicals which contain the element carbon. Pesticides, priority pollutants, etc., belong to this class, (See Inorganics).

PAHs (PNAs)
Polyaromatic hydrocarbons, also called PNAs (polynuclear aromatics). A class of hydrocarbons

that contain fused benzene rings. In the Air program, these compounds are frequently referred to as Polycyclic Organic Matter (POM).

PCBs
Polychlorinated biphenyls. A class of chlorinated organic mixtures primarily previously used as insulator fluid in transformers. The four most common mixtures are called Aroclors 1242, 1248, 1254, and 1260. These designations represent the number of carbon atoms (12) and percent weight chlorine (e.g., 42). Sale of PCBs for new uses was banned by law in 1979.

Percent Recovery
A measure of accuracy determined from the comparison of a reported spike value to its true spike concentration.

Pesticide
Any chemical used to control or eradicate a pest. Subclasses include insecticides (e.g., DDT for insects), herbicides, (e.g., atrazine for weeds), fungicides (e.g., captan for fungi), nematocides (e.g., DBCP for nematodes), etc.

pH
A scale of acidity/alkalinity running from 1.0 to 14. Low values (1-5) represent high acidity, middle values (5-8) neutrality and high values (9-14) high alkalinity.

ppb
Part-per-billion. A unit of measurement that expresses the amount of chemical present ('part') per the amount of sample analyzed ('billion'). For example, a 'ng' (nanogram or one billionth of a gram) per 'g' (gram) of sample is 1 ppb. More common units are µg/Kg (micrograms per kilogram for solids) and µg/L (micrograms per liter for liquids).

ppm
Part-per-million. A unit of measurement which expresses the amount of chemical present ('part') per the amount of sample analyzed ('million'). For example, a 'µg' (microgram or one millionth of a gram) per 'g' (gram) of sample is 1 ppm. More common units are mg/Kg (milligrams per kilogram for solids) and mg/L (micrograms per liter for liquids).

Practical Quantitation Limit (PQL)
The lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

Precision
The reproducibility of an analytical technique, usually measured by analysis of duplicates or

duplicate spikes. Precision is usually expressed in terms of relative standard deviation or relative percent difference, but can be expressed in terms of the variance, range, or other statistic.

Preservative
A chemical or reagent added to a sample to prevent or slow decomposition or degradation of a target analyte or a physical process. Physical and chemical preservation may be used in tandem to prevent simple deterioration.

Quality Control (QC)
The physical procedures within the laboratory used to assess the quality of data (e.g., spikes, blanks, duplicates, calibration, etc).

Raw Data
All documentation associated with the original recording of analytical results pertinent to a specific sample or set of samples. This may include laboratory worksheets, calculation forms, instrument-generated output, analyst notes, etc., from sample receipt through final reporting.

Reference Standard
A chemical of known purity used as a reference ('standard') for the calculation of an analytical result.

Relative Percent Difference (RPD)
Statistic for evaluating the precision of a replicate set.

Semi-Volatile Organics
Organic chemicals which generally contain six to thirty carbon atoms and are amenable to GC, GC/MS or HPLC analysis. (See Extractables).

Solid Waste
Non-liquid, non-soluble, materials, ranging from municipal garbage to industrial wastes, that contain complex, and sometimes hazardous, substances. Solid wastes include sewage, sludge, agricultural refuse, demolition wastes, mining residues, and even liquids, and gases in containers.

Solvent
A substance, usually liquid, capable of dissolving or dispersing one or more other substances.

Standard Operating Procedure (SOP)
A detailed written description of how a laboratory executes a particular procedure or method, intended to standardize its performance.

Standard Reference Material (SRM)
A material of which certain properties have been certified by the National Institute of Standards and Technology (NIST).

Stock Solution
A concentrated solution of analyte(s) or reagent(s) prepared and verified by prescribed procedure(s), and used for preparing working standards or standard solutions.

Subsample
A portion taken from a sample. A laboratory sample may be a subsample of a gross sample; similarly, test portion may be a subsample of a laboratory sample.

Surrogate
Compounds that are added to every blank, sample, LCS, matrix spike, matrix spike duplicate, and standard for most organic analyses. They are used to evaluate analytical efficiency by measuring recovery. Surrogates include brominated, fluorinated, or isotopically labeled compounds that are not expected to be detected in environmental samples.

Target Compounds
Specific compounds that are to be quantified in a sample, based on a standard list of potential compounds.

Traceability
The ability of an analytical standard material used for instrument calibration purposes to be traced to its source. The standards must be traceable via written documentation to sources which produce or sell verified or certified standards, i.e., National Institute for Standards and Technology, USEPA, or vendors preparing standards from those sources which they have certified.

Verification
The process of reviewing data to ensure that data reduction has been correctly performed and that analytical results to be reported correspond to the data acquired and processed.

7.0 Interferences and Pretreatments

7.1 Solvents, reagents and glassware may introduce interferences. These must be demonstrated to be free of interferences by the analysis of a method blank. See the WHG SOP *Reagent, Solvent and Standard Control* (G-008) and *Laboratory Glassware Cleaning* (G-002), for additional details.

7.2 Many interferences can be removed by sample cleanup. The cleanup methods performed by WHG include the following: *Alumina Column Cleanup of Organic Extracts* (OP-009), *Sulfur Cleanup* (OP-007), *Gel-Permeation Chromatography* (OP-006), *Sulfuric Acid* (OP-010), and *Amino-propyl Cleanup of Tissues and Sediments* (OP-008). Only appropriate cleanup techniques must be performed based on the suspected interference and the compounds of interest. For example, sulfuric acid cleanup is not applicable to samples requiring pesticide analysis because this rigorous cleanup will destroy the majority of pesticides. Amino-propyl cleanup cannot be used when Endrin aldehyde is a compound of interest as this pesticide is lost during this cleanup.

7.3 Soapy residue may result in basic conditions on glassware and may cause degradation of the pesticides Aldrin and Heptachlor, and some organophosphorous pesticides. All glassware must be rinsed thoroughly with deionized water and solvent to remove soapy residue. See the WHG SOP (G-002) *Laboratory Glassware Cleaning,* for additional details.

7.4 Phthalate esters can be a major source of contamination if any material containing plasticizers (phthalates) comes in contact with the sample during the extraction process. Use of plastic or any material containing plasticizers (phthalates) should be avoided during extraction or analysis.

8.0 Health and Safety

8.1 The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices shall be followed at all times. Eating, drinking, smoking, or the application of cosmetics is not permitted in the laboratory area. Horseplay of any kind is prohibited. Pipetting by mouth is not permitted. All Personal Protective Equipment (PPE) must be removed before leaving the laboratory area and before entering the employee lounge or eating area. Always wash your hands before leaving the laboratory. All relevant Material Safety Data Sheets (MSDSs) are kept alphabetically in the centrally located file storage, in the common area outside of the Information Technology (IT) offices.

8.2 Approved PPE, which includes Safety Glasses, Gloves and Lab Coats, must be worn at ***all*** times when handling samples, reagents, chemicals, or when in the vicinity of others handling these items, so that dermal contact is avoided. All standards, reagents and solvents shall be handled under a hood using the proper PPE. All flammable solvents must be kept in the flammable storage cabinet, and returned to the cabinet immediately after use. When transporting chemicals, use a secure transporting devise and/or secondary outer container. Chemical storage is properly segregated and adequately ventilated to

reduce the possibility of hazardous reactions. Chemical storage in work areas shall be kept to a minimum. Storage on bench tops or other work surfaces, except temporary, is not permitted.

8.3 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely defined; however, each chemical compound shall be treated as a potential health hazard. From this viewpoint, exposure to chemicals must be reduced to the lowest possible level by whatever means available. All standards and reagents shall be prepared in a hood while using the proper PPE

8.4 Spilled samples, solvents, reagents, and water must be cleaned up from bench tops, instruments and autosampler surfaces immediately. A spill is considered a quantity of hazardous material if it is two times greater than the normal working volume. Concentrated solvents, acids or bases present a moderate to extreme hazard to the skin and mucous membranes. If contact with the skin occurs, immediately flush with large volumes of water. In the case of acidic/basic spills, the *Spill Kit* located in each laboratory shall be utilized before attempting to cleanup the spill. Although procedures are designed to minimize the possibility of an accident, all injuries or accidents, regardless of the nature or severity, are to be reported to the Section Head Supervisor immediately. If an employee discovers a potentially unsafe condition, this must be reported to the Section Head Supervisor immediately. No employee should feel compelled to work in a situation where they do not feel entirely informed, trained, or safe.

8.5 Analytical instrumentation poses the unique possibility of exposure to high voltages. Other than the *routine* instrument maintenance, as listed in the front of every Instrument Maintenance Logbook, at no time shall an instrument operator attempt to maintenance an instrument alone, or without the proper training, supervision or instruction. Caution must always be used in the presence of moving parts (autosamplers) and hot surfaces (injection ports).

8.6 Compressed gas cylinders shall only be moved with the dolly supplied for this specific purpose. The cap must be on the cylinder while it is being moved. The tank must be secured when in its final position. All spent tanks are to be returned in the same manner, and secured until removed by the vendor. Liquid argon or nitrogen represents a potential cryogenic hazard and safe-handling procedures must be used at all times.

8.7 All additional company safety practices shall be followed at all times as written in the WHG *Chemical Hygiene Plan.*

9.0 Equipment and Supplies

9.1 Shaker Table: Lab-line Orbit Shaker, # 3520.

9.2 Drying oven capable of maintaining 105°C and 400°C.

9.3 Dessicator, containing color indicator dessicant.

9.4 250 mL and 500 mL beakers.

9.5 500-mL Erlenmeyer flasks.

9.6 Stainless steel spatulas.

9.7 Concentration apparatus including the following:

- 9.7.1 Kuderna-Danish (K-D) concentrator tubes, 10mL, ground glass.
- 9.7.2 Evaporation flasks, 500mL, that attach to concentrator tubes with clips.
- 9.7.3 Snyder columns, 3-ball macro.
- 9.7.4 Teflon boiling chips.
- 9.7.5 Water bath.
- 9.7.6 N-EVAP by Organomations, Nitrogen blow-down for micro-concentration.
- 9.7.7 Turbo-vap with appropriate concentrator tubes by Zymark, or equivalent, as an alternative to the K-D apparatus.

9.8 Top-loading analytical balance capable of accurately weighing to the nearest 0.01gram.

9.9 Vials including 2mL, 4mL and 10mL for transfer of concentrated extract.

9.10 Syringes including 1mL - 5mL.

9.11 Filter funnels

9.12 Auto-vials, Whatman, 0.45um, PTFE membrane with glass micro-fiber pre-filter and polypropylene housing

Note: All maintenance records including routine upkeep and outside service visits are maintained in the instrument maintenance logbooks for the Lab-line Orbit Shaker Table.

10.0 Reagents and Standards

Use reagent grade chemicals for all reagents. Deionized (DI) water is ASTM Type II laboratory reagent grade water.

10.1 Methylene Chloride, ACS approved, Pesticide grade, see WHG SOP *Reagent, Solvent and Standard Control* (G-008) for additional details regarding solvent purity.

10.2 Acetone, ACS approved, Pesticide grade, see WHG SOP *Reagent, Solvent and Standard Control* (G-008) for additional details regarding solvent purity.

10.3 Hexane, ACS approved, Pesticide grade, see WHG SOP *Reagent, Solvent and Standard Control* (G-008) for additional details regarding solvent purity.

10.4 Sodium Sulfate, granular, anhydrous. Purified by heating to 400°C for 4 hours.

10.5 Glass wool, purified by heating to 400°C for 4 hours.

10.6 Spiking solutions which include the following solutions (see the appropriate WHG analytical SOP cited in Section 3.1.6 for details on the correct spike concentrations and spike volumes):

10.6.1 Surrogate spiking solution
10.6.2 Laboratory Control Sample (LCS) solution
10.6.3 Matrix Spiking (MS) solution.

11.0 Sampling Collection, Preservation, Shipment and Storage

11.1 Sample collection is not applicable to the WHG laboratory operation.

11.2 Please see the WHG *Sample Management* SOP (G-005) that describes the responsibilities of sample custody including all proper documentation, verification, and tracking procedures following Chain of Custody (COC) protocols, sample receipt procedures using the WHG *Sample Receipt Checklist*, which includes the check for proper sample preservation and cooler temperature verification. SOP G-005 also describes how samples are normally shipped or obtained by the laboratory, precautions to be used in opening sample shipments, and sample storage conditions.

11.3 Internal COC procedures for sample tracking includes the use of sample tracking logbooks. These procedures are also described in the *Sample Management* SOP (G-005).

11.4 *Solid samples:* A minimum of 100 grams of sample must be collected in a glass jar with a Teflon lined screw cap. The samples must be refrigerated and maintained at 4°±2°C until extraction and analysis. All solid samples must be extracted within 14 days from the date of collection. The extracts must be refrigerated and maintained at 4°±2°C until analysis. Sample extracts must be analyzed within 40 days from date of extraction.

12.0 Quality Control

12.1 Method Blank

12.1.1 A method blank must be prepared in sodium sulfate once per every 20 samples or per extraction batch, whichever is more frequent. If samples will be extracted for a variety of determinative analyses (*i.e.,* PAH, Pesticide and PCBs within the same extraction batch) a method blank for *each* analysis must be prepared and carried through the same extraction procedures as the samples.

12.1.2 Organic compounds of interest must not be detectable in the method blank at a concentration greater than the reporting limit.

12.1.3 Corrective Action: Extraction of the method blank and all associated samples must be performed until the blank is in control. Samples cannot be analyzed until an acceptable method blank analysis is obtained. Exceptions may be made with approval of the Organic Section Head, Laboratory Director or QA Manager, if the samples associated with the out of control method blank are non-detect for the compound of interest, or if sample concentrations are greater than 10x the blank levels. In such cases, the sample results are accepted without corrective action for the high method blank and the client is notified in a project narrative associated with the sample results.

12.2 Laboratory Control Sample (LCS)

12.2.1 Laboratory control sample (LCS) must be prepared once per every 20 samples or per extraction batch, whichever is more frequent, in sodium sulfate and spiked with a solution prepared from a second source or lot number, other than the source used to verify the accuracy of the standard curve for the determinative analytical method. The LCS contains all target compounds of interest, and is extracted along with the samples as verification of the accuracy of the entire extraction procedure. If samples will be extracted for a variety of determinative analyses (*i.e.,* PAH, Pesticide and PCBs within the same

extraction batch) a LCS for *each* analysis must be prepared and carried through the same procedures as the samples.

12.2.2 The acceptable recovery QC limits are documented in the applicable WHG analytical SOPs noted in Section 3.1.6. The solid recovery limits are continuously monitored and documented in-house through control charts which are updated semi-annually. The WHG SOP *Control Chart Generation* (G-013) provides details explaining how control charts are generated and used for quality control.

12.2.3 Corrective Action: Analysis according to the appropriate WHG analytical SOP must be repeated once to see if an analytical error has occurred. If the LCS recovery is still out of control, re-extract and re-analyze the LCS and all associated samples. Samples cannot be reported until an acceptable LCS is obtained. Exceptions may be made with approval of the Organic Section Head, Laboratory Director or QA Manager, if the samples associated with the out of control LCS are also associated with a matrix spike or matrix spike duplicate pair that is in control. This is an acceptable measure of accuracy of the extraction and analytical procedures. An explanation of this out of control LCS recovery must be included in the project narrative to the client and the sample data reported with the acceptable MS results as batch QC.

12.3 Matrix Duplicate (MD)

12.3.1 Duplicate analyses (matrix or sample duplicate) must be performed once per 20 samples (5% frequency). *For Organic analyses, the matrix duplicate is usually in the form of the matrix spike duplicate, see Section 12.4, below.*

12.3.2 Acceptable relative percent differences (RPD) of duplicates are documented in the applicable WHG analytical SOPs noted in Section 3.1.6. Acceptance criterion is not applicable to sample concentrations less than 5 times the reporting limit. Calculate the RPD as follows:

$$RPD = \frac{R1 - R2}{\frac{[R1 + R2]}{2}} \times 100$$

where:
R1 = sample Replicate #1
R2 = sample Replicate #2

The RPD limits are continuously monitored and documented in-house through control charts which are updated semi-annually. The WHG SOP *Control Chart Generation* (G-013) provides details explaining how control charts are generated and used for quality control.

12.3.3 Corrective Action: Analysis according to the appropriate WHG analytical SOP must be repeated once to see if an analytical error has occurred. If the % RPD still exceeds the control limits; include a project narrative with the results to client noting that there may be potential matrix effects on the precision of the reported organic results as evidenced by the matrix duplicate % RPD exceedance.

12.4 Matrix Spike / Matrix Spike Duplicate (MS/MSD)

12.4.1 Matrix spike / matrix spike duplicate (MS/MSD) samples must be performed once per 20 samples (5% frequency). If samples will be extracted for a variety of determinative analyses (*i.e.,* PAH, Pesticide and PCBs within the same extraction batch) a MS/MSD pair for *each* analysis must be prepared and carried through the same procedures as the samples. If less than 20 samples are prepared in a one-week time frame, a MS/MSD pair will be extracted at the beginning of each week.

12.4.2 The acceptable recovery and %RPD QC limits are documented in the applicable WHG analytical SOPs noted in Section 3.1.6. Calculate the %RPD as described in 12.3.2 above. The solid recovery and %RPD limits are continuously monitored and documented in-house through control charts which are updated semi-annually. The WHG SOP *Control Chart Generation* (G-013) provides details explaining how control charts are generated and used for quality control.

12.4.3 Corrective Action: Analysis according to the appropriate WHG analytical SOP must be repeated once to see if an analytical error has occurred. If the % recovery and/or %RPD still exceeds the control limits and the LCS is compliant; include a project narrative with the results to client noting that there may be potential matrix effects on the accuracy or precision of the reported results as evidenced by MS/MSD recoveries and/or %RPD outside of QC limits.

12.5 Surrogate Spike

12.5.1 Surrogate spikes must be added to QC and field samples to evaluate the extraction method performance.

12.5.2 The acceptable surrogate recovery limits are documented in the applicable WHG analytical SOPs noted in Section 3.1.6. The surrogate recovery limits are continuously monitored and documented in-house through control charts which are updated semi-annually. The WHG SOP *Control Chart Generation* (G-013) provides details explaining how control charts are generated and used for quality control.

12.5.3 Corrective Action: Analysis according to the appropriate WHG analytical SOP must be repeated once to see if an analytical error has occurred. If the % recovery still exceeds the control limits the sample must be re-extracted and re-analyzed to confirm the sample matrix. If *obvious* matrix interferences are noted, consultation with the Organic Section Head, Laboratory Director or QA Manager may be in order to confirm the need for sample re-extraction. If no re-extraction occurs, the surrogate results and reasons for the no re-extract decision must be discussed in the project narrative to the client.

12.6 Standard Reference Materials

12.6.1 Standard reference materials (SRM) are available from the National Institute of Standards and Technology (NIST) and are extracted and analyzed with samples on a project specific basis. These are not used as controls, but to evaluate potential matrix effects in associated samples for the target compounds being evaluated.

12.6.2 Acceptance criteria for SRM analysis will vary from project to project depending upon client data quality objectives (DQOs). Generally, $\pm$ 35% difference (%D) based on the true certified values of the target compounds of interest, or 65% - 135% recovery, serve as advisory acceptance criteria. %D and % recovery are continuously monitored and documented in-house through control charts which are updated semi-annually. The WHG SOP *Control Chart Generation* (G-013) provides details explaining how control charts are generated and used for quality control.

12.6.3 Corrective Action: Analysis according to the appropriate WHG analytical SOP must be repeated once to see if an analytical error has occurred. If the

% recovery and/or %D still exceeds the control limits, and the LCS and MS/MSD pair are compliant, include a project narrative with the results to client noting that there may be potential matrix effects on the accuracy or precision of the reported results as evidenced by SRM % recoveries and/or %D values outside of QC limits. These cases are normally isolated to the SRM, if all other controls are within limits.

13.0 Calibration and Standardization

There are no calibration or standardization requirements for this extraction technique. See the appropriate determinative analytical SOPs noted in Section 3.1.6.

14.0 Procedure

Samples are prioritized by the Organic Section Head or Preparation Group Leader for extraction based on hold time and client due date. The following steps shall be performed as rapidly as possible to avoid the loss of lighter weight, more volatile extractables.

14.1 Sample extraction:

14.1.1 Examine the sample for any signs of heterogeneity. Decant any standing water and discard any sticks or foreign objects that are not representative of the sample and mix well. Weigh a 20-gram aliquot of a well-mixed sample into an appropriate size solvent rinsed beaker. **Note:** Up to 50 grams of sample may be extracted if requested, based on client required reporting limits or other specified instructions. Record the weight to the nearest 0.01g. A smaller weight may be chosen if it is known that the sample concentration is high for the compounds of interest and this has been approved by the Organic Section Head or Laboratory Director.

14.1.2 Add sodium sulfate incrementally to the sample in a 2:1 mass ratio, and mix with a methylene chloride rinsed spatula until the sample is "powdery" or "free flowing". For example, if a 20g-sample aliquot is weighed, then 40g of sodium sulfate must be added to the sample. More sodium sulfate may be needed if the sample is not "free-flowing".

14.1.3 Generally, add one mL of surrogate spiking solution to each sample. The amount of surrogate spike will depend upon the final detection limits, final sample volume and the determinative analytical method. The LCS spiking solution shall be added to the LCS sample at this time. Matrix spiking solution

shall be added to the matrix spike and matrix spike duplicate samples associated with the extraction batch. The amount of LCS and Matrix Spike solution added will depend upon the same factors as the amount of surrogate spike. **Note:** If gel permeation cleanup (GPC) is to be employed, the analyst should either add double the volume of the Surrogate, LCS and MS/MSD spiking solutions, concentrate the final extract to half the normal volume, or employ a dilution factor of 1:2 when calculating the final results. The Organic Section Head or Preparation Group Leader must be consulted if there are any questions regarding the appropriate amount of spiking solutions. *All sample spiking must be "spike witnessed".*

14.1.4 Add the extraction solvent (acetone and methylene chloride [50:50]) to each sample. Use enough solvent to cover the sample during extraction, and add an additional ½ inch of solvent, above the sample.

14.1.5 Place the samples in the beaker rack on the Shaker Table and secure. Up to 25 samples can be loaded at a time. Turn the table on and set to 1.5 to 2.0 x 100 rotations per minute. Allow the samples to shake for 16 hours.

14.1.6 After 16 hours, stop the Shaker Table and transfer the extract solvent, by decanting, into a filter funnel fitted with baked and solvent rinsed glass wool and sodium sulfate, for extract drying. The extract is collected in a solvent rinsed 500-mL Erlenmeyer flask.

14.1.7 Repeat the extraction steps (starting at 14.1.4) twice more with fresh portions of 100% methylene chloride as the extraction solvent for the second and third shakes. The second shake must be 4 hours long and the third shake must be 30 minutes. Combine all three of the resulting extraction portions.

14.1.8 After all three extractions are complete and transferred through the filter funnel, rinse the filter funnel three times with methylene chloride from the laboratory squirt bottles to ensure a complete transfer of the entire extract.

14.1.9 The extract is now ready for concentration.

14.2 Kuderna-Danish (K-D) Concentration:

14.2.1 Transfer the sample extract from the Erlenmeyer flask to the 500-mL K-D flask with the 10-mL concentrator tube attached to the bottom. Place the K-D flask on the water bath with 1-2 boiling chips in the bottom of the tube and the macro

Snyder column on top. The bath temperature should be 85 ± 5°C. Macro-concentrate the sample to less than 10 mL. This will take approximately 15-20 minutes. At the proper rate of distillation, the balls of the column will chatter, but the column should not flood with condensed solvent.

14.2.2 If the extract appears extremely viscous and reduces in volume very slowly, a final volume of greater than10 mL may be used to ensure that there is no loss of surrogates or the compounds of interest. See the Organic Section Head or Laboratory Director for additional guidance on troublesome matrices.

14.2.3 Remove the sample from the bath and allow it to drain and cool for approximately 10 minutes, unless the sample requires solvent exchange. If the sample requires solvent exchange, add 20 mL of the exchange solvent and a new boiling chip to the K-D apparatus. The temperature of the water bath may need to be adjusted to ensure proper distillation of the exchange solvent. Concentrate the solvent exchanged sample to less than 10 mL, remove from the bath and allow to cool.

14.2.4 Move the cooled sample, still in the 10-mL concentrator tube, to the N-EVAP unit for micro-concentration, and bring the extract to the final volume required before cleanup. Refer to Table 1 in Section 23 for determinative method final volumes. The extract must be concentrated under a *gentle* steady stream of nitrogen. The internal walls of the concentrator tube must be rinsed periodically with the appropriate solvent during evaporation. The solvent level of the sample must be positioned to prevent water from condensing into the sample (*i.e.,* the solvent level should be below the level of the water in the bath). If the extract appears extremely viscous and reduces in volume very slowly then a final volume of 5-10 mL should be used to ensure that there is no loss of surrogates or the compounds of interest. **Note**: Micro-concentration may not be needed depending upon the determinative analytical method. Pesticide/PCB samples are typically 10-mL final extract volume and semivolatile samples are typically a 1-mL final extract volume. See Section 23.0 for guidance. Client specifications may be different than this SOP. Always see the Organic Section Head or Laboratory Director for additional guidance when needed.

14.2.5 If the sample in the 10-mL concentrator tube is dark and viscous, an "auto-vial", pre-fitted with a filtration disk, can be employed to remove particulate material. This is particularly evident in heavily contaminated petroleum samples. Reduce the extract to just less than 10-mL. Remove it from the concentrator tube with an appropriate size syringe. Pass it through the auto-vial, and back into the

concentrator tube. Rinse the syringe, tube and auto-vial as needed to ensure a thorough transfer. The extract may now concentrate more easily with the majority of the particulate matter removed. However, do not force the concentration as this may jeopardize the surrogate and the compounds of interest recoveries.

14.2.6 In some heavily contaminated petroleum extracts, it is possible to perform an extra step of hexane exchange to remove the asphaltene material that precipitates out in hexane. This decision must be made with the Organic Section Head or Laboratory Director approval. This may preserve the integrity of surrogates and the compounds of interest. This extract can also be auto-vialed to further remove any unwanted particulate materials. Micro-concentration may then continue.

14.2.7 *Turbo-Vap Concentration*: Pour the sample from the Erlenmeyer flask into the Turbo-vap tube, and place the Turbo-Vap tube in the Zymark unit. Adjust the pressure to 22 PSI, and the temperature to 44°C, and use the Zymark in the sensor mode of operation. Reduce the extract to the final volume required before cleanup, periodically rinsing the interior walls of the Turbo-vap tube with the appropriate solvent during evaporation (refer to Table 1 in Section 23 for final volumes). See Sections 14.2.2 through 14.2.6 for additional guidance with troublesome sample extracts. **Note:** boiling chips are not used for this type of concentration, and do not adjust the temperature if a solvent exchange is to be employed. Micro-concentration may be performed on the turbo-vap unit, however, if a final volume of greater than 1-mL is necessary, the sample must be transferred to a graduated cylinder or other calibrated volumetric flask to determine the final sample volume.

14.2.8 Transfer the sample extract from the concentrator tube to a vial of the appropriate final volume size. The sample may now undergo any necessary cleanup that may be required prior to analysis. See Section 7.2 for WHG sample cleanup SOP references. If the sample does not require cleanup, it may be directly transferred at the correct final volume, with copies of the sample preparation extraction log (Attachment I, Section 23.0), the preparation checklist (Attachment II, Section 23.0) and the client folder, to the analytical instrument room for analysis.

15.0 Data Evaluation, Calculations and Data Reporting

15.1 Procedures for data and record management for organic extraction must adhere to the

Quality Systems Manual, other subordinate documents covering record keeping, and the WHG *Document Control* SOP (G-016). All records must be stored in such a manner as to be safe and accessible for at least 10 years.

15.2 The extraction bench sheets and other relevant laboratory notebooks must follow the specifications in the WHG *Laboratory Notebook Usage* SOP (G-009), and all record keeping and document control practices.

15.3 See the appropriate WHG analytical SOPs noted in Section 3.1.6, for details on sample analysis, data evaluation, calculations and data reporting.

16.0 Method Performance

Initial Demonstration of Proficiency (IDP) is determined by every new analyst during training, and before actual sample analysis. The IDP consists of the extraction and/or analysis of four replicate samples spiked at approximately 10X the determinative method MDL. This process ensures the competency of the individual analysts

16.1 The following information needs to be supplied to the QA Manager for reporting and acceptance of extraction IDP: The *Training Checklist* must be completed by the trainer and the analyst, and supplied with all of the supporting raw data including, calibration standards, and method blanks in order to reconstruct and validate these analyses. The QA Manager will enter the information on to the individual employee spreadsheet. The following information is entered: preparation or analysis date, method name or number, blank ID, the four replicate file IDs, mean recovery, standard deviation and a comparison against the control limits, for precision and accuracy. The solid extraction recovery limits are listed in the determinative method SOPs, see Section 7.2 for analytical method references.

16.2 If any parameter does not meet the control limits, the QA Manager will notify the Organic Section Head or the Preparation Group Leader, and the analyst. The analyst must repeat the IDP until all criteria are met.

16.3 Upon successful completion of the IDP, *The IDP Certification Statement* form will be completed by the analyst, and signed-off by the Laboratory Director and the QA Manager. All of the above information will be retained in the employee-training file kept by the QA Manager.

17.0 Pollution Prevention

See Section 21.0, Waste Management for a discussion on Pollution Prevention.

18.0 Data Assessment and Acceptance Criteria

All results for the organic compounds of interests are reportable without qualification if extraction and analytical holding times are met, preservation (including cooler temperatures) are met, all QC criteria defined in the table below are met, and matrix interference is not suspected during extraction or analysis of the samples. If any of the below QC parameters are not met, all associated samples must be evaluated for re-extraction and/or re-analysis.

QC Parameter	Acceptance Criteria
Method Blank	< reporting limit
Laboratory Control Sample	See the applicable WHG analytical SOP for acceptance criteria
Matrix Duplicate	See the applicable WHG analytical SOP for acceptance criteria
Matrix Spike	See the applicable WHG analytical SOP for acceptance criteria
Matrix Spike Duplicate	See the applicable WHG analytical SOP for acceptance criteria

19.0 Corrective Actions for Non-Compliant Data

Section 12.0, Quality Control, defines the corrective actions that must be taken in instances where QC outliers exist. If the corrective actions have been followed and the data is still unacceptable, reference Section 20.0, Contingencies for Handling Unacceptable Data, for guidance on reporting.

20.0 Contingencies for Handling Unacceptable Data

Section 18.0 outlines sample batch QC acceptance criteria. If non-compliant organic compound results are to be reported, the Organic Section Head and/or the Laboratory Director, and the QA Manager must approve the reporting of these results. The laboratory Project Manager shall be notified, and may chose to relay the non-compliance to the client, for approval, or other corrective action, such as re-sampling and re-analysis. The analyst or Section Head performing the secondary review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

21.0 Waste Management

The Woods Hole Group *Hazardous Waste and Sample Disposal* SOP (G-006), must be

referenced for disposal of used standards, solvents, acids, reagents or other chemicals.

21.1 Once sample batches have completed extraction, the sample containers must be logged back into *Internal Tracking Logbook* and returned to the appropriate sample refrigerator and held for 30 days.

21.2 Once the samples have been held for 30 days, the solid samples must be disposed in a 55-gallon drum labeled "Soil/Solid Waste".

21.3 Once satisfactory organic compound results have been generated, the extracts are held for 30 days, or longer if specified by a client contract, then discarded into a 55-gallon drum labeled "Vial Waste".

21.4 All solvent waste generated during extraction must be stored in satellite containers in the preparation laboratory.

21.5 Once the solvent satellite containers are full, they must be emptied into 55-gallon drums marked "Organic Solvent Waste". Cleanup waste from the HPLC fractionator (silica cleanup) or GPC is emptied into the 55-gallon drum marked "HPLC Solvent Waste".

22.0 References

References in addition to the cyanide distillation and analytical test methods listed in Section 1.0. Identification of Test Methods, used to create this SOP, include the following:

22.1 EPA/600/R-96/027, *Guidance for the Preparation of Standard Operating Procedures (SOPs) for Quality Related Documents*, 1996.

22.2 EPA, 40CFR, Part 136, Appendix B, 7/1997.

22.3 National Environmental Laboratory Accreditation Conference (NELAC) Standard, Chapter 5, 7/1999.

22.4 Smith, Roy-Keith, *Handbook of Environmental Analysis,* 4th Edition, 1999.

23.0 Tables, Diagrams, Flowcharts and Data Validation

Table 1

Method	Solvent For GPC Cleanup	Solvent For Silica Cleanup	Solvent For Analysis	Volume For Cleanup	Volume For Analysis	Effective Final Volume
8081A	NA	NA	HEXANE	NA	10	10
8081A - low	DCM	HEXANE	HEXANE	4	1	2
8081A - ultra low	DCM	HEXANE	HEXANE	4	1	2
8082A	NA	NA	HEXANE	NA[a]	10	10
8082 - low	DCM	HEXANE	HEXANE	4[a]	1	2
8082 - ultra low	DCM	HEXANE	HEXANE	4[a]	1	2
8270C*	NA	NA	DCM	NA	1	1
8270C - low*	NA	NA	DCM	NA	1	1
TPH*	NA	NA	DCM	NA	1	1
EPH	NA	HEXANE	DCM	2	1	2
PAH	NA	NA	DCM	NA	1	1
PAH - low NOAA	DCM	HEXANE	DCM	4	1	2
PAH - SIM	DCM	HEXANE	DCM	4	1	2
Alkylated PAH	DCM	HEXANE	DCM	4	1	2
PCB - 680	NA	NA	HEXANE	NA[a]	1	1
SHC*	NA	NA	DCM	NA	1	1

* - Samples may be hexane exchanged to remove asphaltenes
[a] - Samples may be acid cleaned by GC if necessary

DCM = Dichloromethane or Methylene Chloride

Attachment I

Date:

Analyst: Witness:

Method: 8015 (TPH / SHC) / EPH / 8082 / 680 (PCBs) / 8081A (Pest) / 8270C (BNA / PAH / ALK) / 625 (BNA) / 608 (Pest/PCB) Note:_____

1.) Surrogate ID:
Concentration:

2.) Surrogate ID:
Concentration:

3.) Surrogate ID:
Concentration:

A.) MS / LCS ID:
Concentration:

B.) MS / LCS ID:
Concentration:

C.) MS / LCS ID:
Concentration:

Extraction Type: 3510C (Sep. Fun.) / Shaker / 3550B (Sonication) / 3535(SPE) / 3580A (Waste Dilution)

Cleanup Required: 3660B (Copper) / 3665A (Sulfuric Acid) **or**
Column/Cartridge: 3610A (Alumina) / 3630C (Silica) / 3620B (Florisil) / Amino-propyl, or Carbon, see Cleanup Log
HPLC Cleanup: 3640A (GPC) / 3630C (Silica), see HPLC Log

ETR #	Sample #	Initial Wt./Vol. (g/mL)	pH	Analytical Method	Surr. (mL)	MS/LCS (mL)	Turbo Vap. / KD	Hexane Exchange	Final Vol. (mL)	Final Vol. Equiv. (mL)	Transfer Vol. (mL)	Comments

Attachment II

ETR: ***Client:*** ***Project:***

Combined Extractions

Tests Requested		Separate Extractions	
Aroclor		Aroclor	
Aroclor low		Aroclor low	
Pesticide		Pesticide	
Pesticide low		Pesticide low	
Congener		Congener	
TPH via EPH		TPH via EPH	
TPH via 8015B		TPH via 8015B	
PAH		PAH	
PAH-SIM		PAH-SIM	
PAH low NOAA		PAH low NOAA	
8270		8270	

Combined Extractions #1		Combined Extractions #2	
Aroclor		Aroclor	
Aroclor low		Aroclor low	
Pesticide		Pesticide	
Pesticide low		Pesticide low	
Congener		Congener	
TPH via EPH		TPH via EPH	
TPH via 8015B		TPH via 8015B	
PAH		PAH	
PAH-SIM		PAH-SIM	
PAH low NOAA		PAH low NOAA	
8270		8270	

Required Cleanups			
No cleanups required		Carbon Column	
Copper		Florisil	
Acid		Alumina	
GPC			
Automated Silica Fractionation			
Glass Column Silica Fractionation			

Sample Observations

Sample Volume/ Weight	
	Normal weight/ volume extracted
	Lesser amount used low sample volume provided
	Lesser amount used strong petroleum odor
	Lesser amount used strong naphthalene odor
	Lesser amount used high % moisture
	Lesser amount used strong odor present
	Lesser amount used rocky material present
	Lesser amount used clay-like matrix
	Lesser amount used sediment layer present in 1L bottle
	Lesser amount used sheen present on sample
	Lesser amount used known high target analytes
	Lesser amount used known high non-target analytes
	Other

Extraction Notes	
	Sample not field preserved
	Emulsions during the base/neutral shakes
	Emulsions during the acid shakes
	Difficulty acid or base adjusting
	Extractions performed outside of hold time (notify PM)
	Samples freeze dried/ frozen extracted within hold time

Concentration Notes	
	Normal final volume transferred
	Greater final volume due to extract viscosity
	Greater final volume due to high sample contamination
	Greater final volume due to inability to concentrate further
	Crystals formed during concentration
	Precipitate formed during concentration

Auto-vialing notes	
	Auto-vialing not required
	Auto-vialed for precipitate in extract
	Auto-vialed for sediment in extract
	Auto-vialed for H_2O in extract

Use BACK for additional comments

Analysis of Parent and Alkylated Polynuclear Aromatic Hydrocarbons, Selected Heterocyclic Compounds, Steranes, Diterpanes and Triterpanes by GC / MS - SIM

1.0 Identification of Test Method

This standard operating procedure (SOP) is based on the following analytical test methods:

1.1 USEPA, "Method 8270C Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS)" in Test Methods for Evaluating Solid Waste, SW846, Third Edition, Final Update, December 1996.

2.0 Applicable Matrix or Matrices

2.1 This standard operating procedure (SOP) describes a method for analyzing sample extracts for parent and alkylated polynuclear aromatic hydrocarbons (PAHs), selected heterocyclic compounds, Steranes, Diterpanes and Triterpanes by gas chromatography / mass spectrometry with selected ion monitoring (GC/MS-SIM). This method is appropriate for determining these compounds in the extracts of water, soil, sediment, tissue and petroleum products.

	Approval Signatures	
Laboratory Director	Peter J. Kane	Date: 7/25/02
Section Head	Catherine L. Mather	Date: 7/25/02
Quality Assurance Manager	Gabe Porta	Date: 7/25/02

This SOP is printed from an electronic file.
A signed original is available in the files of Woods Hole Group Environmental Laboratories.

3.0 Detection and Quantitation Limits

3.1 The Method Detection Limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte(s) concentration is greater than zero. It is determined from the analysis of a series of samples, in the given matrix containing that, or those, analyte(s). It is essential that all analytical processing steps be included in the determination of the MDL. MDLs are performed annually or if there is a major change in instrumentation or method procedure.

3.2 Make an estimation of the detection limit using one of the following methods. This estimation assumes a certain degree of analyst experience.

3.2.1 The concentration value that corresponds to the instrument signal/noise in the range of 2.5-5.

3.2.2 The concentration equivalent of 3X the standard deviation of replicate instrument analyses of the analyte or analytes in reagent water.

3.2.3 That region of the standard curve where there is a significant change in sensitivity (*i.e.*, a break in the slope of the standard curve.)

3.2.4 Known lowest level instrumental limitations.

3.3 Prepare a reagent blank that is free of the analytes of interest (*i.e.,* there must not be analytes or interference present at the MDL).

3.4 Prepare a standard that is equal to, or at least in, the same concentration range of, the estimated detection limit (between 1-5 times the estimated MDL). If after analysis, the measured level is less than the estimated detection limit, prepare a standard at a higher concentration, to bring the concentration level to 1-5 times the estimated MDL. If the measured level is greater than the estimated detection limit, prepare a standard at a lower concentration. Alternatively, the standard may be used as is if the concentration of the standard does not exceed 10X the determined MDL (*i.e.,* the standard concentration is .5 ug/L and the determined MDL is .04 ug/L. Multiply .04 x 10 = .4 ug/L. Since .4 (10X the MDL) is less than .5 (the standard spike concentration), the spike level, or standard concentration, *does* exceed 10X the MDL. In this case the MDL must be repeated at a lower standard spike concentration).

3.5 Take a minimum of seven replicates through the entire preparation and analytical method. Calculate the results in the appropriate units. Calculate any concentration found in the blank. If concentrations found in the blank exceed 2X the MDL, the MDL must be repeated.

3.6 To determine that the estimated MDL is a good estimate, and to prevent costly reanalyses, it may be necessary to determine if a lower concentration of the analyte will

result in a lower MDL. To make this determination, start by taking two samples to be used to calculate the MDL and process each through the entire analytical method. If these two indicate a desirable range for MDL determination, proceed with five additional analyses to complete the seven replicates. If these measurements indicate that the range is incorrect, re-estimate the MDL and proceed until the correct range has been determined.

3.7 Calculate the standard deviation of the seven replicate measurements. Multiply the standard deviation by the correct Students' T-Value, depending on the number of replicates.

Replicates:	Students' T-Value:
7	3.143
8	2.998
9	2.896
10	2.821
11	2.764

3.8 To report the MDL, use the pre-prepared excel spreadsheets on the Woods Hole Group (WHG) server. The following information must be supplied: Method name or number; Analyst; Analysis date; Units; Matrix; Instrument used; Concentration analyzed (true value spiked) and *all* of the actual values determined from the seven replicates and their file IDs; Mean concentration; Standard Deviation; Reporting Limit and the Calculated MDL. All supporting raw data and the MDL spreadsheets must be forwarded to the Quality Assurance Manager for review, acceptance and storage of the MDL data. See Table I, Section 23.0 for the current MDL results as determined for aqueous matrix on 12/28/2001, soil/sediment on 01/24/2002, and tissue on 02/01/2002.

3.9 The Practical Quantitation Limit (PQL) or Reporting Limit (RL) for most organic and inorganic analyses, is equivalent to the lowest standard concentration, analyzed with, and included in, any initial calibration curve. The PQL or RL may be greater than the lowest point in the calibration curve, but cannot be lower than the lowest point in the calibration curve. For most organic analyses, the PQL or RL is equivalent to 3 to 5 times the determined MDL. See Table I, Section 23.0 for the current RLs as determined for aqueous matrix on 12/28/2001, soil/sediment on 01/24/2002, and tissue on 02/01/2002.

4.0 Scope and Application

4.1 This method is applicable to the analysis of sample extracts for parent and alkylated polynuclear aromatic hydrocarbons (PAHs), selected heterocyclic compounds, Steranes, Diterpanes and Triterpanes by gas chromatography / mass spectrometry with selected ion monitoring (GC/MS-SIM). Target analytes listed in Tables IIA and IIB are determined and measured in the concentration range of 10 to 5,000 parts per trillion (ng/L) for water samples, and 1 to 500 parts per billion (ug/Kg) for sediment and tissue samples, and 0.1

to 50 parts per million (mg/Kg) in petroleum product samples. Analytes detected over these ranges will be diluted and re-analyzed for accurate quantitation. Lower detection limits can be achieved if large volume injection (LVI, from 1uL to 50uL volume injections) techniques are employed.

4.2 This method is intended to assist in the identification of, or "fingerprinting" of, a source material against a potentially contaminated site and can also provide the identification of petrogenic or pyrogenic contamination.

5.0 Summary of Method

5.1 An aliquot of a well mixed, homogeneous aqueous, solid, tissue or petroleum sample is accurately measured or weighed for sample preparation. Generally, 1L of water sample, 10g of tissue sample, 15g of sediment sample, 20g of soil sample, and 0.1g of petroleum sample. Please refer to the appropriate WHG SOPs for extraction methods and sample preparation information:

- *Method 3510C – Extraction of Water Samples by Separatory Funnel* (OP-001),
- *Tissue Preparation and Homogenization* (OP-003),
- *Method 3545 – Extraction of Soil, Tissue, Vegetation and Sediment Samples by Pressurized Fluid Extraction* (OP-004), and
- *Shaker Table Extraction* (OP-013).
- Refer to SW-846 method 3580A for the preparation of petroleum samples by Waste Dilution.

Water, soil/sediment, tissue and petroleum samples are spiked with surrogate compounds and extracted using methylene chloride or a methylene chloride/acetone mixture. Sample extracts are concentrated and may be exchanged into hexane for optional cleanup and/or fractionation into saturated (f_1) and aromatic (f_2) fractions prior to analysis. See the WHG SOPs *Gel Permeation Chromatography (GPC)* (OP-006) and *Silica Fractionation and Cleanup by HPLC* (OP-014) for additional sample cleanup information and details.

5.2 After cleanup, the extracts are concentrated to a final volume of usually 1 mL, spiked with internal standards, and analyzed by GC/MS-SIM. Analytes are introduced into the GC/MS by injecting a known volume of the calibration standards, quality control samples, and sample extracts into the GC equipped with a narrow-bore capillary column. The GC column is temperature programmed to separate the analytes, which are then detected with a mass spectrometer operating in the selective ion mode. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of the calibration standards. Concentrations are determined using mean relative response factors from a multi-level calibration curve. Response factors for target analytes and surrogate compounds are determined relative to the internal standards. Multi-component analytes (alkylated PAHs) are assigned the response factors of their unsubstituted, parent compounds. Sterane, Diterpane and Triterpane compounds are assigned the response factor of the compound 5B(H)Cholane.

6.0 Definitions

Accuracy
A determination of how close a measured value is to a known true value, usually measured as the percent recovery of a spike analysis.

Aliquot
A measured portion of a sample taken for analysis.

Analyte
The chemical element or compound an analyst seeks to determine; the chemical element of interest.

Analytical Batch
The basic unit for analytical quality control, defined as samples that are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g., groundwater, sludge, and ash).

Analytical Sample
Any solution or media introduced into an instrument, on which an analysis is performed, excluding instrument calibration, initial calibration verification, initial calibration blank, continuing calibration verification, and continuing calibration blank. The following are all analytical samples: undiluted and diluted samples, predigestion spike samples, duplicate samples, serial dilution samplers, analytical spike samples, postdigestion spike samples, interference check samples, laboratory control sample, preparation blank, and linear range analysis sample (LRS).

Area
A term used in gas chromatography that indicates the peak area of a compound exiting a chromatographic column. The size or area of the peak is proportional to the amount of analyte in the sample.

Assessment
The evaluation process used to measure the performance or effectiveness of a system and its elements. Assessment is used as an all-inclusive term to denote any of the following: performance, systems, data and compliance audits, management systems reviews, peer reviews, inspections, or spot assessments.

Audit
A planned and documented investigative evaluation of an item or process to determine its adequacy and effectiveness as well as compliance with established procedures.

Background Correction
A technique usually employed relative to metals analysis, which compensates for variable background contribution to the instrument signal in the determination of trace elements.

Bias
A systematic (consistent) error in test results. Bias is expressed as the difference between the population mean and the true or reference value, or as estimated from sample statistics, the difference between the sample average and the reference value.

Blank
An artificial sample designed to monitor the introduction of artifacts into the measurement process. For aqueous samples, reagent water is used as a blank matrix. A universal matrix does not exist for solid samples; therefore, no matrix is routinely used. There are several types of blanks, which monitor a variety of processes: - *A method blank* is taken through sample preparation and analysis only. It is a test for contamination in the laboratory procedure. – *A storage blank* is stored and analyzed with samples at the laboratory. It is a test for contamination in sample storage as well as sample preparation and analysis. – *A trip blank* is shipped to and from the field with the sample containers. It is not opened in the field and, therefore, provides a test for contamination from sample preservation, site conditions, and transport as well as sample storage, preparation, and analysis. It is most commonly used for volatile organics. – *A field blank* is opened in the field and tests for contamination from the atmosphere as well as those activities listed under *trip blank.*

Blind Performance Evaluation Sample
A sample either submitted to the laboratory or prepared in the laboratory whereby the concentrations of parameters of concern are known by the preparer and not by the laboratory.

BNA
Base, neutral and acid extractable compounds. The terms base, neutral and acid refer to the pH condition of the sample undergoing extraction. Certain compounds extract more efficiently from water under acidic or basic conditions.

Calibration
The systematic determination of the relationship of the response of the measurement system to the concentration of the analyte of interest. Instrument calibration performed before any samples are analyzed is called the initial calibration. Subsequent checks on the instrument calibration performed throughout analysis are called continuing calibration. Calibration is also the act of making a scheduled comparison of instrument performance against national standards for instruments which measure physical parameters such as mass, time, and temperature.

Calibration Curve
The graphical relationship between the known values for a series of calibration standards and instrument responses.

Calibration Factor (CF) (Also see RF and RRF)

The ratio of the instrument response of an analyte to the amount injected. CFs are used in external standard calibrations.

Calibration Standard
A material used to quantitate the relationship between the output of a sensor and a property to be measured. Calibration standards should be traceable to Standard Reference Materials (provided by NIST, EPA, or other recognized standards agencies) or a primary standard.

Capillary Column GC
A GC technique that uses a very long (30-60m) small id (0.2mm) glass column instead of the traditional packed GC column (1.8M by 2mm) for separation of chemicals.

CERCLA
The Comprehensive Environmental Response, Compensation and Liability Act, also known as 'Superfund'. Enacted December 11, 1980, CERCLA provides for identification and cleanup of hazardous materials released over the land and into the air, waterways and groundwater. It covers areas affected by newly released materials and older leaking or abandoned dump sites. CERCLA established the Superfund, a trust fund, to help pay for cleanup of hazardous materials sites. The EPA has authority to collect cleanup costs from those who release the waste material. Cleanup funds come from fines and penalties, from taxes on chemical/petrochemical feed stocks, and the U.S. Department of the Treasury.

Certified Reference Material
A reference material accompanied by a certificate issued by an organization certifying the contents and concentration(s) of the material. (See also Standard Reference Material.)

Chain of Custody
Procedures and associated documents designed to trace the custody of a sample from the point of origin to final disposition, with the intent of legally demonstrating that custody remained intact and that tampering or substitutions were precluded.

Chromatogram
A graph representing the signal output of an instrument (GC or HPLC) which can be used to identify organic chemicals by peak retention time (RT) and to quantitate by peak size.

Clean Water Act (CWA)
Regulates the discharge of nontoxic and toxic pollutants into surface waters. The CWA became effective November 18, 1972, and has been amended significantly since then. Its ultimate goal is to eliminate all discharges into surface waters. EPA sets guidelines and state agencies issue permits (e.g., National Pollutant Discharge Elimination System permits) specifying the types of control equipment and allowable discharges for each facility.

Code of Federal Regulations (CFR)
A collection of the federal regulations established by law and published by the Government Printing Office. Environmental regulations are codified in Title 40 of the CFR.

Coefficient of Variation (Relative Standard Deviation)
A measure of precision (relative dispersion). It is equal to the standard deviation divided by the mean and multiplied by 100 to give a percentage value.

Co-elution
When two organics determined by GC give the same retention time (RT) and cannot be differentiated.

Comparability
Expresses the confidence with which one data set can be compared to another data set measuring the same property. Comparability is assured through the use of established and approved analytical methods, consistency in the basis of analysis (wet weight, volume, etc.) and consistency in reporting units (ppm, ppb, etc.).

Completeness
The amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct normal operations. It is usually expressed as a percentage.

Composite
A sample composed of two or more increments.

Concentration
The amount of chemical (analyte) present per amount of sample. For trace analyses, usually expressed as ppm, ppb, or ppt.

Confirmation
In gas chromatography, an unknown compound in a sample is identified on the basis of its retention time on a specific chromatographic column. Because several compounds may exhibit the same retention time on a given column, a secondary confirmation on a different column or detector is often recommended for additional confidence in the compound identification. This additional confirmation is often referred to as "dual-column" or "second-column" confirmation.

Contract Laboratory Program (CLP)
A program coordinated through the EPA to provide a wide range of analytical services by commercial laboratories in support of investigation, remediation, and enforcement actions at Superfund sites. Laboratories participating in this program are under contract to the EPA and must follow very specific analytical protocols during analyses and data delivery, as specified in the Statement of Work associated with the contract.

Control Chart
A graphical representation of analytical accuracy. Displays the arithmetic mean of a data set, the upper and lower warning limits and the upper and lower control limits.

Corrective Action
A measure taken to rectify conditions adverse to quality and, where necessary, to preclude their recurrence.

Correlation Coefficient
The correlation coefficient is a determination of how closely data "fits" a straight line. It is a number between –1 and 1 that indicates the degree of linear relationship between two sets of numbers.

Data Quality Objective (DQO)
During the planning phase of a project requiring laboratory support, the data user must establish the quality of data required from the investigation. Such statements of data quality are known as DQOs. Qualitative and quantitative statements about the data required to support specific decisions or regulatory actions, DQOs must take into account sampling considerations as well as analytical protocols.

Data Validation
See Validation.

Decafluorotriphenylphosphine (DFTPP)
An organic compound utilized in several GC/MS methods to establish proper mass spectral instrument performance for semi-volatile analyses.

Degrees of Freedom
The number of independent deviations used in calculating an estimate of the standard deviation.

Dissolved Solids
Disintegrated organic and inorganic material contained in water. Excessive amounts make water unfit to drink or use in industrial processes.

Double Blind Performance Evaluation
A sample that contains select parameters at defined levels. The levels are unknown to the laboratory. The laboratory is also unaware that the sample is a performance evaluation sample.

Dry Weight
The weight of a sample based on percent solids. Also, the weight of a sample after drying in an oven at a specified temperature.

Effluent
Treatment or untreated wastewater that flows out of a treatment plant, sewer or industrial outfall. Generally refers to wastes that are discharged into surface waters and are regulated under the Clean Water Act. Effluent limitations are restrictions on quantities, rates and concentrations of wastewater discharges that are established by a state or EPA.

External Standards
A method of quantifying chromatographic data in which standards of known concentrations are analyzed prior to unknown samples. The chromatographic peak area (or height) of a sample component is compared to a calibration curve of a peak area constructed from the standard data for that component. This comparison allows the concentration of the component in the sample to be determined.

Extract
The solution (liquid) remaining after a sample has been contacted with an aqueous solution (for inorganics) or an organic solvent (for organics). The extract, containing the chemical of interest, is then processed and analyzed by AA, ICP, or wet chemical techniques (inorganics and metals) or by GC/MS, or HPLC (organics).

Extractables
Organic chemicals which generally contain six to thirty carbon atoms and are amenable to GC, GC/MS, or HPLC analysis. (Also called Semi-Volatile Organics).

Extraction
The process of isolating chemicals of interest from a sample matrix (e.g., water, soil) when the sample cannot be analyzed directly.

Error
The difference between an observed or measured value and its true value.

False Negative Result
A term used to describe a result that was incorrectly reported as "not detected".

False Positive Result
A term used to describe a result that was incorrectly reported as present. False positives can be checked by analyzing blanks.

Field Blank
A blank that is prepared and handled in the field and analyzed in the same manner as its corresponding client samples.

Field Screening
An investigative technique utilizing analytical chemistry at or near a work site to rapidly determine the presence or absence of environmental contaminants and/or the approximate concentrations of a specific target of compounds.

Finding
An event discovered during an audit which, if continued, is sufficient to render the quality of an item unacceptable or indeterminate.

Flame Ionization Detector (FID)

A gas chromatography detector in which the column effluent gas is mixed with hydrogen and burned in air or oxygen. The ions and electrons produced in the flame generate an electric current proportional to the amount of material in the detector. The FID responds to nearly all organic compounds, but it does not respond to air and water, which makes it exceptionally suited to environmental analysis.

Flash Point
The lowest temperature at which a flammable liquid gives off sufficient vapor to form an ignitable mixture with air near its surface or within a vessel. Combustion does not continue. Used to characterize a waste as hazardous or non-hazardous in terms of flammability.

Full Scan
The process of monitoring all of the ions formed when a molecule is bombarded with electrons in the mass spectrometer.

Gas Chromatography (GC)
A technique for detecting organic compounds by using their physical and chemical properties to separate a mixture. The compounds are identified and quantified with various types of detectors as they exit the chromatograph. Selection of detectors is dependent on the particular compounds of interest.

GC/ECD
A GC with a detector (Electron Capture) selective for halogenated organic chemicals (usually chlorinated pesticides and PCBs), used in Methods 608, 8081, 8082.

Gas Chromatography/Mass Spectrometry (GC/MS)
A technique in which sample analytes are bombarded with electrons as they exit a gas chromatographic column and are fragmented into characteristic ion patterns. The mass spectrometer is the detector. It can determine which fragments are present and therefore the identity of the compounds.

GC/N/P
A GC with a detector (N/P) selective for organic chemicals which contain nitrogen and phosphorus usually organophosphorous or triazine pesticides). Also referred to as GC/TSD (Thermionic Specific Detector).

GC/PID
A GC with a detector (Photo Ionization) selective for aromatic hydrocarbons.

Gravimetric
Analyses based on the direct or indirect weighing of the analyte in question. This technique usually requires the use of an analytical balance with a sensitivity of 0.1 mg or better.

Hazardous Waste
Waste regulated under RCRA that can pose a substantial or potential hazard to human health or the environment when improperly managed. Such wastes possess at least one of four characteristics (ignitability, corrosivity, reactivity, or toxicity) or appear on special hazardous waste lists. The term is not interchangeable with hazardous substance or material.

Headspace
Any area in a container not completely filled by the sample in which gases can collect.

High Resolution GC/MS (HR/GC/MS)
A GC/MS that uses both an electromagnet and permanent magnet to detect ions produced by the ion source. By using both magnets in series, very small differences in mass (0.003) can be detected. This type of instrument is most frequently used where extremely low (ppq) detection limits are important, such as analyses for dioxins and furans.

Holding Time
The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

High Performance Liquid Chromatography (HPLC)
A chromatograph that is used to qualitatively and quantitatively identify organic chemicals, particularly those which are not amenable to GC techniques because of thermal instability.

Hydrocarbons
Chemical compounds that consist entirely of carbon and hydrogen.

Initial Calibration
Analysis of a series of analytical standards at different specified concentrations; used to define the linearity and dynamic range of the response of an instrument to the target compounds prior to the analysis of samples.

Instrument Detection Limit (IDL)
The smallest concentration or amount an instrument can reliably detect.

Instrument Tuning
A technique used in GC/MS procedures to verify that the instrument is properly calibrated to produce reliable mass spectral information.

Internal Standards (IS)
A compound added to every sample or sample extract at a known concentration prior to analysis for the purpose of quantitation.

Injection
Process of introducing a portion of a sample extract into a GC, GC/MS, or HPLC.

Isomers
Chemical compounds with the same molecular weight and atomic composition but differing molecular structure, e.g., n-pentane and 2-methylbutane.

Limit of Quantification (LOQ)
The minimal signal level required to quantitate a specific analyte by a specific procedure at the desired confidence level.

Library Search
A technique in which an unknown mass spectrum of a compound is compared to the mass spectra of compounds contained in a computer library in an effort to identify the compound. Compounds identified in this manner are referred to as tentatively identified compounds (TICs).

Linear Regression
A statistical method for finding a straight line that best fits a set of two or more data points, thus providing a relationship between two or more variables.

Listed Waste
Any waste listed as hazardous under the Resource Conservation and Recovery Act, but which has not been subjected to the Toxic Characteristics Listing Process because the dangers it presents are considered self-evident.

Log-In
The receipt and initial management of an environmental sample. It generally includes identifying who sent the sample; maintaining chain-of-custody; checking report and invoice information; recording analyses requested, including methodology and special instructions; and assigning a discreet in-lab identification, usually a number or bar code.

Mass Chromatogram
The plot of selected ions versus time. The areas under the curves are proportional to the amounts of each compound detected.

Mass Spectrum
A bar graph showing the relative abundance of the ions produced when sample molecules are bombarded by electrons in a mass spectrometer.

Material Safety Data Sheet (MSDS)
A compilation of information required under the OSHA Communication Standard on the identity of hazardous chemicals and their associated health and physical hazards, exposure limits and precautions.

Matrix
The component or substrate which contains the analyte(s) of interest. Examples of matrices are water, soil, sediment, and air. Matrix is not synonymous with phase (liquid or solid).

Matrix Effect
An interference in the measurement of analyte(s) in a sample that is caused by materials in the sample. Matrix effects may cause elevated reporting limits or may prevent the acquisition of acceptable results.

Matrix Modifiers
Chemicals added to samples for metals analysis, which are used to lessen the effects of chemical interferents, viscosity, and surface tension.

Matrix Spike (MS)
An aliquot of a matrix fortified sample spiked with known quantities of specific compounds and subjected to an entire analytical procedure. The percent recovery for the respective compound(s) is a measure of accuracy.

Matrix Spike Duplicate (MSD)
A second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

Maximum Contaminant Level (MCL)
The maximum permissible level of a contaminant in water delivered to any user of a public water system. MCLs are enforceable standards.

Mean
The average of a set of values.

Measurement
The process or operation of ascertaining the extent, degree, quantity, dimensions, or capability with respect to a standard.

Median
The middle value of a set of data when the data set is ranked in increasing or decreasing order.

Method Blank
An analytical control consisting of all reagents, which may include internal standards and surrogate standards, that is carried through the entire analytical procedure. The method bland is used to define the level of laboratory background contamination. Examples of method blanks are a volume of deionized or distilled laboratory water for water samples, a purified solid matrix for soil/sediment samples, or a generated zero air.

Method Detection Limit (MDL)
The minimum concentration of an analyte that, in a given matrix and with a specific method, can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Narrative
In an analytical report, a descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution.

National Pollutant Discharge Elimination System (NPDES)
A provision of the Clean Water Act that prohibits discharge of pollutants into waters within the U.S. unless a special permit is issued by EPA, a state (where delegated), or a tribal government on an Indian reservation.

Nutrient
Any substance assimilated by living a thing that promotes growth. The term is generally applied to nitrogen and phosphorus in wastewater, but is also applied to other essential and trace elements.

Organics
Chemicals which contain the element carbon. Pesticides, priority pollutants, etc., belong to this class, (See Inorganics).

Outlier
A result excluded from the statistical calculations due to being deemed "suspicious" when applying the "Grubbs Test" (or equivalent).

PAHs (PNAs)
Polyaromatic hydrocarbons, also called PNAs (polynuclear aromatics). A class of hydrocarbons that contain fused benzene rings. In the Air program, these compounds are frequently referred to as Polycyclic Organic Matter (POM).

PCBs
Polychlorinated biphenyls. A class of chlorinated organic mixtures primarily previously used as insulator fluid in transformers. The four most common mixtures are called Aroclors 1242, 1248, 1254, and 1260. These designations represent the number of carbon atoms (12) and percent weight chlorine (e.g., 42). Sale of PCBs for new uses was banned by law in 1979.

Percent Difference
When two independent measurements of the same characteristics are available, it is possible to use the percent difference instead of the coefficient of variation to measure precision.

Performance Evaluation (PE)
A type of audit in which a known or characterized value is compared to the result obtained through the routine analysis of a "PE" sample in the laboratory to evaluate the proficiency of an analyst or laboratory.

Performance Evaluation (PE) Sample
A sample of known composition (unknown to the laboratory), provided by an external source (e.g., EPA), which is used to evaluate lab performance.

Periodic Calibration
A calibration that is performed at prescribed intervals for equipment such a balances, thermometers, and balance weights. In general, they are performed on equipment that are distinct, singular purpose units, and are relatively stable in performance.

Percent Recovery
A measure of accuracy determined from the comparison of a reported spike value to its true spike concentration.

Pesticide
Any chemical used to control or eradicate a pest. Subclasses include insecticides (e.g., DDT for insects), herbicides, (e.g., atrazine for weeds), fungicides (e.g., captan for fungi), nematocides (e.g., DBCP for nematodes), etc.

Petroleum Hydrocarbon Fingerprinting
A technique for identifying sources of petroleum products.

pH
A scale of acidity/alkalinity running from 1.0 to 14. Low values (1-5) represent high acidity, middle values (5-8) neutrality and high values (9-14) high alkalinity.

Pollutant
Generally, any substance introduced into the environment that adversely affects the usefulness of a resource.

ppb
Part-per-billion. A unit of measurement that expresses the amount of chemical present ('part') per the amount of sample analyzed ('billion'). For example, a 'ng' (nanogram or one billionth of a gram) per 'g' (gram) of sample is 1 ppb. More common units are ug/Kg (micrograms per kilogram for solids) and ug/L (micrograms per liter for liquids).

ppm
Part-per-million. A unit of measurement which expresses the amount of chemical present ('part') per the amount of sample analyzed ('million'). For example, a 'ug' (microgram or one millionth of a gram) per 'g' (gram) of sample is 1 ppm. More common units are mg/Kg (milligrams per kilogram for solids) and mg/L (micrograms per liter for liquids).

Practical Quantitation Limit (PQL)
The lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

Precision
The reproducibility of an analytical technique, usually measured by analysis of duplicates or duplicate spikes. Precision is usually expressed in terms of relative standard deviation or relative percent difference, but can be expressed in terms of the variance, range, or other statistic.

Preservative
A chemical or reagent added to a sample to prevent or slow decomposition or degradation of a target analyte or a physical process. Physical and chemical preservation may be used in tandem to prevent simple deterioration.

Priority Pollutants
A set of organic and inorganic chemicals identified by EPA as indicators of environmental contamination. A priority pollutant analysis is usually done on wastewater to obtain a discharge permit. See Part 122.

Proficiency Test
See Performance Evaluation.

Qualitative Analysis
An analysis that focuses primarily on the identification of chemicals present in a sample.

Quality Assurance (QA)
An organized program designed to assure that laboratory quality control procedures are appropriate and demonstrate date quality. All those planned and systematic actions necessary to provide adequate confidence in results.

Quality Assurance Program Plan (QAPP)
A written assembly of management policies, objectives, principles, and general procedures that outlines how the laboratory intends to generate data of known and acceptable quality.

Quality Assurance Project Plan (QAPJP)
A written document that presents in specific terms the policies, organization, objectives, functional activities and specific quality assurance/quality control (QA/QC) activities designed to achieve the data quality objectives of a specific project. There are 16 essential elements that EPA has mandated be addressed in a project plan.

Quality Control (QC)
The physical procedures within the laboratory used to assess the quality of data (e.g., spikes, blanks, duplicates, calibration, etc).

Quantitative Analysis
An analysis that focuses primarily on the measurement of the amount of specific analyte(s) present in a sample.

Raw Data
All documentation associated with the original recording of analytical results pertinent to a specific sample or set of samples. This may include laboratory worksheets, calculation forms, instrument-generated output, analyst notes, etc., from sample receipt through final reporting.

Reconstructed Ion Chromatogram (RIC)
The response of the total ions detected versus time. A term applicable only to GC/MS.

Reference Method
Statistic for evaluating the precision of a replicate set.

Reference Standard
A chemical of known purity used as a reference ('standard') for the calculation of an analytical result.

Relative Percent Difference (RPD)
Statistic for evaluating the precision of a replicate set.

Relative Response Factor (RRF)
A measure of the relative response of a compound compared to its internal standard. RRFs are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

Relative Standard Deviation
See Coefficient of Variation.

Resolution
The degree of separation between peaks eluting from a chromatographic column. Sufficient resolution between peaks is required for proper quantitation of unknown analytes.

Resource Conservation and Recovery Act (RCRA)
A federal law that established a regulatory system to track hazardous substances from the time of generation to disposal. The law requires safe and secure procedures to be used in treating, transporting, storing, and disposing, of hazardous substances. RCRA is designed to prevent new and uncontrolled hazardous waste sites.

Response Factor (RF)
A factor derived from the calibration of a compound that is used in the quantitation calculation of sample analytes. A response factor may be derived from an external standard calibration (then called a Calibration Factor) or from an internal standard calibration (then called a Relative Response Factor).

Retention Time
A term used in gas and liquid chromatography describing the time elapsed from sample injection until the specific compound elutes or exits the chromatographic column at the detector. Each

compound has a characteristic retention time on a specific column; therefore, this information is used to qualitatively identify the compounds in the sample.

Relative Retention Time (RRT)
Used to code GC peaks by calculating the ratio between the RT of a GC peak and the RT of a reference peak.

Selected Ion Monitoring (SIM)
A technique in which one or more specific ions are monitored. Because only specific ions are monitored, selected ion monitoring generally provides higher sensitivity than a full scan monitoring. A term applicable only to GC/MS.

Semi-Volatile Organics
Organic chemicals which generally contain six to thirty carbon atoms and are amenable to GC, GC/MS or HPLC analysis. (See Extractables).

Solid Waste
Nonliquid, nonsoluble, materials, ranging from municipal garbage to industrial wastes, that contain complex, and sometimes hazardous, substances. Solid wastes include sewage, sludge, agricultural refuse, demolition wastes, mining residues, and even liquids, and gases in containers.

Solvent
A substance, usually liquid, capable of dissolving or dispersing one or more other substances.

Standard Operating Procedure (SOP)
A detailed written description of how a laboratory executes a particular procedure or method, intended to standardize its performance.

Standard Reference Material (SRM)
A material of which certain properties have been certified by the National Institute of Standards and Technology (NIST).

Stock Solution
A concentrated solution of analyte(s) or reagent(s) prepared and verified by prescribed procedure(s), and used for preparing working standards or standard solutions.

Subsample
A portion taken from a sample. A laboratory sample may be a subsample of a gross sample; similarly, test portion may be a subsample of a laboratory sample.

Superfund
The Response Trust Fund, established by CERCLA as a mechanism for the federal government to take emergency or remedial action to clean up both abandoned and existing disposal sites when there is a release, or potential threat of a release, of a hazardous substance presenting imminent and substantial danger to public health and welfare. See CERCLA.

Surrogate
Compounds that are added to every blank, sample, LCS, matrix spike, matrix spike duplicate, and standard for most organic analyses. They are used to evaluate analytical efficiency by measuring recovery. Surrogates include brominated, fluorinated, or isotopically labeled compounds that are not expected to be detected in environmental samples.

Systems Audit
A systematic on-site qualitative review of facilities, equipment, training, procedures, record keeping, data verification, and reporting aspects of a quality assurance system to arrive at a measure of the capability of the system.

Target Compound List (TCL)
A list of organic compounds that are determined during Superfund site remediations. Created by EPA for use in the Contract Laboratory Program, this list was formerly referred to as the Hazardous Substance List (HSL).

Target Compounds
Specific compounds that are to be quantified in a sample, based on a standard list of potential compounds.

Tentatively Identified Compounds (TICs)
Compounds detected in samples that are not target compounds, internal standards, system monitoring compounds or surrogates. TICs usually consist of up to 30 peaks that are greater than 10% of the peak areas, or heights, of the nearest internal standard. They are subjected to mass spectral library searches for tentative identification.

Traceability
The ability of an analytical standard material used for instrument calibration purposes to be traced to its source. The standards must be traceable via written documentation to sources which produce or sell verified or certified standards, i.e., National Institute for Standards and Technology, USEPA, or vendors preparing standards from those sources which they have certified.

Trip Blank
A sample, usually pure water prepared in the lab, which is taken to the sampling site and then returned with the collected samples. Later analysis will indicate any false positive results in the real samples arising from contamination during shipment.

Validation
A systematic effort to review data for identification of errors, and thereby deleting or flagging suspect values to assure the validity of the data for the user. This process may be done by manual or computer methods.

Verification
The process of reviewing data to ensure that data reduction has been correctly performed and that analytical results to be reported correspond to the data acquired and processed.

Volatile Organics
Organic chemicals which generally contain one to six atoms and are amenable to analysis by the purge/trap technique because of their high vapor pressures. (See Semi-Volatile Organics).

7.0 Interferences and Pretreatments

7.1 Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause inferences that lead to discrete artifacts and/or elevated baselines in the ion current profiles. Demonstrate that all of these materials are free from interferences under the conditions of the preparation and analysis by extracting and analyzing a laboratory method blank with each batch of up to 20 samples.

7.2 Contaminants coextracted from the sample may cause matrix interferences. The extent of matrix interferences will vary considerably from sample to sample, depending upon the nature of the environment being investigated. An interference, which is unique to SIM techniques, can arise from the presence of a coeluting compound, which contains the quantification mass ion. This event results in a positive interference to the reported value for the compound of interest. This interference is controlled to some degree by acquiring data for a confirmation ion. If the ion ratios between the quantification ion and the confirmation ion are not within the specified limits, then interferences may be present. Quantification and confirmation ions should agree within +/- 20% of the calibration standard ion ratios. However, the stability of confirmatory/primary ion abundance ratios may decrease as the IDL is approached. Analysts must apply judgment in evaluating apparent interferences.

7.3 The presence of a large amount of a single alkyl homolog is usually indicative of an interference. For example, the presence of an apparent C_2 - Naphthalene compound in the absence of other C_2 - Naphthalenes or the C_3 - Naphthalenes is probably an analytical interference. An experienced analyst should confirm the determination of any analytical interference that may affect reported results. Confirmation may be obtained by the full scan GC/MS analysis of the sample or analysis by GC/FID.

8.0 Health and Safety

8.1 The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices shall be followed at all times. Eating, drinking, smoking, or the application of cosmetics is not permitted in the laboratory area. Horseplay of any kind is prohibited. Pipetting by mouth is not permitted. All Personal Protective Equipment (PPE) must be removed before leaving the laboratory area and before entering the employee lounge or eating area. Always wash your hands before leaving the laboratory. All relevant Material Safety Data Sheets

(MSDSs) are kept alphabetically in the centrally located file storage, in the common area outside of the Information Technology (IT) offices.

8.2 Approved PPE, which includes Safety Glasses, Gloves and Lab Coats, must be worn at ***all*** times when handling samples, reagents, chemicals, or when in the vicinity of others handling these items, so that dermal contact is avoided. All standards, reagents and solvents shall be handled under a hood. All flammable solvents must be kept in the flammable storage cabinet, and returned to the cabinet immediately after use. When transporting chemicals, use a secure transporting devise and/or secondary outer container. Chemical storage is properly segregated and adequately ventilated to reduce the possibility of hazardous reactions. Chemical storage in work areas shall be kept to a minimum. Storage on bench tops or other work surfaces, except temporary, is not permitted.

8.3 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely defined; however, each chemical compound shall be treated as a potential health hazard. From this viewpoint, exposure to chemicals must be reduced to the lowest possible level by whatever means available. All standards and reagents shall be prepared in a hood while using the proper PPE.

8.4 Spilled samples, solvents, reagents, and water must be cleaned up from bench tops, instruments and autosampler surfaces immediately. A spill is considered a quantity of hazardous material if it is two times greater than the normal working volume. Concentrated solvents, acids or bases present a moderate to extreme hazard to the skin and mucous membranes. If contact with the skin occurs, immediately flush with large volumes of water. In the case of acidic/basic spills, the *Spill Kit* located in each laboratory shall be utilized before attempting to cleanup the spill. Although procedures are designed to minimize the possibility of an accident, all injuries or accidents, regardless of the nature or severity, are to be reported to the Section Head immediately. If an employee discovers a potentially unsafe condition, this must be reported to the Section Head immediately. No employee should feel compelled to work in a situation where they do not feel entirely informed, trained, or safe.

8.5 Analytical instrumentation poses the unique possibility of exposure to high voltages. Other than the *routine* instrument maintenance, as listed in the front of every Instrument Maintenance Logbook, at no time shall an instrument operator attempt to maintenance an instrument alone, or without the proper training, supervision or instruction. Caution must always be used in the presence of moving parts (autosamplers) and hot surfaces (injection ports).

8.6 Compressed gas cylinders shall only be moved with the dolly supplied for this specific purpose. The cap must be on the cylinder while it is being moved. The tank must be secured when in its final position. All spent tanks are to be returned in the same manner, and secured until removed by the vendor. Liquid argon or nitrogen represents a potential cryogenic hazard and safe-handling procedures must be used at all times.

8.7 All additional company safety practices shall be followed at all times as written the WHG *Chemical Hygiene Plan.*

9.0 Equipment and Supplies

If performing any maintenance on any piece of equipment, other then routine daily maintenance, it must documented in the *Instrument Maintenance Logbook* located in the laboratory specific to each instrument.

9.1 Gas Chromatograph - The instrumentation includes a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port is designed for splitless injection onto a capillary column. The injection port includes a silanized glass liner containing a plug of silanized glass wool to reduce high-molecular-weight mass discrimination. The model is HP6890 or equivalent. The injector port will require maintenance on an as needed basis if degradation or contamination is apparent. Please refer to the front of the *Instrument Maintenance Logbook*, which outlines the routine maintenance procedures. The instrument is currently under service contract by Ernie Kirschner of HSS (Hardware & Software Services, LLC).

9.2 Large volume injector, ATAS OPTIC 2 or APEX ProSep 800 Plus XT, or equivalent - Capable of injecting one to fifty microliters of standards and extracts onto the GC column.

9.3 Column - Restek 30-m x 0.25 mm ID, 0.25 um film thickness, fused-silica capillary column with RTX-5 bonded phase, or equivalent.

9.4 Mass Spectrometer - The mass spectrometer must operate at 70ev (nominal) electron energy in the electron impact ionization mode and be tuned to optimize the sensitivity of the instrument to the mass range being monitored (35 - 525 amu). The GC capillary column is fed directly into the ion source of the mass spectrometer. The model is HP5973, or equivalent. The source will require cleaning and/or filament replacement on an as needed basis. Please refer to the instrument hardware manual for detailed procedures, located in the laboratory next to the instrument. This instrument is currently under service contract by Ernie Kirschner of HSS (Hardware & Software Services, LLC).

9.5 Auto sampler - Adapted onto the Gas Chromatograph. The model is HP 6890 series autosampler with a GC autosampler controller, or equivalent.

9.6 Computer - with Windows NT version 4.0 operating software utilizing HP Enviroquant G1701BA Version B.01.00 software.

9.7 Helium - Ultra high purity grade (99.9999% pure).

10.0 Reagents and Standards

10.1 Methylene Chloride, ACS approved, Pesticide grade, see WHG SOP *Reagent, Solvent and Standard Control* (G-008) for additional details regarding solvent purity.

10.2 Acetone, ACS approved, Pesticide grade, see WHG SOP *Reagent, Solvent and Standard Control* (G-008) for additional details regarding solvent purity.

10.3 Hexane, ACS approved, Pesticide grade, see WHG SOP *Reagent, Solvent and Standard Control* (G-008) for additional details regarding solvent purity.

10.4 Methanol, Purge and Trap grade, see WHG SOP *Reagent, Solvent and Standard Control* (G-008) for additional details regarding solvent purity.

10.5 *Custom Mix Calibration Standard* prepared by Supelco which contains all of the parent PAH and Heterocyclic compounds (catalog # 20033962) at 1000ug/mL.

10.6 *5B(H)-Cholane:* (CAS# 80373-86-0) obtained from Chiron AS Norway (catalog # 0641,24) at 1000ug/mL. (This compound is used for calibration and quantitation of all Steranes, Diterpanes and Triterpanes).

10.7 *Carbazole*: neat, or in 2000ug/mL solution. (Additional target compound not contained in the Custom Mix Calibration Standard in 10.5, above).

10.8 *Surrogates:* 2-Methylnaphthalene-d10, Pyrene-d10, and Benzo(b)Fluoranthene-d12 from Cambridge Isotope, neat, or in 200ug/mL solution. Prepare a surrogate solution by taking 2.5mL of each surrogate into 100mL of *Acetone or Methanol* for a 5ug/mL surrogate spiking solution. The solution must be assayed for use by analysis before release to the preparation lab. All compounds must be within 20% of their true value. 1mL is spiked into each QC and field sample. This amount may be adjusted to meet project specific concentrations, as needed.

10.9 *Recovery Correct Surrogates*: SV Internal Standard mix (Naphthalene-d8, Acenaphthalene-d10, Pheneanthrene-d10, and Chrysene-d12) from Restek at 2000ug/mL.

10.10 *Internal Standards (IS):* Fluorene-d10 and Benzo(a)Pyrene-d12 from Cambridge Isotope, neat, or in a 200ug/mL solution. Prepare a 1:8 dilution (1250uL of each IS at 200ug/mL into 10mL of Methylene Chloride) for a 25µg/mL solution. 20uL is spiked into each standard, QC sample and field sample.

10.11 *Laboratory Control Sample, Matrix Spike, and Matrix Spike Duplicate (LCS/MS/MSD):* A solution of 17 priority pollutant parent PAH's from Ultra Scientific, or equivalent, at 2000ug/mL. This is a source separate from the calibration curve. Prepare a spike mix by adding 250uL of the solution to 100mL of *Acetone* for a 5ug/mL LCS/MS/MSD spiking solution. The solution must be assayed for use by analysis before release to the

preparation lab. All compounds must be within 20% of their true value. 1mL is spiked into the LCS and each designated MS/MSD field sample. This amount may be adjusted to meet project specific concentrations, as needed.

10.12 *Alaska North Slope Crude Oil*, neat. Weigh approximately 0.5g into 10mL of Methylene Chloride for a stock solution of approximately 50mg/mL. Then prepare a 1:10 dilution (100uL of standard into 900uL of Methylene Chloride) spiked with 20uL of the internal standard solution, for a working standard of approximately 5.0 mg/mL.

10.13 *Independent Reference Material (IRM) 1491*, PAH's in toluene. Prepare a 1:10 dilution of the working standard, 100uL of standard into 900uL of methylene Chloride, for use as the independent verification check of the calibration standards. Spike this standard with 20uL of the internal standard solution. The PAH's are at certified concentrations. See the corresponding *Certificate of Analysis* for the true values of each analyte.

10.14 *SRM 1944 – PAH's in sediment and SRM 1974a – PAH's in Tissue*, from the National Institute of Standards & Technology (NIST). Please refer to the individual certifications for the assigned true values. These SRMs may be extracted and analyzed with sample batches as part of the overall QC evaluation if requested by the client. Other certified SRMs may be used on a project specific basis.

10.15 Prepare the *Working Stock Standard* (all resulting concentrations at 10µg/mL) in 10mL of Methylene Chloride (CH_3Cl_2) as follows. (**Note:** If any compounds are received neat, a stock standard in the range of 200-2000ug/mL must be prepared. Then, adjust the "Volume Added" below, as needed, so the resulting concentration is 10µg/mL, the same final concentration as the other components.)

Component	**Volume Added**	**Final Volume in (CH_3Cl_2)**
Custom Supelco Mix	100 µL of 1000 µg/mL	10 mL
5B(H)Cholane	100 µL of 1000 µg/mL	10 mL
SV IS Mix	50 µL of 2000 µg/mL	10 mL
Carbazole	50 µL of 2000 µg/mL	10 mL
2-Methylnaphthalene-d10	500 µL of 200 µg/mL	10 mL
Pyrene-d10	500 µL of 200 µg/mL	10 mL
Benzo(b)Fluoranthene-d12	500 µL of 200 µg/mL	10 mL

6 Level Curve Preparation for Individual Components

Calibration Level	Volume of Working Std. Added (10 ug/mL)	Volume of CH_3Cl_2 added
Level 1 - 10 ng/mL	1 µL	999 µL
Level 2 - 25 ng/mL	2.5 µL	997.5 µL
Level 3 - 250 ng/mL	25 µL	975 µL
Level 4 - 500 ng/mL (also Continuing Calibration Level)	50 µL	950 µL
Level 5 - 1,250 ng/mL	125 µL	875 µL
Level 6 - 5,000 ng/mL	500 µL	500 µL

Note: 20 µL of the 25µg/mL Internal Standard (Fluorene-d10 and Benzo(a)Pyrene-d12) is added to each calibration level. *A minimum of a 5-level curve must be analyzed, but 6-levels may be analyzed and evaluated.*

11.0 Sample Collection, Preservation, Shipment and Storage

11.1 Sample collection is not applicable to the WHG laboratory operation.

11.2 Please see the *Sample Management* SOP (G-005) that describes the responsibilities of sample custody including all proper documentation, verification, and tracking procedures following Chain of Custody (COC) protocols, sample receipt procedures using the *Sample Receipt Checklist*, which includes the check for proper sample preservation and cooler temperature verification. SOP G-005 also describes how samples are normally shipped or obtained by the laboratory, precautions to be used in opening sample shipments, and sample storage conditions.

11.3 Internal COC procedures for sample tracking includes the use of sample tracking logbooks. Theses procedures are also described in the *Sample Management* SOP (G-005).

11.4 *Aqueous* samples should be collected in 1L or 2L amber glass bottles and stored without preservative at 4°C. *Soil/sediment and tissue* samples should be collected in glass soil jars and stored at 4°C, or if desired, frozen. The minimum amount of sample needed to reach the reporting limits in Section 23.0 for this method for aqueous samples is 1L, for solid and tissue matrices is 10-20 grams and for petroleum product samples is 0.1 grams. Additional sample is needed (approximately 3X the minimum amount) if MS/MSD analyses are to be performed.

11.5 The hold time for this method is 7 days for the extraction of aqueous samples and 14 days for the extraction of solid and tissue samples. There is no extraction holding time applied to petroleum product samples. If a sediment or tissue samples are frozen, this suspends

the holding time until removal from the freezer. All extracts must be analyzed within 40 days of the extraction date.

12.0 Quality Control

Quality control (QC) samples are necessary to monitor both the sample extraction and instrument analysis procedures.

12.1 Method Blank

12.1.1 A method blank must be extracted (spiked with surrogates and internal standards) and analyzed once per every 20 samples or per extraction batch, whichever is more frequent.

12.1.2 An *acceptable* method blank analysis must not contain any target compound in Table II at concentrations 5 times greater than the reporting limit. The presence of analytes at concentrations greater than 5 times the reporting limit will warrant application of a "B" qualifier to that target compound(s) on all associated report forms, and perhaps reextraction of all associated samples. Surrogate and internal standard recoveries must meet the QC limits for the method blank, see Section 12.6. Re-extraction *corrective action* that would exceed the sample holding time criteria should be discussed with the client, Laboratory Director, QA Manager and/or Section Head prior to implementation. Exceptions may be made with approval of the Section Head if the samples associated with an out of control method blank are non-detect for the affected compound(s) or if the concentrations of the affected compound(s) are greater than 10x the blank level in the samples. In such cases, the sample results are accepted without corrective action for the high method blank result. The client must be notified, via the project narrative, of any method blank non-compliance associated with the sample results.

12.2 Laboratory Control Sample (LCS)

12.2.1 The laboratory control sample (LCS) contains 17 priority pollutant parent PAH's and is from a second/separate source, to verify the accuracy of the calibration curve, see Section 10.11. The LCS is extracted along with the samples. An LCS must be extracted and analyzed once per every 20 samples or per extraction batch, whichever is more frequent.

12.2.2 The acceptable recovery QC limits are 40%-140% for an aqueous, solid, tissue, and product LCS's. All recovery limits are continuously monitored and documented in-house through control charts which are updated semi-annually. The WHG SOP *Control Chart Generation* (G-013) provides details explaining how control charts are generated and used for quality control.

12.2.3 Corrective Action: Repeat analysis or check to see if an analytical error has occurred. If the LCS recovery is still out of control, re-extract and re-analyze the LCS and all associated samples. Samples cannot be analyzed until an acceptable LCS is obtained. Exceptions may be made with approval of the Section Head if the samples associated with the out of control LCS are also associated with a matrix spike and matrix spike duplicate that is in control which demonstrates an isolated problem pertaining to the LCS only. An explanation of this out of control LCS recovery must be included in the project narrative to the client and the sample data reported with the acceptable MS/MSD results as batch QC.

12.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

12.3.1 Matrix spike and matrix spike duplicate analyses must be performed once per 20 samples per matrix (5% frequency).

12.3.2 The acceptable recovery QC limits are 40%-140% for an aqueous, solid, tissue, and product MS/MSD's. The acceptable RPD limit is 50%. All recovery limits are continuously monitored and documented in-house through control charts which are updated semi-annually. The WHG SOP *Control Chart Generation* (G-013) provides details explaining how control charts are generated and used for quality control.

12.3.3 Corrective Action: Repeat analysis or check to see if an analytical error has occurred. If the % recovery or %RPD still exceeds the control limits and the associated LCS is within control, include a project narrative with the results to client noting that there may be potential matrix effects on the accuracy or precision of the affected results as evidenced by the matrix spike and matrix spike duplicate exceedance.

12.4 Matrix or Sample Duplicates

12.4.1 Laboratory matrix or sample duplicates are analyzed if requested by the client. The QC limit is 50% RPD for target compounds found above 5 times the reporting limit.

12.4.2 Corrective Action: If the %RPD exceeds the 50% control limit and the associated MS/MSD %RPD is within 50%, include a project narrative with the results to client noting that there may be potential matrix effects on the precision of the results isolated to this sample, as evidenced by the matrix duplicate exceedance and the MS/MSD acceptance. If both the sample/duplicate and the MS/MSD exceed the control limits, include a project narrative with the results to client noting that there may be potential matrix effects on the precision of the results as evidenced by the sample/duplicate and the MS/MSD exceedances.

12.5 Surrogates

12.5.1 Surrogates are monitored at 30%-150% recovery for all matrices. The recovery limits are continuously monitored and documented in-house through control charts which are updated semi-annually. The WHG SOP *Control Chart Generation* (G-013) provides details explaining how control charts are generated and used for quality control. Recovery limits will be replaced by control charted values when enough data points are generated.

12.5.2 Corrective Action: Check to see if an analytical or dilution error occurred and re-calculate. If only one surrogate falls below the 30% recovery limit, but is above 10% recovery, the exceedance is noted, with approval of the Section Head, and the results are reported to the client with a notation in the case narrative. If all surrogates are recovered below the 30% limit, re-extract the sample and report the re-extract results along with the original results, if re-extraction occurred beyond the holding time, and the re-extract surrogates are within the QC limits. If the surrogates are recovered below 30% in the re-extract, this confirms a suspected matrix interference on the surrogates, and only the original analysis needs to be reported. If the chromatogram shows obvious matrix interference, no re-analysis or re-extraction is necessary. *This decision must be made with approval of the Section Head.* Surrogate outliers and sample re-extracts must be noted in the case narrative to the client.

12.6 Internal Standards

12.6.1 Internal standards are added to every field sample, QC sample, standard, and method blank. The acceptance limits are 50-200% of the internal standard response (or area) of the daily continuing calibration verification standard.

12.6.2 Corrective Action: Check to see if an analytical, dilution or spiking error occurred. If the chromatogram shows obvious matrix interference, no re-analysis is necessary. *This decision must be made with approval of the Section Head.* Note the exceedance in the case narrative to the client. If no obvious interference is present, re-analyze the extract. If internal standards are now within the acceptance limits, report only the re-analysis, as long as the re-analysis occurred within the 40-day analytical hold time. If the re-analysis occurred outside of the 40-day analytical hold time, both the original and re-analysis must be reported. If the internal standards again are outside the acceptance limits, after re-analysis, either within or outside of the 40-day hold time, report only the original analysis, and include a narrative to the client that the suspected matrix interference on the internal standards was confirmed by sample re-analysis.

12.7 Standard Reference Materials (SRM's)

12.7.1 Standard reference materials (SRM) are available from the National Institute of Standards and Technology (NIST) and are extracted and analyzed with samples

on a project specific basis. These are not used as controls, but to evaluate potential matrix effects in associated samples for the target compounds being evaluated.

12.7.2 Acceptance criteria for SRM analysis will vary from project to project depending upon client data quality objectives (DQOs). Generally, ± 35% difference (%D) based on the true certified values of the target compounds of interest, or 65% - 135% recovery, serve as advisory acceptance criteria. %D and % recovery are continuously monitored and documented in-house through control charts which are updated semi-annually. The WHG SOP *Control Chart Generation* (G-013) provides details explaining how control charts are generated and used for quality control.

12.7.3 Corrective Action: Repeat analysis and/or check to see if an analytical error has occurred. If the % recovery or %D still exceeds the control limits and the associated LCS and/or MS/MSD are within control, include a project narrative with the results to client noting that the observed recovered of the SRM are isolated to this sample as evidenced by the LCS and/or MS/MSD acceptance.

13.0 Calibration and Standardization

Prior to the analysis of any standards or samples, the instrument acquisition and process methods must be set up. This includes the GC run parameters and the SIM mode acquisition ion entries into the different SIM acquisition retention time windows. An initial calibration must be analyzed to establish linearity of the instrument. First, the mass spectrometer must be tuned to the meet the abundance criteria for PFTBA, then DFTPP.

13.1 PFTBA Manual Tuning

13.1.1 Prior to initial calibration, and each day prior to sample analysis, tune the mass spectrometer using PFTBA (Perfluorotributylamine - calibration gas) to maximize the sensitivity of the instrument in the mass range of interest, 35-525 amu. The use of PFTBA for MS tuning maximizes the sensitivity of the analysis within the mass/charge (m/e) range being monitored. *If only the PTFBA tune is required, per client request or project specific DQOs, the DFTPP tune is Section 13.2 does not need to be evaluated.*

13.1.2 To acquire the PFTBA Tune:

- Click on the "Instrument" icon to open the Chem Station.
- Go into "Instrument Control" in the "GC/MS Top Environmental" screen.
- Go to "View" and select "Manual Tune".
- Go to "File" and select "Load Tune Values". Select the PFTBA.U file.

- Go back into "File" and select "Generate Report". The calibration gas will automatically turn ON, equilibrate for approximately 20 seconds, and generate a report. Evaluate the PFTBA tune against the parameters below.

PFTBA Ion	Relative Abundance
m/e 69	Base Peak with > 150,000 counts
m/e 219	30% to 60% of Base Peak
m/e 502	2% to 6% of Base Peak

If the PFTBA tune meets the criteria, "Save" the tune values, and exit the program.

13.1.3 If the PFTBA does not meet the criteria above, the following corrective actions may be attempted by an experienced mass spectrometrist:

- Adjust the ion focus value up or down while the calibration gas valve is open and continue to scan until the desired abundances are achieved.
- Adjust the entrance lens value up or down while the calibration gas valve is open and continue to scan until the desired abundances are achieved.
- Save the tune parameters under PFTBA.U.

13.2 DFTPP Tuning - ***Only*** performed on a project specific basis, if requested by the client, or included in a project specific Quality Assurance Plan (QAP).

13.2.1 Before the analytical standards are analyzed, the mass spectrometer must be evaluated for the proper ion criteria for DFTPP (decafluorotriphenylphosphene), if specifically requested by the client or included in a project specific QAP. Generally, 1uL of a 50 ng/mL solution is evaluated. A larger volume or lesser concentration may be evaluated if using large volume injections.

13.2.2 To acquire the DFTPP tune:

- Click on the "Instrument" icon to open the Chem Station, if not already open.
- Go into the "GC/MS Top Environmental" screen.
- Go into "Sequence".
- Edit the "Sample Table Log" by entering the "Vial" number starting at position 1, the "Data File ID" (for the DFTPP tune the nomenclature is "T" for Tune "2" for instrument number 2, the date, and the tune number "01, 02, etc." such as, T2060501, T2060502, etc.), the acquisition method, DFTPP.m, and finally the "Sample Name" (*i.e.*, "DFTPP 50 ng/mL") When complete, click "OK".
- Go back into "Sequence" and "Save" the sequence as the date, such as, S060501.s. The ending "01" indicates the first sequence created on 06/05.
- Go back into "Sequence" and "Load and Run" the sequence that was just saved.

13.2.3 After the analysis of the DFTPP, evaluate the tune as follows:

- Enter into the "Environmental Data Analysis" (off-line) screen.
- Go to "File" and under method, select the method, DFTPP.m, that the tune was analyzed under, and then select the tune data file.
- Go into "Tuner" and select "Eval DFTPP", then select "AutoFind DFTPP to Screen", to evaluate the tune file. The software will evaluate the tune by selecting three scans of the DFTPP peak and will display the ion intensities on the screen. That is, one scan at the apex, one scan either directly preceding **or** following the apex, and one background subtracted scan, 20 seconds before the beginning of the DFTPP peak. If the criteria below are met, repeat but select "AutoFind to Printer", for a hardcopy of the tune evaluation for the record.

13.2.4 If the "AutoFind" tune evaluation does not meet the criteria below, manual evaluation of the tune can be performed by attempting either of the options below:

- Blow up the DFTPP peak on the screen and select the scan at the apex of the peak, and the scans immediately preceding **and** following the apex, and average them. Go into "Tuner" and select "Evaluate DFTPP to Screen", or "Evaluate DFTPP to Printer", as described above, OR,
- Take the average of the scans across the entire peak and average them. Go into "Tuner" and select "Evaluate DFTPP to Screen", or "Evaluate DFTPP to Printer", as described above.

13.2.5 The following DFTPP mass intensity criteria must be used:

DFTPP KEY MASSES AND ABUNDANCE CRITERIA

Mass	m/e Abundance criteria
51	30-60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40-60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5-9 percent of mass 198.
275	10-30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17-23 percent of mass 442.

Tune acceptance must be verified at the beginning of every analytical shift, and prior to the analysis of any standards. If the DFTPP tune does not meet the criteria above, the PFTBA must be re-evaluated, and adjustments made by an experienced mass spectrometrist, to obtain an acceptable DFTPP tune, before continuing with any analysis.

13.3 GC Instrumental Conditions

13.3.1 Inject an aliquot of 1uL to 50uL into the capillary column of the gas chromatograph at the following conditions. Injection volume (using the Large Volume Injector, LVI) amount will be dictated by project specific DQOs.

GC Parameter	Setting
Injector Temp:	60 - 300 °C (or see LVI settings, 13.5)
Transfer Line Temp:	300 °C
Initial Oven Temp:	40 °C
Initial Hold Time:	1 minute
Ramp Rate:	6 °C / minute
Final Temperature:	290 °C
Final Hold Time:	18 minutes
Total runtime:	60 minutes
Mode:	Splitless / Constant Flow (or see LVI settings, 13.5)
Purge:	50 mL / minute – on at 0.80 minutes (or see LVI settings, 13.5)
MS Temperature	300 °C

13.4 Mass Spectrometer Conditions

13.4.1 The effluent from the GC capillary column is fed directly into the ion source of the mass spectrometer. The MS is operated in the SIM mode using appropriate retention time windows to include the quantification and confirmation ions for each PAH as shown in Table II. For each retention time window the ions 191, 217, and 218 are included for Sterane, Diterpane and Triterpane quantification, if requested by the client.

13.5 ProSep Injection Port Parameters for Large Volume Injections (LVI)

ProSep Parameter*	Setting*
Injector Temp:	60 - 300 °C
Initial Hold Time:	30 sec. - 3 minutes
Flow Rate:	0.5 - 5.0 mL / minute
Purge:	0.5- 5.0 mL / minute, ON at desired time
Injection Volume:	1uL - 50uL

* = The settings listed may vary from project to project, based on client specific DQOs. *Injection temperature, hold time, flow rate, purge time and injection volume can effect chromatographic resolution and detection limits.* All parameters listed above can be set within the above setting ranges. Only a trained and experienced mass spectrometrist has the authority to change any setting. All standards and samples must be acquired using the same set of parameters. If any parameters are changed, a new initial calibration must be analyzed and accepted before any samples can be analyzed.

13.6 Data Acquisition Parameters

13.6.1 SIM Windows must be set up that bracket the expected retention times for each target analyte. These windows include the quantitation (primary) and confirmation ions for each parent PAH and Alkyl homolog group. To establish the expected retention time widow ranges, the mid-level calibration standard must be analyzed in full scan mode. The resulting full scan analysis will dictate the windows in which the selected ions will be monitored. The table below lists the windows and the ions that are monitored within each window. Depending upon the length of the analytical GC column, the time each window is selectively monitored may vary. The retention time windows must be shifted accordingly, when instrument maintenance is performed, (*i.e.,* the column is clipped).

Window Number	Selected Ions Monitored
# 1	136, 128, 180, 162, 217, 138, 152, 134, 127, 218, 96, 166, 148, 191, 192
# 2	142, 156, 180, 162, 218, 152, 141, 155, 166, 191, 192, 194, 176, 148, 217, 150
# 3	164, 162, 168, 194, 184, 154, 153, 139, 170, 183, 156, 155, 152, 169, 176, 180, 218, 191, 192, 217, 182
# 4	174, 155, 184, 179, 217, 182, 176, 166, 183, 165, 218, 196, 170, 169, 180, 191, 192
# 5	188, 179, 194, 198, 139, 196, 184, 183, 195, 191, 217, 210, 178, 180, 208, 192, 218, 167
# 6	191, 194, 198, 206, 234, 101, 240, 211, 192, 195, 212, 207, 235, 217, 210, 202, 208, 226, 220, 216, 218, 234
# 7	240, 220, 230, 236, 217, 240, 258, 189, 226, 234, 244, 229, 218, 315, 248, 149, 228, 216, 242, 191, 192, 330, 262, 167
# 8	264, 244, 256, 260, 217, 221, 276, 262, 252, 240, 270, 229, 218, 357, 258, 253, 242, 284, 191, 192, 372, 248
# 9	276, 139, 284, 218, 138, 277, 191, 192, 278, 270, 217

13.6.2 The "dwell" time for each window should be set to 30, and the resolution should be set to "high".

13.7 Initial Calibration

13.7.1 Before analysis of sample extracts, establish a multi-point response factor calibration curve showing the linear range of the analysis for all target analytes in Table IIA and IIB. Use standard concentrations of 10, 25, 250, 500, 1250, and 5000, ng/mL to construct the curve. See Section 10.15 for the preparation of the standard solutions for the initial calibration curve.

13.7.2 Construct an analytical sequence using the HP Enviroquant software:

- Click on the "Instrument" icon to open the Chem Station
- Go into the "GC/MS Top Environmental" screen
- Go into "Sequence"
- Edit the "Sample Table Log" by entering the "Vial" number starting at position 1, the "Data File ID" (for the initial calibration curve the nomenclature is "I" for initial calibration "2" for instrument number 2, the date, and the standard number "01, 02, etc." such as, I2060501, I2060502, etc.), the acquisition method (such as, ALKPAH0605.m, which indicates the type of method and the date the method was created), and finally the "Sample Name" (such as, "Alk-PAH 10ng/mL", for the first standard concentration level, etc.). When complete, click "OK".
- Go back into "Sequence" and "Save" the sequence as the date, such as, S060501.s. The ending "01" indicates the first sequence created on 06/05.
- Go back in to "Sequence" and "Print" the sequence that was just saved. This will become part of the instrument run log. See Section 15.0 for additional instrument run log details.
- Go back into "Sequence" and "Load and Run" the sequence that was just saved.

An example initial calibration sequence, created on 06/05, follows:

I2060501 (10 ng/mL standard)
I2060502 (25 ng/mL standard)
I2060503 (250 ng/mL standard)
I2060504 (500 ng/mL standard)
I2060505 (1250 ng/mL standard)
I2060506 (5000 ng/mL standard)
A2060501 (Alaska North Slope Crude Reference Oil)
Q2060501 (IRM 1491)
B2060501 (rinse blank)

13.7.3 When the sequence has finished running, the Enviroquant software will generate "Not Reviewed" quantitation reports. All reports must be "Quant Reviewed" before they can become part of the initial calibration acquisition method for sample analysis.

- Enter into the "Environmental Data Analysis" (off-line) screen.

- Go to "File" and under method, select the method (ALKPAH0605.m) that the initial calibration standards were analyzed under, then select the first data file.
- Go into "Quant" and select "QEdit Quant Results" to process the data files. See Section 15.0 for manual integration details and processing of Alkylated PAH standards.
- When processing is complete for the first standard, "Save" the changes and "Exit". Re-print the re-processed data file by "Generating Quant Report", and save the hard copy for each level of the initial calibration.
- Repeat these steps for all initial calibration standards analyzed within the sequence.
- When all levels have been processed, go into "IntiCal", and select "Update Levels", and enter all levels for the initial calibration at the proper concentrations. Note: The C_1 - C_4 Alkyl homolog group responses *must be hand entered* into the calibration curve using the responses of the parent PAHs. For a *mixed* Alkyl homolog series, assign the alkylated phenanthrenes/anthracenes the response of phenanthrene, and the alkylated fluoranthenes/pyrenes the response of pyrene.
- After all responses are entered, "Save" the completed method and print the resulting response factor summary by selecting "Response Factors to Printer".
- Additionally, the response for 5B(H)cholane *must be hand entered* into the calibration curve for quantitation of all Steranes, Diterpanes and Triterpanes listed in Table IB. When all of these have been entered, "Save" this completed method (as S&T0605.m, for example) and print the resulting response factor summary by selecting "Response Factors to Printer".
- Acceptance Criteria: 30% RSD for all target compounds. All calibration standards must be analyzed within 12-18 hours.

13.7.4 If using fewer than six calibration solutions in the initial calibration, standards must only be excluded from either extreme. That is, the 10 ng/mL or the 5,000 ng/mL solutions may be dropped to generate a five-level initial calibration. However, an intermediate-level calibration standard must not be dropped to convert a failing six-level initial calibration curve into a passing five-level initial calibration curve. Reduction in the number of calibration standards must also reduce the linear dynamic range used to quantify analytes in samples. The resulting average response factor for each target analyte in the initial calibration curve will be used by the computer software to calculate actual sample concentrations. See Section 15.0 for additional calculation details.

13.7.5 The following *corrective actions* are recommended for failing initial calibrations:

- Perform instrument maintenance and repeat the initial calibration, OR,
- Qualify all results reported for the analyte failing in the initial calibration, including all alkylated compounds quantified using the suspect average response, and any non-detects. If the failure of the suspect average response

appears related to a loss in MS sensitivity, instrument maintenance and repeat the initial calibration curve must be performed.

The choice of corrective action must be made in consultation with the Section Head, QA Manager, Project Manager and/or the client. The reasoning for choosing the second option must be documented in the project narrative to the client.

13.7.6 Complete the initial calibration by filling out the *Initial Calibration Checklist*. An example of the checklist can be found in Section 23.0. The initial calibration, along with any corresponding continuing calibration data and sample data, is then forwarded for secondary review.

13.8 Initial Calibration Verification - ICV (IRM 1491)

13.8.1 The analysis of IRM 1491 must follow the initial calibration curve. All PAH's in this verification standard are at a certified concentrations. See the corresponding *Certificate of Analysis* for the true value of each PAH. **Note:** If this standard was analyzed immediately following the initial calibration curve, it must be re-"Calculated and Generated" in the "Qedit" field, against the completed initial calibration curve method and then re-processed, before it can be reviewed for acceptability.

After final processing, calculate the percent recovery of each PAH by using the following calculation:

% Recovery = Found Amount / True Value x 100

Acceptance Criteria: All recoveries must be +/- 20% of the true values. (**Note**: the *total* of the Benzo(b&k)fluoranthene pair is used for evaluation).

13.9 Alaska North Slope Crude Reference Oil (ANS)

13.9.1 The ANS crude oil reference standard is analyzed following each initial calibration curve. Analysis of this reference oil is to establish the integration patters of the Alkyl PAH homolog groups, and to establish the current instrument quantitation and confirmation ion ratios. Analysis of this standard following the initial calibration ensures the retention time windows in the SIM mode of acquisition have been set up properly.

13.9.2 The analysis of the ANS standard is for reference and is subject to the acceptance criteria below. The ANS reference standard does not need to be analyzed daily, or prior to the analysis of samples, under this SOP. However, if instrument maintenance is performed, such as removing a significant section of the analytical column consisting of one "loop" or more, this will result in a retention time shift

that may effect the SIM acquisition windows. Even if the response of the parent PAH's are acceptable after this type of instrument maintenance, and an initial calibration does not need to be repeated, the ANS must be analyzed to update and/or confirm the SIM acquisition windows.

Alaska North Slope Crude – Monitored Analytes and Ratios for Acceptance

Analyte/Ratio	D2/P2	D3/P3	D2/C2	D3/C3	DEC3/ P3	S-Nap/ S-DBT	Naph	DBT	Phen	Chry	C30H52	Total
Accpt. Range	0.83-1.11	0.83-1.45	3.21-8.45	3.31-8.15	1.29-2.65	2.24-3.58	414-987	145-265	183-336	34-52	71-555	7840-16184

The above acceptance ranges are based on control charting. The following defines the monitored analytes:

D2/P2 = C2-Dibenzothiophenes/C2-Phenanthrene Anthracenes expressed as a ratio
D3/P3 = C3-Dibenzothiophenes/C3-Phenanthrene Anthracenes expressed as a ratio
D2/C2 = C2-Dibenzothiophenes/C2-Chrysenes expressed as a ratio
D3/C3 = C3-Dibenzothiophenes/C3-Chrysenes expressed as a ratio
DEC3/P3 = C3-Decalins/C3-Phenanthrene Anthracenes expressed as a ratio
S-Nap/S-DBT = The sum of C1 through C4-Naphthalenes/ The sum of C1 through C4-Dibenzothiophenes expressed as a ratio
Naph = Naphthalene result (calculated concentration)
DBT = Dibenzothiophene result (calculated concentration)
Phen = Phenanthrene result (calculated concentration)
Chry = Chrysene result (calculated concentration)
C30H52 = 17a(H),21B(H)-hopane result (calculated concentration)
Total = Total PAH result (calculated concentration)

13.9.3 The ANS reference standard is processed against the completed initial calibration curve method, as with the IRM, Section 13.8.1, above. See Section 15.2 for information regarding manual integration of the Alkyl PAH homolog clusters. Once all Alkyl PAH homolog clusters have been integrated, print a "detailed" report for this standard. The hardcopy of this standard will be used for reference when processing field samples for this method, until such a time that a new ANS standard needs to be analyzed.

14.0 Procedure

14.1 Daily PFTBA Tuning is not required. See Section 13.1 for details.

14.2 Evaluate the DFTPP tune as described in Section 13.2, if required.

14.3 Continuing Calibration Verification

A continuing calibration verification (CCV) standard, at the concentration of the mid-level of the initial calibration curve, must be analyzed at the beginning and end of every analytical sequence, and every 12-18 hours within the sequence, to confirm instrument stability, via response factor, for each calibrated PAH.

14.3.1 After successful analysis of the DFTPP tune, "Edit" the "Sample Table Log" to include the 500 ng/mL CCV standard (C2060501, where "C" is for CCV, "2" is for instrument number 2, followed by the date, and "01" for the first CCV analyzed this day), and acquire the CCV against the correct initial calibration method. "Save", then "Load and Run" the sequence, as in Section 13.6.2.

14.3.2 When the sequence has finished running, the Enviroquant software will generate a "Not Reviewed" quantitation report. All reports must be "Quant Reviewed" against the acquisition method for sample analysis.

- Enter into the "Environmental Data Analysis" (off-line) screen.
- Go to "File" and under method, select the method that the CCV was analyzed under, then select the CCV data file.
- Go into "Quant" and select "QEdit Quant Results" to process the CCV file. See Section 15.0 for manual integration details and processing of Alkylated PAH standards. **Note:** The Alkyl homolog groups may be deleted from the report. Only the parent PAH compounds are monitored for %D and the following acceptance criteria.
- When processing is complete, go into "ConCal", and select "Evaluate Data File as Continuing Calibration".

14.3.3 Acceptance Criteria: Compare the CCV resulting response against the average response for the initial calibration for each calibrated PAH, and calculate the % difference (%D). See Section 15.0 for the calculations. The %D for each calibrated PAH must be below 30%. If multiple CCVs are analyzed within an analytical sequence, each CCV must be analyzed within 12-18 hours of the previous CCV and each CCV, including the ending CCV must meet the acceptance criteria.

- If the CCV meets the acceptance criteria, save the hard copy for each CCV standard and include it with the *Continuing Calibration Checklist*. An example of the checklist can be found in Section 23.0.
- Go back into "ConCal" and select "Update Continuing Calibration" and save the method updated to the opening CCV of the day.

14.3.4 If the CCV does not meet the 30%D criteria for each calibrated PAH, the following *corrective actions* are recommended:

- Perform instrument maintenance and repeat the initial calibration, and re-analyze all affected samples, OR,

- Qualify all results reported for the failing CCV with a "J" qualifier, including all alkylated compounds quantified using the suspect response, and any non-detects. If the failure of the suspect response appears related to a loss in MS sensitivity, instrument maintenance and repeat analysis of the initial calibration curve, and all affected samples, must be performed.

The choice of corrective action must be made in consultation with the Section Head, QA Manager, Project Manager and/or the client. The reasoning for choosing the second option must be documented in the project narrative to the client.

14.4 Daily Analytical Sequence

14.4.1 Samples are prioritized for analysis by the Organic Section Head or GC/MS Group Leader based on client due date and sample analytical hold time. Samples are retrieved from the sample storage refrigerator, spiked with 20uL of the internal standard solution from Section 10.10, and loaded into the instrument autosampler trays following the generalized sequence below.

Tune – (T2060501 at 50 ng/mL, if required by the project QAP)
CCV – (C2060501 at 500 ng/mL)
Method Blank – (ID from sample preparation batch)
LCS – (ID from sample preparation batch)
SRM – (ID from sample preparation batch)
Samples (up to 12-18 hours of analytical time)
CCV – (C2060502 at 500 ng/mL)
Samples (up to 12-18 hours of analytical time)
CCV – (C2060503 at 500 ng/mL)

14.4.2 Samples are processed from "Not Reviewed" data files, to "Quant Reviewed" data files in a similar way the standards were previously processed. See Section 15.0 for details on sample processing. If a CCV fails the criteria outlined in Section 14.3.3, all samples since the last acceptable CCV must be re-analyzed.

14.4.3 If the on-column concentration of any PAH compound exceeds the calibration range of 5000 ng/mL, the sample must be diluted, re-spiked with the appropriate amount of internal standard and re-analyzed. Assuming all samples are at a 1mL final volume, the following example dilutions would apply. Adjust the volumes accordingly for other sample final volume amounts.

1:2 dilution = 500uL of sample : 500uL CH_3Cl_2 and 10uL of IS
1:4 dilution = 250uL of sample : 750uL CH_3Cl_2 and 15uL of IS
1:5 dilution = 200uL of sample : 800uL CH_3Cl_2 and 16uL of IS
1:10 dilution = 100uL of sample : 900uL CH_3Cl_2 and 18uL of IS, etc.

15.0 Data Evaluation, Data Reporting and Calculations

15.1 After sample analysis, "Not Reviewed" quantitation reports are generated by the software system. It is expected that situations will arise when the automated quantitation procedures of the chromatographic software provide inappropriate quantitations or integrations. This normally occurs when there is compound co-elution, baseline noise or matrix interference with the priority pollutant PAH compounds. However, with *alkylated* PAH homolog groups, a range or cluster of peaks, is evaluated and manual integration must be performed for each PAH homolog group or cluster.

15.2 Identification of the priority pollutant PAH compounds is based on gas chromatographic relative retention times (RRTs) from the analysis of the mid-level initial calibration standard. For these compounds, manual quantitations are performed, if necessary, by integrating the area of the quantitation ion or peak. For *alkylated* PAHs, the homolog groupings (*i.e.,* C_3- Naphthalenes) appear in the extracted ion current profiles (EICPs) as a cluster of isomers. Establish the pattern of each cluster, and the retention time window for the cluster, by analysis of the reference crude oil, Alaska North Slope (ANS) Crude. Integrate peaks within the cluster by straight-line integration to the baseline, taking into account background noise in the EICPs. See the most recently generated "detailed" Alkylated PAH reference spectrum hardcopy, that is based on the most recent analysis of the Alaska North Slope Crude Oil, for a cluster by cluster example of each integration for each alkylated PAH homolog group. Table III, in Section 23.0, lists the representative ion(s) used for quantitation and confirmation of each parent PAH and alkylated PAH homolog group.

Note: Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system.

15.3 From EICP of the quantification (primary) mass ions and the confirmatory mass ions, identify all target analytes according to the following criteria:

- The characteristic masses of each analyte of interest should maximize in the same, or within one scan of each other.

- The retention time should fall within $\pm$ 10 seconds of the retention time of the parent PAH from the preceding CCV. **Note:** When evaluating alkyl homolog groups, the retention time of the most intense peak within the group may not have the exact retention time of the most intense peak in the ANS reference standard. Analyst judgement and referral to each Homolog groups' retention time window is essential for identification. Apply analyst judgment regarding corrective action when this criteria is not met.

- The relative peak heights of the primary ion compared to the confirmation or secondary ion masses for parent compounds should fall within $\pm$ 50 percent of the

relative intensities of these masses in a the reference mass spectrum (*i.e.,* the mid-level of the initial calibration curve and/or the Alaska North Slope Crude Oil).

Note: The relative intensities of the primary and secondary ions may vary widely within a given group of alkyl homologs (*i.e.,* C_3 - Naphthalenes). Thus, the pattern of each alkyl homolog cluster, and the retention time window for the cluster, will be the primary identification criteria for alkyl homologs. In some instances, a parent compound that does not meet secondary ion confirmation criteria may still be determined to be present in a sample after close inspection of the data by the experienced mass spectrometrist. Supportive data includes the presence of the secondary ion, but ratio value greater than $\pm$ 50 percent of the primary ion, which may be caused by an interference of the secondary ion.

15.4 In instances where manual integration has been performed, the analyst must identify such edits or manual procedures by initialing and dating the changes made to the quantitation report. The revised hard copy, printed as a "detailed" report, displaying the manual integration, including an "m" qualifier next to the modified or manually integrated compound(s), shall be included in the raw data for secondary review. These requirements apply to all standards, QC samples, field samples and blanks.

15.5 To calculate the ***Relative Standard Deviation*** (RSD) of all target analytes and surrogate compounds for the initial calibration use the formula below. The RSD of each target compound and surrogate must be below 30%. Additionally, use the initial six-point calibration to determine ***Relative Response Factors*** (RRF_Is) at each concentration level. Average the RRF_Is, to generate mean RRF_Is, for quantification of all target analytes and surrogate compounds. The RRF_Is are based on the internal standard compounds, and are calculated using the formula below. (The relative response factors for the continuing calibration verifications (RRF_Cs) are calculated using the same formula). See Section 23.0, Table II, for the listing of target compounds and their associated internal standards for quantification.

$$\mathbf{RSD = SD \ / \ mean\ RRF_I \ x \ 100}$$

where:

SD = Standard deviation between the five points, for that target analyte.

$$\mathbf{RRF_I = (A_c \ x \ C_{IS}) \ / \ (A_{IS} \ x \ C_c)}$$

where:

A_c = Area of the characteristic ion for the standard compound to be measured.
A_{IS} = Area of the characteristic ion for the representative internal standard compound.
C_{IS} = Concentration of the representative internal standard compound (ng/mL).
C_c = Concentration of the standard compound to be measured (ng/mL).

Note: Assign the response factor of the parent compound to the alkyl homolog cluster, unless using an authentic representative isomer(s) for each level of alkylation.

15.6 Based on the mean RRF_Is, calculate the ***Sample Extract Amount*** for each target analyte and surrogate in the extracts using the following formula:

$$\mathbf{Q_e = (A_a \times Q_{IS}) / (A_{IS} \times RRF_I)}$$

where:

Q_e = Sample extract amount (ng) of target analyte, from quantitation report.
A_a = Area of the characteristic ion for the target analyte.
A_{IS} = Area of the characteristic ion for the representative internal standard compound.
Q_{IS} = Amount of internal standard compound added to each extract (ng).

15.7 Calculate the ***Sample Concentration*** (C) for each compound by the following formula:

$$\mathbf{C = (Q_e / V_s) \times DF}$$

where:

C = Concentration in sample (ng/L water, ug/Kg sediment/tissue, or mg/Kg product).
V_s = Original volume or weight of sample extracted.
DF = Dilution factor or fraction of the original extract to which internal standard added.

Report alkyl homologs as total C_1, total C_2, total C_3 and total C_4.

15.8 If the response of any target compound in a sample exceeds the linear response range, as defined by the initial calibration standards in Section 13.0, dilute the extract so that the concentrations of all target compounds fall within the range of the calibration curve. If the response of any target compound in a sample exceeds the MDL but is below the reporting limit (RL), qualify the reported concentration with a "J". If any target compound is found in the method blank and in the associated sample(s), qualify the reported concentration with a "B".

15.9 Calculate the ***Surrogate Recoveries*** relative to the internal standards by the following formula:

$$\mathbf{\%R_{sc} = (A_{sc} / A_{is}) \times (Q_{is} / Q_{sc}) \times (100 / RRF_{sc}) \times DF}$$

where:

Q_{is} = Amount of the representative internal standard (ng).
DF = Dilution factor or fraction of the original extract.

15.10 If ***Surrogate Recovery Correction*** is required, apply the following formula:

$$\mathbf{C / \%R_{SC} = C_{RC}}$$

where:

C = Concentration in sample (ng/L water or ug/Kg sediment/tissue, from 15.7, above).
$\%R_{SC}$ = Surrogate recovery as a decimal amount (*i.e.,* 93.2% recovery as 0.932).
C_{RC} = Concentration in sample, recovery corrected.

15.11 Compare response factors for each compound in the ***Continuing Calibration Verification*** (CCV), to those of the initial calibration curve by determining the percent difference.

$$\textbf{Percent Difference (\%D)} = ([RRF_I - RRF_C] / RRF_I) \times 100$$

where:

RRF_I = Mean response factor from initial calibration.
RRF_C = Response factor from CCV.

15.12 All results must be reported to two significant figures. All solids including soils, sediments, and sludges must be reported on a dry-weight basis. Tissue results may be reported in wet-weight depending upon client request. Petroleum results are reported "as received" or on a wet-weight basis.

15.13 The primary analyst does data entry, or upload of the data, into the LIMS system. The LIMS is "linked" to the instrument, so the analyst must choose the sample(s) to be reported from that instrument's analytical sequence. All associated preparation and instrumental QC samples and dilutions are also chosen. Once the data/samples have been selected and "associated" with the proper QC samples, the batched data set is sent to print.

15.14 The laboratory generates two types of data packages from the LIMS: "Commercial" for routine projects, and "Full Deliverable" or "CLP-like" for fully data validated projects. A Commercial package consists of sample results and the associated method blank and LCS results. A Full Deliverable package includes all sample results, all preparation and instrumental QC results and the associated supporting raw data. Check the "Report Type" on the project folder to ensure all required deliverables are included. The checklists used for primary and secondary review of the analytical results can be found in Section 23.0. A secondary review is performed on all data.

15.15 Procedures for data and record management must adhere to the Quality Systems Manual, other subordinate documents covering record keeping, and the *Document Control* SOP,

G-016. All records shall be stored in such a manner as to be safe and accessible for at least 10 years.

15.16 Notebooks: Laboratory notebooks are designed to accommodate the specific analysis. Instrument printouts are used to document run sequences, and each daily sequence printout is filed in a three-ring notebook. Each page is numbered as it is generated each day the instrument is operated. If a sample requires re-analysis or re-extraction for any reason, a notation is made next to the sample entry on the sequence log. Requests for re-extraction are further documented in the "Request for Re-extraction" logbook. After one month of sample analysis, the sequence run log is permanently bound, assigned an internal ID number, and filed accordingly. Such files shall be archived so as to remain available for at least 10 years. All laboratory notebooks must follow the specifications in the *Laboratory Notebook Usage* SOP, G-009, and all record keeping and document control practices.

15.17 Electronic records: All data files from computers, attached to instruments, shall be backed up daily onto the proper directory on the server. The backups shall be stored so as to be accessible for 10 years. Movement of the data files to the server is the responsibility of the primary analyst. Server backup and storage is the responsibility of the IT department.

16.0 Method Performance

16.1 Initial Demonstration of Proficiency (IDP) is determined by every new analyst during training, and before actual sample analysis. The IDP consists of the preparation and/or analysis of four replicate samples spiked at approximately 10X the Alkylated PAH-SIM MDL. This process ensures the competency of the individual analysts

16.1.1 The following information needs to be supplied to the QA Manager for reporting and acceptance of the Alkylated PAH-SIM IDP: The *Training Checklist* must be completed by the trainer and the analyst, and supplied with all of the supporting raw data including, calibration standards, and method blanks in order to reconstruct and validate these analyses. The QA Manager will enter the information on to the individual employee spreadsheet. The following information is entered: preparation or analysis date, method name or number, blank ID, the four replicate file IDs, mean recovery, standard deviation and a comparison against the control limits, for precision and accuracy. The aqueous and solid limits for precision are 40%-140% recovery and for accuracy are 50%RPD.

16.1.2 If any parameter does not meet the control limits, the QA Manager will notify the Section Head and the analyst. The analyst must repeat the IDP until all criteria are met.

16.1.3 Upon successful completion of the IDP, *The IDP Certification Statement* form will be completed by the analyst, and signed-off by the Laboratory Director and

the QA Manager. All of the above information will be retained in the employee-training file kept by the QA Manager.

17.0 Pollution Prevention

See Section 21.0, Waste Management for a discussion on Pollution Prevention.

18.0 Data Assessment and Acceptance Criteria

All Alkylated PAH-SIM results are reportable without qualification if analytical holding times are met, preservation (including cooler temperatures) are met, and all QC criteria defined in the table below are met. If any of the below QC parameters are not met, all associated samples must be evaluated for re-analysis. See Sections 12.0 and 13.0 for additional QC discussion including corrective actions for any QC outliers.

QC Parameter	Acceptance Criteria
Initial Calibration Curve	30% RSD for all target analytes with exception for 10% of target analytes to be >30%, but ≤ 40%
IRM 1491	+/- 20% recovery of the true values
Continuing Calibration Verification	Analyzed every 12-18 hours, ≤ 30%D for all target analytes with exception for 10% of target analytes to be >30%, but ≤ 40%
Method Blank	</= 5X the reporting limit
Laboratory Control Sample	40-140%R for all target analytes
Matrix Spike / Matrix Spike Duplicate	40-140%R for all target analytes, 50% RPD between the duplicates.
Sample / Sample Duplicate	50% RPD between the duplicates.
Surrogates	30% - 150% recovery
Internal Standards	50% - 200% of the daily CCV area for the Internal Standards
SRM	+/- 35% D or 65% - 135% recovery

19.0 Corrective Actions for Non-Compliant Data

Section 12.0, Quality Control, defines the corrective actions that must be taken in instances where QC outliers exist. If the corrective actions have been followed and the data is still unacceptable, reference Section 20.0 for guidance on reporting non-compliant data.

20.0 Contingencies for Handling Unacceptable Data

Section 18.0 outlines sample batch QC acceptance criteria. If non-compliant Alkylated PAH-SIM results are to be reported, the Section Head and/or the Laboratory Director, and the QA Manager must approve the reporting of these results. The laboratory Project Manager shall be notified, and may chose to relay the non-compliance to the client, for approval, or other

corrective action, such as re-sampling and re-analysis. The analyst or Section Head performing the secondary review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

21.0 Waste Management

The Woods Hole Group *Hazardous Waste and Sample Disposal* SOP (G-006), must be referenced for disposal of used standards, solvents, acids, reagents or other chemicals.

21.1 Once satisfactory Alkylated PAH-SIM results have been generated, the extracts are held for 30 days, or longer if specified by a client contract, then discarded into a 55-gallon drum labeled "Vial Waste".

22.0 References

References in addition to the analytical test methods listed in Section 1.0. Identification of Test Methods, used to create this SOP, include the following:

22.1 EPA/600/R-96/027, *Guidance for the Preparation of Standard Operating Procedures (SOPs) for Quality Related Documents*, 1996.

22.2 EPA, 40CFR, Part 136, Appendix B, 7/1997.

22.3 National Environmental Laboratory Accreditation Conference (NELAC) Standard, Chapter 5, 7/1999.

22.4 The Woods Hole Group Environmental Laboratory *Quality Systems Manual*, Rev. 2.0, 5/2001.

22.5 Smith, Roy-Keith, *Handbook of Environmental Analysis,* 4th Edition, 1999.

22.6 Evaluation of Dredged Materials Proposed for Discharge in Waters of the US-Testing Manual, US EPA & US Army Corps of Engineers, 2/98, Table 8-2.

23.0 Tables, Diagrams, Flowcharts and Data Validation

Table IA: Method Detection Limits (MDLs) and Reporting Limits (RLs) for PAH, Alkyl PAH, and Heterocyclic Target Compounds

Note: *MDLs and RLs are determined for each "parent" PAH only. RLs for Alkyl PAHs are based on the associated parent PAH.*

Aqueous:

Analyte	Spike Conc.	MDL	RL
Naphthalene	20 ng/L	2.09	10 ng/L
2-Methylnaphthalene	20 ng/L	1.49	10 ng/L
1-Methylnaphthalene	20 ng/L	1.29	10 ng/L
Biphenyl	20 ng/L	1.14	10 ng/L
2-Chloronaphthalene	20 ng/L	1.49	10 ng/L
2,6-Dimethylnaphthalene	20 ng/L	1.40	10 ng/L
Acenaphthylene	20 ng/L	2.10	10 ng/L
Acenaphthene	20 ng/L	1.50	10 ng/L
Dibenzofuran	20 ng/L	1.39	10 ng/L
Fluorene	20 ng/L	1.55	10 ng/L
2,3,5-Trimethylnaphthalene	20 ng/L	1.77	10 ng/L
Phenanthrene	20 ng/L	4.10	10 ng/L
Anthracene	20 ng/L	1.66	10 ng/L
1-Methylphenanthrene	20 ng/L	2.32	10 ng/L
Fluoranthene	20 ng/L	2.78	10 ng/L
Pyrene	20 ng/L	5.16	10 ng/L
Benzo[a]anthracene	20 ng/L	1.92	10 ng/L
Chrysene	20 ng/L	1.38	10 ng/L
Benzo[b]fluoranthene	20 ng/L	6.41	10 ng/L
Benzo[k]fluoranthene	20 ng/L	7.74	10 ng/L
Benzo[e]pyrene	20 ng/L	1.35	10 ng/L
Benzo[a]pyrene	20 ng/L	1.73	10 ng/L
Perylene	20 ng/L	1.19	10 ng/L
Indeno[1,2,3-cd]pyrene	20 ng/L	1.87	10 ng/L
Dibenz[a,h]anthracene	20 ng/L	2.46	10 ng/L
Benzo[g,h,i]perylene	20 ng/L	1.72	10 ng/L

Table IA (cont): Method Detection Limits (MDLs) and Reporting Limits (RLs) Soil/Sediment:

Analyte	Spike Conc.	MDL	RL
Naphthalene	2 ug/Kg	1.22	1 ug/Kg
2-Methylnaphthalene	2 ug/Kg	0.28	1 ug/Kg
1-Methylnaphthalene	2 ug/Kg	0.24	1 ug/Kg
Biphenyl	2 ug/Kg	0.16	1 ug/Kg
2-Chloronaphthalene	2 ug/Kg	0.26	1 ug/Kg
2,6-Dimethylnaphthalene	2 ug/Kg	0.26	1 ug/Kg
Acenaphthylene	2 ug/Kg	0.24	1 ug/Kg
Acenaphthene	2 ug/Kg	0.38	1 ug/Kg
Dibenzofuran	2 ug/Kg	0.26	1 ug/Kg
Fluorene	2 ug/Kg	0.26	1 ug/Kg
2,3,5-Trimethylnaphthalene	2 ug/Kg	0.26	1 ug/Kg
Phenanthrene	2 ug/Kg	0.29	1 ug/Kg
Anthracene	2 ug/Kg	0.27	1 ug/Kg
1-Methylphenanthrene	2 ug/Kg	0.30	1 ug/Kg
Fluoranthene	2 ug/Kg	0.34	1 ug/Kg
Pyrene	2 ug/Kg	0.30	1 ug/Kg
Benzo[a]anthracene	2 ug/Kg	0.28	1 ug/Kg
Chrysene	2 ug/Kg	0.23	1 ug/Kg
Benzo[b]fluoranthene	2 ug/Kg	0.37	1 ug/Kg
Benzo[k]fluoranthene	2 ug/Kg	0.27	1 ug/Kg
Benzo[e]pyrene	2 ug/Kg	0.29	1 ug/Kg
Benzo[a]pyrene	2 ug/Kg	0.31	1 ug/Kg
Perylene	2 ug/Kg	0.33	1 ug/Kg
Indeno[1,2,3-cd]pyrene	2 ug/Kg	0.22	1 ug/Kg
Dibenz[a,h]anthracene	2 ug/Kg	0.26	1 ug/Kg
Benzo[g,h,i]perylene	2 ug/Kg	0.95	1 ug/Kg

Note: The above Soil/Sediment MDL includes GPC cleanup.

Table IA (cont): Method Detection Limits (MDLs) and Reporting Limits (RLs) Tissue:

Analyte	Spike Conc.	MDL	RL
Naphthalene	4 ug/Kg	0.48	2 ug/Kg
2-Methylnaphthalene	4 ug/Kg	0.34	2 ug/Kg
1-Methylnaphthalene	4 ug/Kg	0.28	2 ug/Kg
Biphenyl	4 ug/Kg	0.22	2 ug/Kg
2-Chloronaphthalene	4 ug/Kg	0.26	2 ug/Kg
2,6-Dimethylnaphthalene	4 ug/Kg	0.25	2 ug/Kg
Acenaphthylene	4 ug/Kg	0.33	2 ug/Kg
Acenaphthene	4 ug/Kg	0.37	2 ug/Kg
Dibenzofuran	4 ug/Kg	0.36	2 ug/Kg
Fluorene	4 ug/Kg	0.66	2 ug/Kg
2,3,5-Trimethylnaphthalene	4 ug/Kg	0.32	2 ug/Kg
Phenanthrene	4 ug/Kg	0.79	2 ug/Kg
Anthracene	4 ug/Kg	0.77	2 ug/Kg
1-Methylphenanthrene	4 ug/Kg	0.76	2 ug/Kg
Fluoranthene	4 ug/Kg	0.76	2 ug/Kg
Pyrene	4 ug/Kg	0.51	2 ug/Kg
Benzo[a]anthracene	4 ug/Kg	0.46	2 ug/Kg
Chrysene	4 ug/Kg	0.70	2 ug/Kg
Benzo[b]fluoranthene	4 ug/Kg	0.38	2 ug/Kg
Benzo[k]fluoranthene	4 ug/Kg	0.58	2 ug/Kg
Benzo[e]pyrene	4 ug/Kg	0.59	2 ug/Kg
Benzo[a]pyrene	4 ug/Kg	0.57	2 ug/Kg
Perylene	4 ug/Kg	0.53	2 ug/Kg
Indeno[1,2,3-cd]pyrene	4 ug/Kg	0.45	2 ug/Kg
Dibenz[a,h]anthracene	4 ug/Kg	0.40	2 ug/Kg
Benzo[g,h,i]perylene	4 ug/Kg	0.50	2 ug/Kg

Note: The above Tissue MDL includes Silica cleanup.

Table IB: Reporting Limits for Steranes, Diterpanes and Triterpanes

Note: *MDLs are NOT analyzed for the Steranes, Diterpanes and Triterpanes listed in the table below. The RLs for Steranes, Diterpanes and Triterpanes are assumed from the PAHs above, for the same matrices,*

Analyte	Aqueous RL	Soil/Sediment RL	Tissue RL
5a,14B,17B-pregnane	10 ng/L	1 ug/Kg	2 ug/Kg
5a,14B,17B,20-methylpregnane	10 ng/L	1 ug/Kg	2 ug/Kg
13B,17a-diachloestane(20S)	10 ng/L	1 ug/Kg	2 ug/Kg
13B,17a-diachloestane(20R)	10 ng/L	1 ug/Kg	2 ug/Kg
5a,14B,17B-chloestane(20R)	10 ng/L	1 ug/Kg	2 ug/Kg
5a,14B,17B-chloestane(20S)	10 ng/L	1 ug/Kg	2 ug/Kg
5a,14B,17B,24-methylcholestane(20R)	10 ng/L	1 ug/Kg	2 ug/Kg
5a,14B,17B,24-methylcholestane(20S)	10 ng/L	1 ug/Kg	2 ug/Kg
5a,14a,17a,24-ethylcholestane(20S)	10 ng/L	1 ug/Kg	2 ug/Kg
5a,14B,17B,24-ethylcholestane(20R)	10 ng/L	1 ug/Kg	2 ug/Kg
5a,14B,17B,24-ethylcholestane(20S)	10 ng/L	1 ug/Kg	2 ug/Kg
5a,14a,17a,24-ethylcholestane(20R)	10 ng/L	1 ug/Kg	2 ug/Kg
C20 Diterpane	10 ng/L	1 ug/Kg	2 ug/Kg
C21 Diterpane	10 ng/L	1 ug/Kg	2 ug/Kg
C22 Diterpane	10 ng/L	1 ug/Kg	2 ug/Kg
C23 Diterpane	10 ng/L	1 ug/Kg	2 ug/Kg
C24 Diterpane	10 ng/L	1 ug/Kg	2 ug/Kg
C25 Diterpane	10 ng/L	1 ug/Kg	2 ug/Kg
C24 Tetracyclic Terpane	10 ng/L	1 ug/Kg	2 ug/Kg
C26 Tetracyclic Terpane (1)	10 ng/L	1 ug/Kg	2 ug/Kg
C26 Tetracyclic Terpane (2)	10 ng/L	1 ug/Kg	2 ug/Kg
C28 Tetracyclic Terpane (1)	10 ng/L	1 ug/Kg	2 ug/Kg
C28 Tetracyclic Terpane (2)	10 ng/L	1 ug/Kg	2 ug/Kg
C29 Tetracyclic Terpane (1)	10 ng/L	1 ug/Kg	2 ug/Kg
C29 Tetracyclic Terpane (2)	10 ng/L	1 ug/Kg	2 ug/Kg
18a(H)-22,29,30-trisnorhopane(Ts)	10 ng/L	1 ug/Kg	2 ug/Kg
17a(H)-22,29,30-trisnorhopane(Tm)	10 ng/L	1 ug/Kg	2 ug/Kg
17B(H)-22,29,30-trisnorhopane	10 ng/L	1 ug/Kg	2 ug/Kg
17a(H),21B(H)-22,29,30-bisnorhopane	10 ng/L	1 ug/Kg	2 ug/Kg
17a(H),21B(H)-30-norhopane	10 ng/L	1 ug/Kg	2 ug/Kg
18a(H)-30-Neonorhopane	10 ng/L	1 ug/Kg	2 ug/Kg
17B(H),21a(H)-normoretane	10 ng/L	1 ug/Kg	2 ug/Kg
18a(H)-oleanane	10 ng/L	1 ug/Kg	2 ug/Kg
17a(H),21B(H)-hopane-C30H52	10 ng/L	1 ug/Kg	2 ug/Kg
17B(H),21a(H)-moretane	10 ng/L	1 ug/Kg	2 ug/Kg
22S-17a(H),21B(H)-30-homohopane	10 ng/L	1 ug/Kg	2 ug/Kg

Analyte	Aqueous RL	Soil/Sediment RL	Tissue RL
22R-17a(H),21B(H)-30-homohopane	10 ng/L	1 ug/Kg	2 ug/Kg
17B(H),21B(H)-hopane	10 ng/L	1 ug/Kg	2 ug/Kg
17B(H),21a(H)-homomoretane	10 ng/L	1 ug/Kg	2 ug/Kg
Hop-22(29)-ene(diploptene)	10 ng/L	1 ug/Kg	2 ug/Kg
22S-17a(H),21B(H)-30-bishomohopane	10 ng/L	1 ug/Kg	2 ug/Kg
22R-17a(H),21B(H)-30-bishomohopane	10 ng/L	1 ug/Kg	2 ug/Kg
17B(H),21a(H)-bishomohopane	10 ng/L	1 ug/Kg	2 ug/Kg
17B(H),21B(H)-30-homohopane	10 ng/L	1 ug/Kg	2 ug/Kg
22S-17a(H),21B(H)-trishomohopane	10 ng/L	1 ug/Kg	2 ug/Kg
22R-17a(H),21B(H)-trishomohopane	10 ng/L	1 ug/Kg	2 ug/Kg
22S-17a(H),21B(H)-tetrakishomohopane	10 ng/L	1 ug/Kg	2 ug/Kg
22R-17a(H),21B(H)-tetrakishomohopane	10 ng/L	1 ug/Kg	2 ug/Kg
22S-17a(H),21B(H)-pentakishomohopane	10 ng/L	1 ug/Kg	2 ug/Kg
22R-17a(H),21B(H)-pentakishomohopane	10 ng/L	1 ug/Kg	2 ug/Kg

Table IIA: PAH, Alkyl PAH, and Heterocyclic Target Compounds

Compound	Surrogate and IS Reference	Compound	Surrogate and IS Reference
Decalin	3,A	Naphthobenzothiophene	3,B
C_1-Decalins	3,A	C_1-Naphthobenzothiophene	3,B
C_2-Decalins	3,A	C_2-Naphthobenzothiophene	3,B
C_3-Decalins	3,A	C_3-Naphthobenzothiophene	3,B
C_4-Decalins	3,A	Benzo[a]anthracene	3,B
Naphthalene	3,A	Chrysene	3,B
C_1-Naphthalenes	3,A	C_1-Chrysenes	3,B
C_2-Naphthalenes	3,A	C_2-Chrysenes	3,B
C_3-Naphthalenes	3,A	C_3-Chrysenes	3,B
C_4-Naphthalenes	3,A	C_4-Chrysenes	3,B
2-Methlynaphthalene	3,A	Benzo[b]fluoranthene	3,B
1-Methlynaphthalene	3,A	Benzo[k]fluoranthene	3,B
Acenaphthylene	3,A	Benzo[e]pyrene	3,B
Acenaphthene	3,A	Benzo[a]pyrene	3,B
Biphenyl	3,A	Perylene	3,B
Benzothiophene	3,A	Indeno[1,2,3-c,d]pyrene	3,B
2,6-Dimethylnaphthalene	3,A	Dibenz[a,h]anthracene	3,B
Dibenzofuran	3,A	Benzo[g,h,i]perylene	3,B
2,3,5-Trimethylnaphthalene	3,A		
Fluorene	3,A	Biomarker Compounds	
C_1-Fluorenes	3,A	17a(H),21B(H) – hopane	3,A
C_2-Fluorenes	3,A	5B(H) - cholane	3,A

Compound	Surrogate and IS Reference	Compound	Surrogate and IS Reference
C_3-Fluorenes	3,A		
Dibenzothiophene	3,A	Recovery Corrected	
C_1-Dibenzothiophenes	3,A	Surrogate Compounds	
C_2-Dibenzothiophenes	3,A	Naphthalene-d_8	1,A
C_3-Dibenzothiophenes	3,A	Acenaphthene-d_{10}	2,A
C_4-Dibenzothiophenes	3,A	Phenanthrene-d_{10}	3,A
Phenanthrene	3,A	Chrysene-d_{12}	4,B
Anthracene	3,A		
C_1-Phenanthrenes/Anthracenes	3,A	Surrogate Compounds	
C_2-Phenanthrenes/Anthracenes	3,A	2-Methylnaphthalene-d_{10}	5,A
C_3-Phenanthrenes/Anthracenes	3,A	Pyrene-d_{10}	6,B
C_4-Phenanthrenes/Anthracenes	3,A	Benzo(b)fluoranthene-d_{12}	7,B
1-Methylphenanthrene	3,A		
Carbazole	3,A	Internal Standards	
Fluoranthene	3,B	Fluorene-d_{10}	A
Pyrene	3,B	Benzo(a)pyrene-d_{12}	B
C_1-Fluoranthrenes/Pyrenes	3,B		
C_2-Fluoranthrenes/Pyrenes	3,B		
C_3-Fluoranthrenes/Pyrenes	3,B		
C_4-Fluoranthrenes/Pyrenes	3,B		

Note: Alkylated phenanthrenes and anthracenes, and alkylated fluoranthenes and pyrenes are quantified together as total alkylated phenanthrene/anthracenes (using the phenanthrene parent response factor) and total alkylated fluoranthenes/pyrenes (using the pyrene parent response factor).

Table IIB: Sterane, Diterpane and Triterpane Target Compounds

Compound	Surrogate and IS Reference
5a,14B,17B-pregnane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
5a,14B,17B,20-methylpregnane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
13B,17a-diachloestane(20S)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
13B,17a-diachloestane(20R)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
5a,14B,17B-chloestane(20R)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
5a,14B,17B-chloestane(20S)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
5a,14B,17B,24-methylcholestane(20R)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
5a,14B,17B,24-methylcholestane(20S)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
5a,14a,17a,24-ethylcholestane(20S)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
5a,14B,17B,24-ethylcholestane(20R)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
5a,14B,17B,24-ethylcholestane(20S)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)

Compound	Surrogate and IS Reference
5a,14a,17a,24-ethylcholestane(20R)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C20 Diterpane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C21 Diterpane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C22 Diterpane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C23 Diterpane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C24 Diterpane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C25 Diterpane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C24 Tetracyclic Terpane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C26 Tetracyclic Terpane (1)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C26 Tetracyclic Terpane (2)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C28 Tetracyclic Terpane (1)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C28 Tetracyclic Terpane (2)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C29 Tetracyclic Terpane (1)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
C29 Tetracyclic Terpane (2)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
18a(H)-22,29,30-trisnorhopane(Ts)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
17a(H)-22,29,30-trisnorhopane(Tm)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
17B(H)-22,29,30-trisnorhopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
17a(H),21B(H)-22,29,30-bisnorhopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
17a(H),21B(H)-30-norhopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
18a(H)-30-Neonorhopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
17B(H),21a(H)-normoretane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
18a(H)-oleanane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
17a(H),21B(H)-hopane-C30H52	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
17B(H),21a(H)-moretane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
22S-17a(H),21B(H)-30-homohopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
22R-17a(H),21B(H)-30-homohopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
17B(H),21B(H)-hopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
17B(H),21a(H)-homomoretane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
Hop-22(29)-ene(diploptene)	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
22S-17a(H),21B(H)-30-bishomohopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
22R-17a(H),21B(H)-30-bishomohopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
17B(H),21a(H)-bishomohopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
17B(H),21B(H)-30-homohopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
22S-17a(H),21B(H)-trishomohopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
22R-17a(H),21B(H)-trishomohopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
22S-17a(H),21B(H)-tetrakishomohopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
22R-17a(H),21B(H)-tetrakishomohopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
22S-17a(H),21B(H)-pentakishomohopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)
22R-17a(H),21B(H)-pentakishomohopane	5B(H)-cholane (Surr) / Fluorene-d_{10} (IS)

Table IIIA: PAH, Alkyl PAH and Sterane, Diterpane and Triterpane Quantification (Primary) and Confirmation Ions

Compound	Quantification & Confirmation Ions	Compound	Quantification & Confirmation Ions
Decalin	138, 96	Naphthobenzothiophene	234, 189
C_1-Decalins	152	C_1-Naphthobenzothiophene	248
C_2-Decalins	166	C_2-Naphthobenzothiophene	262
C_3-Decalins	180	C_3-Naphthobenzothiophene	276
C_4-Decalins	194	Benzo[a]anthracene	228, 226
Naphthalene	128, 127	Chrysene	228, 226
C_1-Naphthalenes	142, 141	C_1-Chrysenes	242, 241
C_2-Naphthalenes	156, 141	C_2-Chrysenes	256, 241
C_3-Naphthalenes	170, 155	C_3-Chrysenes	270, 255
C_4-Naphthalenes	184, 169, 141	C_4-Chrysenes	284, 269, 241
2-Methylnaphthalene	142, 141	Benzo[b]fluoranthene	252, 253, 125
1- Methylnaphthalene	142, 141	Benzo[k]fluoranthene	252, 253, 125
Acenaphthylene	152, 153	Benzo[e]pyrene	252, 253, 125
Acenaphthene	154, 153	Benzo[a]pyrene	252, 253, 125
Biphenyl	154	Perylene	252
Benzothiophene	134	Indeno[1,2,3-c,d]pyrene	276, 277, 138
2,6-Dimethylnaphthalene	156, 155	Dibenz[a,h]anthracene	278, 279, 139
Dibenzofuran	168, 139	Benzo[g,h,i]perylene	276, 277, 138
2,3,5-Trimethylnaphthalene	170, 155		
Fluorene	166, 165	Biomarker Compounds and ALL Steranes, Diterpanes and Triterpanes	
C_1-Fluorenes	180, 165		191, 217, 218
C_2-Fluorenes	194, 179	17a(H),21B(H) – hopane	191
C_3-Fluorenes	208, 193	5B(H) - cholane	217, 315, 330
Dibenzothiophene	184, 152, 139		
C_1-Dibenzothiophenes	198, 184, 197	Surrogate Compounds	
C_2-Dibenzothiophenes	212, 197	2-Methylnaphthalene-d_{10}	152, 150
C_3-Dibenzothiophenes	226, 211	Pyrene-d_{10}	212, 211
C_3-Dibenzothiophenes	240	Benzo(b)fluoranthene-d_{12}	264, 260
Phenanthrene	178, 176		
Anthracene	178, 176	Surrogates for Recovery Correction	
C_1-Phenanthrenes/Anthracenes	192, 191		
C_2-Phenanthrenes/Anthracenes	206, 191	Naphthalene-d_8	136, 134
C_3-Phenanthrenes/Anthracenes	220, 205	Acenaphthene-d_{10}	164, 162

Compound	Quantification & Confirmation Ions	Compound	Quantification & Confirmation Ions
C_4-Phenanthrenes/Anthracenes	234, 219, 191	Phenanthrene-d_{10}	188, 184
1-Methylphenanthrene	192, 191	Chrysene-d_{12}	240, 236
Carbazole	167, 139		
Fluoranthene	202, 101	Internal Standards	
Pyrene	202, 101	Fluorene-d_{10}	176, 174
C_1-Fluoranthrenes/Pyrenes	216, 215	Benzo(a)pyrene-d_{12}	264, 260
C_2-Fluoranthrenes/Pyrenes	230		
C_3-Fluoranthrenes/Pyrenes	244		
C_4-Fluoranthrenes/Pyrenes	258		

Note: Alkylated phenanthrenes and anthracenes, and alkylated fluoranthenes and pyrenes are quantified together as total alkylated phenanthrene/anthracenes (using the phenanthrene parent response factor) and total alkylated fluoranthenes/pyrenes (using the pyrene parent response factor).

Initial Calibration Checklist

Standards Analyzed:								
File IDs:								
Analysis Date:				**Tune Date (PFTBA):**				
Instrument:	**BNA #**							

Review Items	N/A	Yes	No	If No, why is data reportable? (Narrate)	2nd Level
1. Is a copy of the analytical sequence attached?					
A. Tune					
1. Did PFTBA meet tune criteria? Did DFTPP meet tune criteria?				*Include tune raw data with ICAL and circle the tuning method (at left).*	
2. Were all initial calibration standards injected within 12-18 hours?					
B. Initial Calibration					
1. Were at least 5-levels of each compound analyzed? (Confirm all levels present and raw data consistent with summary report.)					
2. Was the Primary Ion used for all compounds?				☒ Secondary ion used due to interferences for compound(s)_____.	
3. Are the Average RFs for ALL compounds > 0.01?					
4. Are %RSD <±30% for ALL compounds?					
5. Are ALL compounds quantitated using Ave. Rf.? (Verify with Compound List Report)					
6. Is the parent Rf entered for ALL Homologs?					
7. 5B(H)cholane Rf entered for Hopane and all Steranes, Diterpanes & Triterpanes?					
8. Is the Separate Source Check Standard, IRM 1491, included? Is the acceptance criteria met? (± 20%D) **If not, explain below.** (*Note: Use **Total** Benzo(b+k)fluoranthene result.*)				**Notes:**	
9. If *FULL* ALK-PAH, is the ANS crude analyzed and included? **If not, explain below.**					
C. Other					
1. Were isometric pairs adequately resolved (i.e., Benzo(b) and Benzo(k)fluoranthene)?					

Analyst: _____ **Date:** _____ **2nd Level Reviewer:**_____ **Date:**_____

Comments:

Continuing Calibration Checklist

Standard Analyzed:		**List CCV IDs and Times:**	
Run Date:			
Instrument:	**BNA #**		

Review Items	N/A	Yes	No	Reason why data reportable? NARRATE w/ effected ETRs.	2nd Level
1. Is a copy of the Analytical sequence attached?					
A. Tune					
1. Did PFTBA meet the Tune criteria before ICAL? Did DFTPP meet the tune criteria?				*Include tune raw data with ICAL and circle the tuning method (at left).*	
2. Were all CCVs injected within 12-18 hours of each other? ***(Including ending CCV?)***					
B. Continuing Calibration					
1. Was the correct ICAL method used as a reference for CCV (Check the "*Quant File ID*" and "*Method ID*" above)? Verify ICAL has been reviewed (was an ICAL checklist completed?), and note any narrations with the associated data. (**Note**: Remember to update to daily CCV and save the method!)				**Notes:**	
2. Are the Internal Standard Areas between 50 -200 % of the areas observed in the last ICAL?				☒ Since the last ICAL, instrument maintenance was performed which changed the area response and retention times of the IS compounds. The change was maintenance related and should not influence the sensitivity and detection of the compounds of interest within the sequence.	
3. Are the CCV RFs for ALL compounds 0.01?					
4. Is the %D ±30% for ALL compounds?					
5. If *FULL* ALK-PAH, is the ANS crude analyzed and included?					
C. Other					
1. Are isomeric pairs adequately resolved (i.e., Benzo(b) and Benzo(k)fluoranthene)?					

Analyst: _____ **Date:** _____ **2nd Level Reviewer:**_____ **Date:**_____

Comments:

Data Review Checklist

Extraction Date:		**Blank ID#:**		**LCS ID#:**	
Instrument ID:	**BNA #**	**ICAL File : Date:**			
Analysis Date:		**CCV IDs & Times:**			

Review Items **A. Tune**	**N/A**	**Yes**	**No**	**Reason why data reportable? NARRATE w/ ETR.**	**2nd Level**
1. Did PFTBA meet the Tune criteria before the ICAL? Did DFTPP meet the Tune criteria?				**PFTBA Date(s):** *Circle tuning method(s) used, at left.*	
B. Initial Calibration Verification					
1. Has an Initial Calibration Checklist been completed for all ICALs? (**Note** any QC anomalies).				**Notes:**	
2. Was the correct ICAL method used for sample quantitation? (Check *"Quant File ID" and compare w/ Method(s) above*). If wrong, data needs to be reprocessed w/ the correct Method(s) above.					
C. Continuing Calibration Verification					
1. Has a CCV Checklist been completed for each Analytical Batch? (**Note** any QC anomalies).				**Notes:**	
2. Were all samples injected between CCVs that were 12-18 hours apart *(including ending CCV)*?					
3. If *FULL* ALK-PAH, is the ANS crude included?					
D. Sample Results					
1. Was the correct analysis performed? Is all paperwork present? (Check ETR worksheet & comments).					
2. Is the header information correct? (If not, 2nd bring data package back to the Lab for corrections.)					
3. Sample analyses done within preparation and analytical holding time (HT)? *If No, list samples and reasons:* **[Prep**.=Aqu.-7 days; Soil -14 days; **Analytical** = 40 days**]** Sample(s) Reason(s) HT _____ _____ _____ _____ _____ _____				1. HT had expired before receipt of sample(s).-***Narrate*** 2. Sample received with < 3 days left for extraction. 3. Client requested analysis after HT expired.*-***Narrate*** 4. Re-extraction done after HT expired.-***Narrate*** 5. Other:_____	
4. Are surrogates within QC limits? *If No, list Samples/Surrogates/Reasons:* Sample(s) Surrogate(s) Reason(s) _____				6. Surrogate %R outside QC limits due to matrix effect. MS/MSD surr. %R demonstrated same effect.-***Narrate*** 7. Surrogate %R outside QC limits due to matrix effect since re-extraction/re-analysis demonstrated the same effect. ***Report original and Narrate.*** 8. Surrogate %R outside QC limits due to obvious matrix interferences. Explain/***Narrate***:_____ *(Analyst has confirmed w/ Section Head.)* 9. Surrogate %R outside QC limits; however, there wasn't sample left to re-extract. -***Narrate/PM notified***. 10. Surrogate %R outside QC limits; re-extraction outside HT; both sets of data are reported.-***Narrate/PM notified***. 11. Surrogate %R outside QC limits; however, at the client's request, the data were flagged and released without further investigation. *-***Narrate*** 12. Surrogates diluted out.	

D. Sample Results (continued)	**N/A**	**Yes**	**No**	**Reason why data reportable? NARRATE w/ ETR.**	**2nd Level**
5. Is largest compound diluted to upper half of calibration range? *If no, list sample(s):* Sample(s) Dilution(s) Reason(s) ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____				13. At the client's request, the sample was analyzed with minimum dilution even though some compounds were outside of calibration range. *-***Narrate*** 14. Largest compound diluted to acceptable concentration based on normal sample dilution volumes. 15. Sample showed matrix inhomogeneity. Duplicate analysis (or Re-extraction) was within calibration range, both analyses are reported.-***Narrate*** 16. Other:____	
6. Are there any samples with elevated reporting limits due to dilution? *If Yes, list sample(s):* Sample(s) Dilution(s) Reason(s) ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____ ____				17. Dilution required to prevent contamination of the instrument due to non-target compounds.-***Narrate*** 18. Diluted for target analytes. 19. Limited sample volume available.-***Narrate/PM notified.*** 20. FV greater than routine method SOP.-***Narrate*** 21. Waste Dilution/Product sample. 22. High moisture content. (Low %solids) 23. Diluted due to nature of extract(s):____-***Narrate*** 24. Other:____	
7. Are multiple runs reported for a single sample? *If Yes, list samples(s):* Sample(s) Dilution/Other Reason(s) ____ ____ ____ ____ ____ ____ ____ ____ ____				25. The sample was run at multiple dilutions to obtain the lowest reporting limit for each compound analyzed. -***Narrate.*** 26. Duplicate/Multiple samples reported to show/confirm results due to QC failure (i.e. IS(s) out; Surrogate(s) out; CCV anomaly; MB/LCS anomaly). -***Narrate***	
8. Are the Internal Standards all within QC limits? (response is 50-200% of CCAL and RTs within windows) *If No, list*: Sample(s) Reason(s) ____ ____ ____ ____ ____ ____				27. Re-analysis confirmed matrix effect is responsible for the IS criteria not being met.-***Narrate/Report original*** 28. IS criteria not met due to obvious matrix interference. *(Analyst has confirmed w/ Section Head)* Explain:____-***Narrate*** 29. Upon consultation with the client, re-extraction/re-analysis not performed to meet this criteria.*-***Narrate***	
9. If manual integrations were performed, is a before and after quantitation report present, technique marked, and justification given with analyst's initials/date?					
E. Preparation/Matrix QC					
1. LCS done per prep batch and all compounds within QC limits? *If No, list LCS & Compounds:* ____ ____				30. MS/MSD %R and all Sample and Method Blank surrogate recoveries good; indicates problem was confined to the LCS.-***Narrate*** 31. Re-extraction not possible due to insufficient sample.*-***Narrate***	
2. Method Blank done per preparation batch and all surrogate recoveries OK?				32. Sample surrogates OK and no compound > RL in samples associated with blank. *-***Narrate***	
3. Are any compounds present in the Method Blank RL? *If Yes, list Blank and Compounds:* Blank ID#: Compound > RL: ____ ____				33. Compound(s) is a common lab contaminant and is present at a concentration <5x RL. (PAHs) 34. Sample results are > 20x higher than blank. 35. Re-extraction not possible due to insufficient sample.*-***Narrate***	
4. MS/MSD done per batch or per 20 field samples and are all %R and %RPDs within laboratory QC limits? *If No, list*: MS/MSD ID: Compounds Out: ____ ____				36. LCS showed acceptable results indicating sample matrix effects.-***Narrate*** 37. MS/MSD not possible due to limited sample; LCS done and recoveries are within QC limits. 38. Done per batch, but not associated w/ this ETR. **List ETR#**:____	

D. Sample Results (continued)	N/A	Yes	No	Reason why data reportable? NARRATE w/ ETR.	2nd Level
5. MS/MSD run at same dilution as sample?				39. Insufficient sample volume prevented analyzing the MS/MSD at the same dilution as the sample. 40. MS/MSD required analysis at a dilution to bring spiked compounds within calibration range because the native sample had high concentrations of targets.	
F. Other					
1. Date/time of analysis verified between sample header (raw) and sample header (report) as correct?					
2. Graphs included for ALL *FULL* ALK-PAH samples?					
3. Are all non-conformances documented properly?				Review checklist, start or append to narrative under *F: \shared\narrtemp\ETR#.doc*	
4. Calculations checked for error?				**2nd Level Check ~10%**	
5. Transcriptions checked for error?				**2nd Level Check ~10%**	
6. All client/project specific requirements met?				* Review ETR comments and /or Project Initiation Form.	

Analyst: _____ **Date:** _____ **2nd Level Reviewer :** _____ **Date:** _____

Comments:_____

Total Petroleum Hydrocarbons
Gas Chromatography and Flame Ionization Detector Technique
Method 8100 (Modified)

1.0 METHOD REFERENCE

1.1 Test Methods for Evaluating Solid Waste, SW-846, Third Edition, (USEPA, Office of Solid Waste and Emergency Response, Washington, DC, September 1986).

1.2 "Methodology for Comparison of Petroleum Oil by Gas Chromatography," American Society for Testing and Materials (ASTM) Method D 3328-78 (1982).

1.3 Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), Massachusetts DEP, Wall Experiment Station, January 1998.

2.0 SCOPE AND APPLICATION

2.1 This method is applicable to the quantification and qualitative fingerprinting of petroleum products in water, soil, and sludge samples. Extractable petroleum hydrocarbon in petroleum products such as kerosene, aviation fuels, diesel and heating oils may be analyzed by this method but products with primarily volatile constituents such as gasoline range organic compounds are not amenable to this method.

2.2 The reporting limit for aqueous samples is 1 ug/L and for soil samples is 25 ug/Kg.

2.3 The qualitative identification is dependent on the product pattern, how weathered it may be and how much is present. This is the subjective aspect of the analysis that requires an experienced analyst. Care should be taken to ensure consistency in petroleum identification.

	Approval Signatures	
Laboratory Director	Peter J. Shane	Date: 7/16/99
Section Head	Norman [illegible]	Date: 7/16/99
Quality Assurance Manager	Gail Hymes	Date: 7/16/99

3.0 SUMMARY OF METHOD

3.1. Aqueous samples are extracted with methylene chloride employing Separatory Funnel extraction (Method 3510C) or Continuous Liquid/Liquid extraction (Method 3520C). Soil samples are extracted by sonication (Method 3550B) in a methylene chloride - acetone mixture or on the Dionex with methylene chloride. The Dionex is a pressurized fluid extractor (Method 3545). The extract may be treated with silica gel (Method 3630C) to remove non-petroleum hydrocarbon contaminates, if indicated. The extract is concentrated to the appropriate volume for analysis and the cleanup technique is applied, if necessary. The extract is injected into a gas chromatograph (GC) fitted with a capillary column. Target analytes are resolved on the column and detected using a flame ionization detector (FID). Concentrations are calculated from the FID response. Identification of the petroleum product or products present are made by comparison to reference standards.

3.2. Petroleum hydrocarbons are quanitatively identified over the range from n-C_9 alkane isomer to the n-C_{36} isomer. Quantitation is performed using a standard mixture of n-alkanes. Qualitative identifications are conducted against specific petroleum hydrocarbon product analyzed under the same conditions as the samples of interest. The distinctive "fingerprint" of the standards are matched to the samples by an experienced analyst.

4.0 SAMPLE HANDLING AND PRESERVATION

4.1. Aqueous samples are collected in a pre-cleaned 1-L amber glass bottle with a teflon lined screw cap. Samples should be preserved with HCl to pH<2 and stored at 4°C. Extraction should be performed within 14 days of collection; extract should be analyzed within 40 days of extraction.

4.2. Soil samples are collected in a pre-cleaned 250 mL soil jar with teflon lined screw cap. Samples should be preserved by cooling to 4°C. Extraction should be performed within 7 days of collection; extract should be analyzed within 40 days of extraction. Approximately 100 g of soil is required for the analysis although more may be collected to provide a representative sample.

5.0 GENERAL POINTS

5.1. Samples should be inspected for particulates while still in the sample bottle. Particulates should be noted on the appropriate benchsheets and reporting forms as they can interfere with the extraction by causing an emulsion in the separatory funnel during the draining steps.

5.2. Emulsions can form during the extraction especially in samples with high concentrations of petroleum contamination. This may require mechanical means to disperse such as glass stirring rods or centrifugation. Alternatively, filtration of emulsions through pre-dried sodium sulfate can be employed. Additional filtration through sodium sulfate after emulsion reduction is required to ensure adequate sample drying has been achieved.

5.3. The injector system of the GC can become contaminated with non-volatizable components from prepared samples, decreasing the resolution and responsiveness of the system. High molecular weight polyaromatic hydrocarbons (PAH) in the calibration mix can act as indicators of chromatographic problems. C_{36} response decreases with increased injector contamination and is a good indicator compound. Maintenance of the analytical system should be performed when system performance degrades.

6.0 EQUIPMENT AND REAGENTS

6.1 See the appropriate SOP's for the extraction procedures, equipment and reagents needed as indicated in Section 3.1 above.

6.2. **Gas chromatograph** - Programmable; heating range from 60°C to 310°C; splitless-type inlet system; flame ionization detector (Hewlett-Packard HP 5890 Series II GC or similar).

6.2.1 Chromatography Column - 95% dimethyl-5%diphenyl polysiloxane, fused silica, capillary column,:0.32mm ID x 30m length, 0.25μm film thickness (Rtx-5, Restek Corporation, SN 10255, or equivalent).

6.2.2. Data Acquisition System - Computerized system for collecting, storing, and processing detector output (Turbochrom, Perkin-Elmer).

6.2.3. Gases - High purity hydrogen, air, and helium.

6.3. **Laboratory Supplies** - Syringes, pipettes, autosampler vials, crimper.

6.4. **Reagents**

6.4.1. Methylene Chloride - HPLC grade of better.

6.4.2. Acetone - Optima grade or equivalent

6.4.3. Silica gel - column chromatography grade,.60-200 mesh, dried at 110°C for 24 hours.

6.4.4. Hexane - Optima grade or equivalent.

6.5. **Analytical Standards**

6.5.1. **Surrogate Spiking Solution** – 5-alpha-androstane at 100 ug/mL in acetone. 5-alpha-androstane is commercially available from Restek at a concentration of 10000 ug/mL. To prepare a working standard, add 1.0 mL to a 100 mL volumetric flask and dilute to volume with acetone. The solution should be transfered to a 40 mL glass vial with teflon lined cap and stored at 4°C. Discard after 6 months.

6.5.2. **Matrix Spike Solution** - Diesel fuel #2 at approximately 10000 ug/mL. This solution is prepared from neat commercially available product. It is prepared to produce a solution of approximately 10000 ug/mL. Weigh out approximately 1000 mg or 1.0 grams of diesel fuel into a 100 mL volumetric flask and dilute to volume with acetone. One mL of this solution can then be spiked into each matrix spike or blank spike sample. Store at 4°C. Discard after 6 months.

6.5.3. **Calibration Standard Solution** - A working solution is prepared from stock solutions by diluting 1 mL of the 2000 ug/mL alkane stock solution in a 10 mL volumetric with methylene chloride. This solution is at 200 ug/mL which also can be used for the optional seventh point in an initial calibration. Subsequent dilution's can be made to create the rest of the calibration curve. The solution should be transfered to a 15 mL glass vial with teflon lined cap and stored at 4°C. Discard after 6 months.

An alkane stock solution can be commercially obtained (Ultra SMA 310). This standard is a mixture of the following alkanes at 2000 ug/mL: Nonane (n-C_9), Decane (n-C_{10}), Dodecane (n-C_{12}), Tetradecane (n-C_{14}), Hexadecane n-C_{16}), Octadecane (n-C_{18}), Nonadecane (n-C_{19}), Eicosane (n-C_{20}), Docosane (n-C_{22}), Tetracosane (n-C_{24}), Hexacosane (n-C_{26}), Octacosane (n-C_{28}), Triacontane (n-C_{30}) and Hexatriacontane (n-C_{36}). Alternatively another commercial mix can be used with all of the alkanes from C_{10} to C_{25}. One mix can be used for initial calibration and the one mix for ortho-Terphenyl.

6.5.4. **Petroleum Hydrocarbon Reference Standards** - For chromatographic library and pattern matching. The Library should include (but not neccessarily be limited to) standards of PAHs, gasoline, kerosene, fuel oil #2, diesel fuel, fuel oil #4, fuel oil #6, asphalt, used motor oil, lubricating oil, paint thinner, creosote, cutting oil, coal tar, and hydrolic oil. Prepare reference standard solutions by adding measured quantities of reference materials to methylene chloride. Dilute to appropriate concentration for use (approximately 2000 - 5000 ug/mL). Because reference materials cannot always be obtained as certified materials, the source of the reference standards should be documented, i.e. fuel oil #2 obtained from a particular fuel oil company on a particular date.

7.0 SAMPLE ANALYSIS

7.1. Instrument Setup

The basic GC parameters are as follows:

Injector A Temp	300°C
Detector Temp	350°C
Equil. Time	0.1 minutes
Oven Temp	60°C
Initial Value	60°C
Initial Time	2 minutes
Rate 1	10°/minute
Intermediate Value	300°C
Time	10 min.
Rate 2	25°/minute
Final Value	310°C
Final Time	3 minutes
Purge/Valve A ON	1 minute

7.2. Initial Calibration

7.2.1. Before samples can be analyzed, the instrument must be calibrated for the analysis. This is done by injecting a series of normal alkane standards in the carbon range of n-C_9 to n-C_{36} into the injection port of the GC. The volume injected is 1 *u*L.

7.2.2. A seven point calibration curve is prepared using the alkane mixture that was commercially obtained. The range of the curve is 1 ug/mL to 200 ug/mL.

A 200 ug/mL standard is prepared from stock parent standards by diluting 2mLs of 2000 ppb alkane stock and 0.2 mL 10000 ppb of 5-alpha-androstane to 10 mL final volume. This standard is used as the high point of the calibration curve as well as to prepare other calibration standards as described below.

Final concentration of Standard (ug/mL):	Volume of 200 ug/mL added- *u*L:	Volume of solvent added-*u*L:
150	750	250
100	500	500
50	250	750
10	50	950
5	25	975
1	5	995

7.2.3. Calculate a response factor (Rf) for each alkane in each standard using the area response and the amount of standard material. Calculate the relative standard deviation percentage (%RSD) of the Rf for each alkane across the calibration curve. The value for each alkane should not exceed 25% for the curve to be deemed valid. The average response factor for the weight ranges are calculated and used for sample quantitation (see below, Section 7.2.4). If any individual alkane exceeeds 25%, then the weight range response factors may be evaluated, and used, if %RSD for the average of the range meets the criteria.

If the curve still does not meet criteria, the analyst should check the calculation of the standard preparation that was performed. If chromatographic problems are indicated by the standard chromatograms already analyzed, then the injection port should be prepped. This consists of cutting 6 to 12 inches off of the column, changing the

liner and the septa. If the system shows poor sensitivity after this cleaning, the detector jet should be cleaned or changed.

The gold seal at the base of the injection port should be replaced whenever major maintenance is performed.

7.2.4. The alkanes are divided into two molecular weight ranges. The average Rf for each range is calculated and used for sample quantitation. If the individual alkanes meet acceptance criteria, then the range response factors are assumed to be valid (see above, Section 7.2.3). If the %RSD for the individual alkanes is outside of limits, a check may be made using the weight range Rf. If this average meets acceptence criteria, the average Rf may be used for sample quantitation.

7.2.5. The ranges are defined as:

- C_9 to C_{18} aliphatics
- C_{19} to C_{36} aliphatics

7.2.6. Alternately the chromatogram can be divided into three molecular weight ranges to meet specific project requirements. This type of reporting is performed only if specifically requested by client. The ranges are defined as:

- Light weight hydrocarbons - C_9 to less than C_{16}
- Midweight hydrocarbons - C_{16} to less than C_{20}
- Heavy weight hydrocarbons - C_{20} to C_{36}

7.3. **Continuing Calibration**

7.3.1 On a daily basis a continuing calibration is performed using a 100 ug/mL alkane standard. The calculated Rf of the individual alkanes in the continuing calibration are compared to the average Rf in the initial calibration. The percent difference (%D) between the Rf's must be less than or equal to 25% for all alkanes except C_{36}. The minimum %D for C_{36} is 50%. (A low response for C_{36} is an indication that the GC liner should be replaced.) This same criteria is applied if using the weight range Rf for calculations. Additionally, the response ratio between C_{28} and C_{20} should be determined. The ratio should be ≥ 0.85.

7.3.2. Analysis of samples must be bracketed by a valid continuing calibration check standard. If the ending standard to a batch of samples is not valid, the analyst must take great care in evaluating these samples. The standard must be reviewed to determine if the samples were properly analyzed. An anomalous condition may have caused the standard to be unacceptable and the samples acceptable. Qualitative information may still be available when quantitative information is not possible. A clear data narrative is essential in cases where standards may be in question. The Section Head, Laboratory Manager and/or the QA Manager should be consulted and should approve reporting of anomolous analytical results.

7.3.3. The analyst judgment from continuous daily use of the instrument is important in determining the validity of a continuing calibration. Even if the %D criteria are met, the peak shape may have deteriorated to a point where maintenance is required and a new initial calibration is in order.

7.3.4. The ratio of phytane to n-C_{18} must be 60% or better for the test to appropriately provide weathering information. If the ratio is acceptable, it is assumed that the n-C_{17} to pristane ration is also acceptable.

7.4. Prepared Samples

7.4.1 The following sequence is recommended for analysis of sample extracts:

* Primer
* Instrument blank (Methylene chloride or Hexane - dependant on extract solvent).
* Initial calibration standards 1 to 200 ug/mL.
* Instrument blank.
* Independent Check Standard (100 ug/mL from a separate source).
* Instrument blank.
* Continuing calibration standard (100 ug/mL).
* Instrument blank.
* Samples 1 to 20.
* Continuing calibration standard (100 ug/mL).
* Instrument blank.
* Samples 1 to 20.
* Instrument blank
* Continuing calibration standard (100ug/mL).

7.4.2. Quantitation shall be determined via collective integration of all resolved and unresolved complex mixtures, UCMs, (i.e., hump) above the baseline. The contribution from the solvent front and surrogate compound are excluded from the total area. The total area is divided into the two ranges and a result is calculated. The results from each range are summed to calculate a value for the total petroleum hydrocarbons.

7.5. Qualitative Identification

7.5.1. The chromatograms produced by the analysis are compared to reference chromatograms for qualitative identification. The reference chromatograms are stored as hard copy reports as well as electronically in the data acquisition software. Electronic storage allows for evaluation using computer software.

7.5.2. The qualitative analysis can be time consuming. Retention time information for the alkanes and any UCM's (Unresolved Complex Mixtures) is essential. The graphical comparison of sample patterns to standard patterns is extremely useful in the interpretation of results. Hard copy reports of comparisons should be retained for future reference.

7.5.3. Degrees of confidence in the qualitiative identification of product contamination should be included as report qualifiers. The following definitions should be used.

MATCH - This level of identification indicates an exact match or nearly exact match between the sample and the reference standard. Indicate the name of the product in the product source information section of the data sheet (i.e. "#2 fuel oil")

PROBABLE MATCH - This indicates a nearly exact match, with the exception of small differences that can be specifically attributed to the presence of extraneous components or moderate weathering effects. Indicate the name of the component, that is the probable match, and the reference (i.e. "Probable Mineral Spirits with some sludge contamination" or "Probable #4 Fuel oil, slightly weathered")

INDETERMINATE - This level indicates that the sample is too different from any reference to make a definitive identification. Indicate the median boiling point of the product as either light-weight (≤ n-C15), mid-weight (n-C16 to <nC20), or heavy-weight (≥ n-C20). Include the range of alkanes that the product spans and indicate the degree of weathering (if it is apparent), (i.e. "Indeterminate mid-weight product, heavily weathered" or "Indeterminate heavy-weight product, n-C17 to n-C32 present")

MISMATCH - This level of identification should only be used when a client has submitted a possible source for comparison with the sample and the source doesn't match the sample. Use this in conjunction with one of the other 3 levels of identification for both the sample and the suspected source.

7.5.4. The degree of weathering can be approximated using the ratios. Note that weathering information can only be evaluated in cases where samples contain products which contain n-C_{17} and n-C_{18} (primarily fuel oil #2 contaminated samples).

Pristane ratio = Area Pristane/Area n-C_{17}
Phytane ratio = Area Phytane/Area n-C_{18}

Pristane or Phytane ratio	Degree of Weathering
< 1.0	Unweathered or Slightly
1.0 - 2.0	Moderately Weathered
> 2.0	Highly Weathered
Pristane & Phytane degraded	Extremely Weathered

For extremely weathered samples the start and end of the UCM can be used to project a tentative identification of the fuel oil. There will be little to no resolvable chromatographable peaks.

7.5.5. **Identification of Products** - The identification of petroleum products by this method is complicated and relies heavily upon the experience of the analyst with this and other gas chromatographic analyses. The following questions may need to be answered to gather sufficient data to make an identification.

- Is there a UCM? No UCM in the low range may indicate the presence of gasoline. A low range UCM may indicate the presence of a petroleum based lubricant. Mid range UCM may indicate the presence of fuel oil. High range UCM may indicate heavy lubricating oil or asphalt materials.

- Is there one or two distinct molecular weight ranges in the chromatogram? If there are two this may indicate a cutting oil/lubricating oil.

- Are there well resolved peaks and do they have the same retention times as standard alkanes?

- Are pristane and phytane present? Can the degree of weathering be determined?

8.0 CALCULATIONS

8.1. Aqueous Samples - For calculation of weight range use the following formulas.

$$C_f = Area_p \times Rf \times \frac{V_f}{V_i} \times DF \times 1000$$

C_f = final sample concentration (ug/L)
$Area_p$ = measured area of peak (or peaks)
V_i = initial volume extracted (mL)
V_f = final extract volume (mL)
DF= dilution factor of sample or extract
Rf = response factor from calibration standard calculated as

$$Rf = \frac{Concentration_p}{Area_p}$$

Concentration $_p$ = concentration of peak or total concentration of range
$Area_p$ = area of peak or total area across range

8.2. **Soil Samples** - For calculation of weight range use the following formulas.

$$C_f = Area_p \times Rf \times \frac{V_f}{W_i} \times DF \times 1000$$

C_f = final sample concentration (ug/L)
$Area_p$ = measured area of peak (or peaks)
W_i = initial weight extracted (g dryweight)
V_f = final extract volume (mL)
DF= dilution factor of sample or extract
Rf = response factor from calibration standard calculated as

$$Rf = \frac{Concentration_p}{Area_p}$$

Concentration $_p$ = concentration of peak or total concentration of range
$Area_p$ = area of peak or total area across range

8.3 Calculate Petroleum Hydrocarbon Total by adding the calculated results of both ranges together. Note: see section 9.2 for reporting instructions for ranges with values below reporting limits.

8.4. **Percent Relative Standard Deviation**

Calculate % RSD by: $$\%RSD = \frac{SD}{\bar{x}} \times 100 \qquad SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N-1}}$$

where:
% RSD = percent relative standard deviation
x = average of RF's
SD = standard deviation
xi = analytical results of each level in the final reporting units
N = number of results (levels)

8.5. **Percent Difference**

$$\%D = \frac{Rf_{ical} - Rf_{ccal}}{Rf_{ical}} \times 100$$

8.6 **Relative Percent Difference**

$$RPD = \frac{|R1 - R2|}{\frac{[R1 + R2]}{2}} \times 100$$

where:
R1 = result one, i.e. MS
R2 = result two, i.e. MSD

8.7. **Percent Surrogate Recovery**

$$\% \text{ Surrogate Recovery} = \frac{C_{surrogate}}{C_{spike}} \times 100$$

$C_{surrogate}$ = calculated surrogate concentration from sample analysis
C_{spike} = concentration of surrogate spiked into the sample

8.8. **Percent Matrix Spike Recovery**

$$\% \text{ Matrix Spike Recovery} = \frac{Csp - Csa}{Ca} \times 100$$

Csp = concentration obtained in spiked sample
Csa = concentration obtained in sample
Ca = concentration of spike added

9.0 REPORTING RESULTS

9.1 For projects requiring qualitative results report from the possible choices listed in section 7.5.3. The reporting program offers these selections properly phrased so that the wording is consistent each time.

9.2 For projects requiring quantitative results report the numerical result as calculated in section 8.1 or 8.2 for each weight range and as calculated in section 8.3 the total TPH concentration. Report results to 2 significant figures.

9.2.1 For samples having results for 1 range less than the range reporting limit, the total TPH is equal to the result of the range which is above the reporting limit.

9.2.2 For samples having results less than the reporting limit in each range, the total TPH is less than the single range reporting limit, NOT the sum of the 2 ranges.

9.3 The limit of detection and thus the reporting limit for a hydrocarbon range is the highest value calculated for the individual alkanes within the hydrocarbon range. The limit of detection, and thus the reporting limit for total TPH, is the same as a single range limit.

10.0 QUALITY CONTROL

10.1. **Laboratory QC Samples**

10.1.1. **Method Blank** - A method blank must be extracted with every batch of samples. It consists of reagent water spiked with 1 mL of the 100 ug/mL surrogate solution. This extraction will demonstrate the background contamination of the apparatus in the laboratory. The acceptance criteria for the blank is that the values should be not greater than two times the reporting limit.

10.1.2. **Surrogate Standard** - The recovery of the surrogate compound (5-alpha-androstane) in the method blank and samples must be monitored to assure method performance. Acceptance criteria are 25 to 120% recovery until lab statistically determined limits are calculated. If surrogate recoveries are low and the procedure is suspect, the analysis should be repeated.

10.1.3. **Lab Control Spike (LCS)** - One second source LCS is extracted with every daily batch of samples. This consist of one liter of reagent water spiked with 1 mL of a 10000ug/mL diesel fuel standard. The surrogate is also spiked. This extraction will demonstrate the overall efficiency of the extraction procedure. Recovery should be within 40 - 120% of the true value.

10.2. Matrix Specific QC Samples

10.2.1. **Matrix Spikes** - Prepared and analyzed at a frequency of 2 per 20 samples extracted (as an MS/MSD pair), and at least 1 pair per week. It is preferable to extract samples that have been selected specifically by the client. If none have been assigned then the analyst in the laboratory must choose a representaive sample from each type of matrix prepared. The samples selected for matrix spikes are spiked with 1 mL of the same spiking solution used in the LCS. The samples are also spiked with surrogate. The relative percent difference (%RPD) between the duplicates is calculated, and should not exceed 30%.

10.2.2. **Duplicate Samples** – (Usually in the form of an MS/MSD pair.) Prepare and analyze an environmental sample in duplicate at a frequency of 2 per 20 samples, when requested by the client as a non-spiked duplicate. Select representative samples from each type of matrix analyzed. The relative percent difference (%RPD) between the duplicates is calculated, and should not exceed 30%.

10.2.3. **Sample Surrogate Recoveries** - Recoveries are monitored and evaluated against the same recovery limits as the method blank surrogate recovery limits. If recoveries are outsidethe control limits, data should be closely evaluated to determine if laboratory error of matrix effects are the cause. A repeat analysis and if necessary reextraction is required to verify recoveries outside of control limits. In some cases, if surrogate recovery of the method blank and LCS are in control, the sample may be qualified as having low recoveries and the data used qualitatively. This may be the case when obvious interferences from a UCM are observed. In all cases, the Section Head, Laboratory Manager and/or the QA Manager should be involved in the decisions about the validity of the data. A project narrative is used to explain any out of control situation and the corrective measures that are employed by the laboratory.

10.3. Method Performance

10.3.1. Method Detection Limit (MDL) studies must be performed annually or whenever significant changes occur to the instrumentation. Method detection limits are determined annually by preparation and analysis of seven replicate samples. Samples for soil MDL analysis are clean sand spiked with 2.5 ug/Kg of the n-alkane standard and a separate MDL of 50 ug/Kg of #2 fuel oil standard. Samples for water MDL analysis are deionized water spiked with 2.5 ug/mL of the n-alkane standard and a separate MDL of 50 ug/mL of #2 fuel oil. The MDL is calculated using student T statistics as 3.14 x the standard deviation of the mean of the seven replicate results.

10.3.2. Initial Demonstration of Proficiency (IDP) must be performed by each analyst who performs this method. Analyst proficiency is demonstrated for this method by performing the analysis of a method blank and four replicates of laboratory control spikes (LCS) on non-consecutive days. The analyst must demonstrate 80%-120% recovery of the true value spiked for the n-alkanes. Records of proficiency are kept on file by the laboratory Quality Assurance Manager.

10.4. Corrective action

10.4.1. Corrective action may be indicated if any of the follow conditions exist:

* Established QC limits are consistently not met, particularly when trends are becoming evident.
* Blanks, LCSs, or surrogates show laboratory contamination or low percent recoveries.
* The pristane to C17 and phytane to C18 ratios are less than 60 %.

In all of the above cases the analyst performing the analysis should be the first point of contact to determine if there are true QC concerns. The Section Head should coordinate efforts with the analyst and the QA Manager to determine any underlying QC problem. If situations are noted, they must be recorded in hard copy form for future referral in the event the same situation arises.

Total Petroleum Hydrocarbons
Gas Chromatography and Flame Ionization Detector
Method 8100 (Modified)

SOP Addendum for Saturated Hydrocarbons

Section 1.0 - No modifications.

Section 2.0 - The reporting limit for aqueous samples is 34 ug/L C_9-C_{40} and 1 ug/L individual alkane. The reporting limit for soil/sediment samples is 14,000 ug/Kg C_9-C_{40} and 400 ug/Kg individual alkane.

Section 3.0 - Petroleum hydrocarbons are quantitatively identified over the range from n-C_9 alkane isomer to the n-C_{40} isomer.

Section 4.0 - No modifications.

Section 5.0 - No modifications.

Section 6.0 – 6.5.1 - ortho-Terphenyl at 100 ug/mL in acetone. Ortho-Terphenyl is commercially available from Restek (cat # 31097) at a concentration of 10,000 ug/mL. To prepare a working standard, add 1.0 mL to a 100 mL volumetric flask and dilute to volume with acetone.

6.5.2 - Alkanes at 50 ug/mL in acetone. An Alkane stock solution is commercially available from Ultra (cat # SMA-310). To prepare a working standard, add 5.0 mL to a 100 mL volumetric flask and dilute to volume with acetone. This standard is a mixture of the following alkanes at 1,000 ug/mL: Nonane (C_9), Decane (C_{10}), Dodecane (C_{12}), Tetradecane (C_{14}), Hexadecane (C_{16}), Octadecane (C_{18}), Nonadecane (C_{19}), Eicosane (C_{20}), Docosane (C_{22}), Tetracosane (C_{24}), Hexacosane (C_{26}), Octacosane (C_{28}), Triacontane (C_{30}) and Hexatriacontane (C_{36}),

6.5.3 - A working solution is prepared from stock solutions by diluting 4 mL of the 500 ug/mL alkane stock solution in a 10 mL volumetric with methylene chloride. This solution is at 200 ug/mL which also can be used for the optional seventh point in an initial calibration. An Alkane stock solution is commercially available from Accustandard (cat # DRH-008S-R1). This standard is a mixture of the following alkanes at 500ug/mL: Nonane (C_9), Decane (C_{10}), Undecane (C_{11}), Dodecane (C_{12}), Tridecane (C_{13}), Tetradecane (C_{14}), Pentadecane (C_{15}), Hexadecane (C_{16}), Heptadecane (C_{17}), Octadecane (C_{18}), Nonadecane (C_{19}), Eicosane (C_{20}), Heneicosane (C_{21}), Docosane (C_{22}), Tricosane (C_{23}), Tetracosane (C_{24}), Pentacosane (C_{25}), Hexacosane (C_{26}), Hexacosane (C_{27}), Octacosane (C_{28}), Nonacosane (C_{29}), Triacontane (C_{30}), Hentriacontane (C_{31}), Dotriacontane (C_{32}), Tritriacontane (C_{33}), Tetratriacontane (C_{34}), Pentatriacontane (C_{35}), Hexatriacontane (C_{36}), Heptatriacontane (C_{37}), Octatriacontane (C_{38}), Tetracontane (C_{40}), Pristane and Phytane.

Section 7.0 - The basic GC parameters are as follows:

Injector Temp	280°C
Detector Temp	350°C
Equil. Time	0.1 minutes
Oven Temp	60°C
Initial Value	60°C
Initial Time	1.2 minutes
Rate 1	15°/minute
Time	1.0 minute
Rate 2	20°/minute
Final Value	300°C
Final Time	25 minutes
Purge/ Valve ON	0.6 minutes

7.2.5 - The range is defined as:

- C_8 to C_{40} aliphatics

7.3.1 – The percent difference (%D) between the Rf's must be less than or equal to 25% for all analytes.

7.5 – Qualitative identification is performed on a project specific basis.

Section 8.0 - No modifications.

Section 9.0 – 9.2.2 The reporting limit generated for the TEM (Total Extractable Material) is based on one quantitative range n-C_8 to n-C_{40}.

Section 10.0 – 10.1.2 The acceptance criteria for the surrogate compound (ortho-Terphenyl) in the method blank and samples is 40%-140%.

10.1.3 - The acceptance criteria for the spike compounds (n-alkane mix) in the laboratory control sample is 40%-140%.

10.2.1 - The acceptance criteria for the spike compounds (n-alkane mix) in the laboratory control sample is 25%-120%. The relative percent difference (%RPD) between the duplicates is calculated, and should not exceed 30%.

Total Organic Carbon in Soil, Sediment and Water

1.0 Identification of Test Method

This standard operating procedure is based on the following TOC analytical test methods:

1.1 USEPA, "Method 9060 Total Organic Carbon," in Test Methods for Evaluating Solid Waste, SW846, Third Edition, Final Update, December 1996.

1.2 USEPA, "Organic Carbon, Total (Combustion or Oxidation) 415.1," in Methods for Chemical Analyses of Water and Wastes, EPA-600/4-79-020, Revised March 1983.

1.3 Perkin Elmer, "PE 2400 Series II CHNS/O Analyzer User's Manual," The Perkin-Elmer Corporation, April 1998.

1.4 USEPA, Region II, Lloyd Kahn, "Determination of Total Organic Carbon in Sediment", July 27, 1988.

2.0 Applicable Matrix or Matrices

2.1 This method is applicable to the determination of Total Organic Carbon in water and other aqueous samples (drinking, surface and saline waters, domestic and industrial wastes) and solid samples (soils, sediments, sludges).

	Approval Signatures	
Laboratory Director	Peter J. Kane	Date: 1/22/03
Section Head	Nancy A Rose	Date: 1/22/03
Quality Assurance Manager	Gale Potra	Date: 1/22/03

This SOP is printed from an electronic file.
A signed original is available in the files of Woods Hole Group Environmental Laboratories.

3.0 Detection and Quantitation Limits

3.1 The Method Detection Limit (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 indicative of the accuracy, precision, and sensitivity of the analytical method. It is essential that all analytical processing steps be included in the determination of the MDL. The Total Organic Carbon MDL is performed annually or if there is a major change in instrumentation or method procedure. The procedures described in 40CFR Part 136 must be followed to determine the MDL. Total Organic Carbon MDLs are performed by analyzing seven to ten replicates of a low-level Total Organic Carbon spike (at 3-5x the expected MDL) in reagent water or a clean sand. The MDL is calculated by multiplying the standard deviation of the replicates by the corresponding Student T test value (*i.e.*, 3.143 for seven replicates). MDL results are on file in the laboratory QA department.

3.1.1 Prepare a reagent blank that is free of the Total Organic Carbon and Total Organic Carbon interference.

3.1.2 Prepare a standard that is equivalent to, or at least in, the same concentration range of, the estimated method detection limit (between 1-5 times the estimated MDL). If after analysis the measured level is less than the estimated detection limit, prepare a standard at a higher concentration, to bring the concentration level to 1-5 times the estimated MDL. If the measured level is greater than the estimated detection limit, prepare a standard at a lower concentration. Alternatively, the standard may be used as is if the concentration of the standard does not exceed 10X the determined MDL (*i.e.,* the standard concentration is 0.5 μg/L and the determined MDL is 0.04 μg/L. Multiply 0.04 x 10 = 0.4 μg/L. Since 0.4 (10X the MDL) is less than 0.5 (the standard spike concentration), the spike level, or standard concentration, *does* exceed 10X the MDL. In this case the MDL must be repeated at a lower standard spike concentration). The Total Organic Carbon MDL standards have historically been prepared at a concentration of 3.00 mg/L and 10.00 mg/Kg.

3.1.3 A minimum of seven replicates are taken through the entire combustion and analytical procedures. Calculate the results in the appropriate units. Calculate any concentration found in the blank. If concentrations found in the blank exceed 2X the MDL, the MDL must be repeated.

3.1.4 Calculate the standard deviation of the seven replicate measurements. Multiply the standard deviation by the correct Students' T-Value, depending on the number

of replicates. For seven replicates, use 3.143 as the Student's T-Value constant.

3.1.5 To report the MDL, use the pre-prepared Excel spreadsheets on the Woods Hole Group (WHG) server. The following information must be supplied: Method name or number; Analyst; Analysis date; Units; Matrix; Instrument used; Concentration analyzed (true value spiked) and *all* of the actual values determined from the seven replicates and their file IDs; Mean concentration; Standard Deviation; Reporting Limit and the Calculated MDL. All supporting raw data and the MDL spreadsheets must be forwarded to the Quality Assurance Manager for review, acceptance and storage of the MDL data.

3.1.6 The MDL for Total Organic Carbon in an aqueous matrix as determined on 10/09/02 is 1.2932 mg/L. The MDL for Total Organic Carbon in a solid matrix as determined on 07/11/02 is 1.839 mg/Kg.

3.2 The Practical Quantitation Limit (PQL) or Reporting Limit (RL) is the level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. **For Total Organic Carbon, the PQL is 0.01% (or 100mg/Kg) for solid samples, and 3mg/L for aqueous samples.**

4.0 Scope and Application

4.1 The organic carbon in a sample consists of a variety of organic compounds in various oxidation states. Some of these compounds may be oxidized by biological or chemical processes and can be measured by the Biochemical Oxygen Demand or Chemical Oxygen Demand tests (see WHG SOPs W-012 for BOD and W-013 for COD). To measure the amount of organically bound carbon; the organic carbon molecules are broken down into single carbon units, and converted into a form that can be measured quantitatively.

4.2 The PE 2400 Series II CHNS/O Analyzer can simultaneously determine carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) in organic material. In the CHN mode, the PE 2400 Series II CHNS/O Analyzer uses a combustion method to convert the sample elements to simple gases (CO_2, H_2O, and N_2). The resulting gases are homogenized and controlled to exact conditions of pressure, temperature, and volume. The homogenized gases are allowed to de-pressurize through a column where they are separated in a stepwise steady-state manner and detected as a function of their thermal conductivity and reported as a percentage for solid samples, and in mg/L for aqueous samples. Treated with phosphoric acid prior to analysis, the Total Organic Carbon (TOC) content is determined by the amount of CO_2 in the sample. If the sample is analyzed

without pretreatment, the Total Carbon (TC) content is determined. Total Inorganic Carbon can be determined by subtraction of the TOC from the TC values.

4.3 This method is applicable to the measurement of TOC in solid samples ≥ 100mg/Kg or ≥ 0.01%, dry weight, and in aqueous samples ≥ 3mg/L. According to the instrument manufacturer, a sample of up to 70% carbon can be analyzed without dilution.

5.0 Summary of Method

5.1 Solid: A 2-5g solid sample is homogenized, dried at 103 - 105°C, re-homogenized, and the particle size is reduced by mortar and pestle. The sample is pre-treated with phosphoric acid to convert the inorganic carbon (*i.e.,* carbonate and bicarbonate in the form of CO_2) prior to analysis. The sample is re-dried at 103 - 105°C and a 1-10mg aliquot is removed for analysis, by weighing on the Microbalance, which is linked to the TOC analyzer.

5.2 Aqueous: Aqueous samples are collected HCl preserved, to a pH of ≤ 2. A 10mL aliquot of sample is transferred to a beaker and pretreated with phosphoric acid. A 1mL aliquot of treated sample is removed and dried at 103 - 105°C in pre-baked tin boat prior to analysis.

5.3 Organic carbon is measured using combustion and a carbonaceous analyzer. The sample is oxidized in a pure oxygen environment, introduced into a furnace by a 60-slot Autosampler, then combusted. The carrier gas (O_2) is combined with the carbon content of the combusted sample to form CO_2. Elements, such as halogens and sulfur, are removed by scrubbing reagents in the combustion zone. A thermoconductivity detector then measures the CO_2. The amount of CO_2 derived from a sample is directly proportional to the concentration of organic carbonaceous material in the sample.

6.0 Definitions

Accuracy
A determination of how close a measured value is to a known true value, usually measured as the percent recovery of a spike analysis.

Aliquot
A measured portion of a sample taken for analysis.

Analyte
The chemical element or compound an analyst seeks to determine; the chemical element of

interest.

Analytical Batch
The basic unit for analytical quality control, defined as samples that are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g., groundwater, sludge, and ash).

Analytical Sample
Any solution or media introduced into an instrument, on which an analysis is performed, excluding instrument calibration, initial calibration verification, initial calibration blank, continuing calibration verification, and continuing calibration blank. The following are all analytical samples: undiluted and diluted samples, pre-digestion spike samples, duplicate samples, post-digestion spike samples, laboratory control sample, and method blank sample.

Assessment
The evaluation process used to measure the performance or effectiveness of a system and its elements. Assessment is used as an all-inclusive term to denote any of the following: performance, systems, data and compliance audits, management systems reviews, peer reviews, inspections, or spot assessments.

Bias
A systematic (consistent) error in test results. Bias is expressed as the difference between the population mean and the true or reference value, or as estimated from sample statistics, the difference between the sample average and the reference value.

Blank
An artificial sample designed to monitor the introduction of artifacts into the measurement process. For aqueous samples, reagent water is used as a blank matrix. A universal matrix does not exist for solid samples; therefore, no matrix is routinely used. There are several types of blanks, which monitor a variety of processes: 1) A *method blank* is taken through sample preparation and analysis only. It is a test for contamination in the laboratory procedure. 2) An *instrument blank* (including initial and continuing calibration blanks) monitors any instrument drift during analysis. 3) A *field blank* is opened in the field and tests for contamination from the atmosphere as well as provides a test for contamination from sample preservation, site conditions, and transport as well as sample storage, preparation, and analysis.

Calibration
The systematic determination of the relationship of the response of the measurement system to the concentration of the analyte of interest. Instrument calibration performed before any samples

are analyzed is called the initial calibration. Subsequent checks on the instrument calibration performed throughout analysis are called continuing calibration. Calibration is also the act of making a scheduled comparison of instrument performance against national standards for instruments which measure physical parameters such as mass, time, and temperature.

Calibration Curve
The graphical relationship between the known values for a series of calibration standards and instrument responses.

Calibration Standard
A material used to quantitate the relationship between the output of a sensor and a property to be measured. Calibration standards should be traceable to Standard Reference Materials (provided by NIST, EPA, or other recognized standards agencies) or a primary standard.

Certified Reference Material
A reference material accompanied by a certificate issued by an organization certifying the contents and concentration(s) of the material. (See also Standard Reference Material.)

Colorimetric
Analyses based on the measurement of the color that develops during the test-specific reaction. The intensity of color development is proportional to concentration and is usually measured at a specified wavelength on a spectrophotometer.

Concentration
The amount of chemical (analyte) present per amount of sample. For trace analyses, usually expressed as ppm, ppb, or ppt.

Contract Laboratory Program (CLP)
A program coordinated through the EPA to provide a wide range of analytical services by commercial laboratories in support of investigation, remediation, and enforcement actions at Superfund sites. Laboratories participating in this program are under contract to the EPA and must follow very specific analytical protocols during analyses and data delivery, as specified in the Statement of Work associated with the contract.

Control Chart
A graphical representation of analytical accuracy. Displays the arithmetic mean of a data set, the upper and lower warning limits and the upper and lower control limits.

Corrective Action
A measure taken to rectify conditions adverse to quality and, where necessary, to preclude their

recurrence.

Correlation Coefficient
The correlation coefficient is a determination of how closely data "fits" a straight line. It is a number between –1 and 1 that indicates the degree of linear relationship between two sets of numbers.

Distillation
A procedure used to extract the analyte from the sample matrix.

Dry Weight
The weight of a sample based on percent solids. Also, the weight of a sample after drying in an oven at a specified temperature.

Error
The difference between an observed or measured value and its true value.

False Negative Result
A term used to describe a result that was incorrectly reported as "not detected". False negatives can be monitored by analysis of instrument blanks.

False Positive Result
A term used to describe a result that was incorrectly reported as present. False positives can be monitored by analysis of method and instrument blanks.

Field Blank
A blank that is prepared and handled in the field and analyzed in the same manner as its corresponding field samples.

Hazardous Waste
Waste regulated under RCRA that can pose a substantial or potential hazard to human health or the environment when improperly managed. Such wastes possess at least one of four characteristics (ignitability, corrosivity, reactivity, or toxicity) or appear on special hazardous waste lists. The term is not interchangeable with hazardous substance or material.

Holding Time
The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

Initial Calibration
Analysis of a series of analytical standards at different specified concentrations; used to define the linearity and dynamic range of the response of an instrument to the target compounds prior to the analysis of samples.

Linear Regression
A statistical method for finding a straight line that best fits a set of two or more data points, thus providing a relationship between two or more variables.

Material Safety Data Sheet (MSDS)
A compilation of information required under the OSHA Communication Standard on the identity of hazardous chemicals and their associated health and physical hazards, exposure limits and precautions.

Matrix
The component or substrate which contains the analyte(s) of interest. Examples of matrices are water, soil, sediment, and air. Matrix is not synonymous with phase (liquid or solid).

Matrix Effect
An interference in the measurement of analyte(s) in a sample that is caused by materials in the sample. Matrix effects may cause elevated reporting limits or may prevent the acquisition of acceptable results.

Matrix Spike (MS)
An aliquot of a matrix fortified sample spiked with known quantities of specific compounds and subjected to an entire analytical procedure. The percent recovery for the respective compound(s) is a measure of accuracy.

Matrix Spike Duplicate (MSD)
A second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

Method Blank
An analytical control consisting of all reagents, that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background contamination. Examples of method blanks are a volume of deionized or distilled laboratory water for water samples, a purified solid matrix for soil/sediment samples, or a generated zero air.

Method Detection Limit (MDL)
The minimum concentration of an analyte that, in a given matrix and with a specific method, can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Percent Recovery
A measure of accuracy determined from the comparison of a reported spike value to its true spike concentration.

pH
A scale of acidity/alkalinity running from 1.0 to 14. Low values (1-5) represent high acidity, middle values (5-8) neutrality and high values (9-14) high alkalinity.

ppb
Part-per-billion. A unit of measurement that expresses the amount of chemical present ('part') per the amount of sample analyzed ('billion'). For example, a 'ng' (nanogram or one billionth of a gram) per 'g' (gram) of sample is 1 ppb. More common units are µg/Kg (micrograms per kilogram for solids) and µg/L (micrograms per liter for liquids).

ppm
Part-per-million. A unit of measurement which expresses the amount of chemical present ('part') per the amount of sample analyzed ('million'). For example, a 'µg' (microgram or one millionth of a gram) per 'g' (gram) of sample is 1 ppm. More common units are mg/Kg (milligrams per kilogram for solids) and mg/L (micrograms per liter for liquids).

Practical Quantitation Limit (PQL)
The lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

Precision
The reproducibility of an analytical technique, usually measured by analysis of duplicates or duplicate spikes. Precision is usually expressed in terms of relative standard deviation or relative percent difference, but can be expressed in terms of the variance, range, or other statistic.

Preservative
A chemical or reagent added to a sample to prevent or slow decomposition or degradation of a target analyte or a physical process. Physical and chemical preservation may be used in tandem to prevent simple deterioration.

Quality Control (QC)
The physical procedures within the laboratory used to assess the quality of data (e.g., spikes, blanks, duplicates, calibration, etc).

Quantitative Analysis
An analysis that focuses primarily on the measurement of the amount of specific analyte(s) present in a sample.

Raw Data
All documentation associated with the original recording of analytical results pertinent to a specific sample or set of samples. This may include laboratory worksheets, calculation forms, instrument-generated output, analyst notes, etc., from sample receipt through final reporting.

Reference Standard
A chemical of known purity used as a reference ('standard') for the calculation of an analytical result.

Relative Percent Difference (RPD)
Statistic for evaluating the precision of a replicate set.

Solid Waste
Non-liquid, non-soluble, materials, ranging from municipal garbage to industrial wastes, that contain complex, and sometimes hazardous, substances. Solid wastes include sewage, sludge, agricultural refuse, demolition wastes, mining residues, and even liquids, and gases in containers.

Standard Operating Procedure (SOP)
A detailed written description of how a laboratory executes a particular procedure or method, intended to standardize its performance.

Standard Reference Material (SRM)
A material of which certain properties have been certified by the National Institute of Standards and Technology (NIST).

Stock Solution
A concentrated solution of analyte(s) or reagent(s) prepared and verified by prescribed procedure(s), and used for preparing working standards or standard solutions.

Subsample
A portion taken from a sample. A laboratory sample may be a subsample of a gross sample; similarly, test portion may be a subsample of a laboratory sample.

Traceability
The ability of an analytical standard material used for instrument calibration purposes to be traced to its source. The standards must be traceable via written documentation to sources which produce or sell verified or certified standards, i.e., National Institute for Standards and Technology, USEPA, or vendors preparing standards from those sources which they have certified.

Verification
The process of reviewing data to ensure that data reduction has been correctly performed and that analytical results to be reported correspond to the data acquired and processed.

7.0 Interferences and Pretreatments

7.1 To determine the TOC content, the inorganic fractions (carbonate and bicarbonate) must be removed prior to analysis by lowering the pH of the sample to ≤ 2. Care must be taken in sample pretreatment when removing the inorganic carbon, to minimize the potential of loss of volatile organic carbon present in the sample. However, in many surface and ground water samples, the volatile organic carbon contribution to TOC is negligible.

7.2 Maintaining the samples at 4°C, and analyzing within the specified holding time minimizes bacterial decomposition and volatilization of the organic material.

7.3 Elements, such as halogens and sulfur, are removed by scrubbing reagents in the combustion zone. Large and/or complex organic molecules such as tannins, lignins, or humic acids may be oxidized slowly. If these compounds are suspected to be present it is advisable to check the efficiency of the oxidation procedure with a selected representative sample, and adjust the analysis (sample size) as needed.

7.4 Chlorides at a concentration of greater than 0.1% may completely inhibit the oxidation of organic matter. The sample size may need to be adjusted to compensate for this interference.

7.5 Oils from skin, or contact with any organic material, such as plastic containers and rubber tubing, can contaminate samples. Handle the weighing tins with tweezers.

7.6 Sample heterogeneity can be a major source of imprecision in TOC results. Recommend to clients to perform a client-specific duplicate, to evaluate precision and representativeness of the TOC results to the site.

8.0 Health and Safety

8.1 The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices shall be followed at all times. Eating, drinking, smoking, or the application of cosmetics is not permitted in the laboratory area. Horseplay of any kind is prohibited. Pipetting by mouth is not permitted. All Personal Protective Equipment (PPE) must be removed before leaving the laboratory area and before entering the employee lounge or eating area. Always wash your hands before leaving the laboratory. All relevant Material Safety Data Sheets (MSDSs) are kept alphabetically in the centrally located file storage, in the common area outside of the Information Technology (IT) offices.

8.2 Approved PPE, which includes Safety Glasses, Gloves and Lab Coats, must be worn at ***all*** times when handling samples, reagents, chemicals, or when in the vicinity of others handling these items, so that dermal contact is avoided. All standards, reagents and solvents shall be handled under a hood using the proper PPE. All flammable solvents must be kept in the flammable storage cabinet, and returned to the cabinet immediately after use. When transporting chemicals, use a secure transporting devise and/or secondary outer container. Chemical storage is properly segregated and adequately ventilated to reduce the possibility of hazardous reactions. Chemical storage in work areas shall be kept to a minimum. Storage on bench tops or other work surfaces, except temporary, is not permitted.

8.3 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely defined; however, each chemical compound shall be treated as a potential health hazard. From this viewpoint, exposure to chemicals must be reduced to the lowest possible level by whatever means available. All standards and reagents shall be prepared in a hood while using the proper PPE

8.4 Spilled samples, solvents, reagents, and water must be cleaned up from bench tops, instruments and autosampler surfaces immediately. A spill is considered a quantity of hazardous material if it is two times greater than the normal working volume. Concentrated solvents, acids or bases present a moderate to extreme hazard to the skin and mucous membranes. If contact with the skin occurs, immediately flush with large volumes of water. In the case of acidic/basic spills, the *Spill Kit* located in each laboratory shall be utilized before attempting to cleanup the spill. Although procedures are designed to minimize the possibility of an accident, all injuries or accidents, regardless of the nature or severity, are to be reported to the Section Head Supervisor immediately. If an employee discovers a potentially unsafe condition, this must be reported to the Section Head Supervisor immediately. No employee should feel

compelled to work in a situation where they do not feel entirely informed, trained, or safe.

8.5 Analytical instrumentation poses the unique possibility of exposure to high voltages. Other than the *routine* instrument maintenance, as listed in the front of every Instrument Maintenance Logbook, at no time shall an instrument operator attempt to maintenance an instrument alone, or without the proper training, supervision or instruction. Caution must always be used in the presence of moving parts (autosamplers) and hot surfaces (injection ports).

8.6 All additional company safety practices shall be followed at all times as written in the WHG *Chemical Hygiene Plan.*

8.7 All TOC standard solutions must be handled with caution. See pages 5-3 through 5-5 of the PE 2400 Series II CHNS/O Analyzer User's Manual for additional and specific Warnings and Precautions.

9.0 Equipment and Supplies

9.1 Instrument: Perkin Elmer 2400 Series II CHNS/O Analyzer,

9.2 Detector: Thermal Conductivity,

9.3 Mortar and pestle,

9.4 Oven at 103° - 105°C, and Desiccator,

9.5 Class-A, volumetric flasks of various volumes,

9.6 Perkin-Elmer Microbalance, Model AD-6, linked to the instrument,

9.7 Tweezers (Anti-Magnetic),

9.8 Tin Boats (Small and Large),

9.9 Filter Aid 400 (High-density glass beads),

9.10 Gas-tight syringes of various measuring sizes, including 10μL for direct sample spiking,

9.11 Okidata Microline 320 Turbo-9 Pin Printer,

Note: All maintenance records including routine upkeep and outside service visits are maintained in the instrument maintenance logbooks. See the Manufacturers User's Manual for detailed troubleshooting instructions and routine maintenance, as needed.

10.0 Reagents and Standards

Use reagent grade chemicals for all reagents. Deionized (DI) water is ASTM Type II laboratory reagent grade water. All reagents and standards must be stored at 4°C and expire 6 months from preparation, unless otherwise indicated below. All reagents and standards must be documented in the Wet Chemistry Standard Logbook.

10.1 ASTM Type II Water: Boiled, cooled and capped to eliminate CO_2.

10.2 Phosphoric Acid solution: Add 20mL of H_3PO_4 to 400mL of ASTM Type II water. Mix thoroughly and cool to room temperature before use. Store in a glass bottle and keep at room temperature. This solution is stable for 6 months.

10.3 Potassium Hydrogen Phthalate (KHP): *Calibration Solution* (10,000mg/L equivalent to 10,000mg/Kg Carbon, or 1.0 % TOC). Dissolve 2.128g of potassium hydrogen phthalate (primary standard grade) in ASTM Type II water, and dilute to 100mL in a volumetric flask. This stock may be stored up to six months at 4°C. Discard solution if discoloration or any signs of bacterial growth are observed. **Note:** When preparing this solution for the *Lloyd Kahn* Calibration method, double the weight (4.256g) to 100mL in a volumetric flask for a 2% TOC solution. This will be the stock for the highest point of the calibration curve. Appropriate dilutions can then be made from this stock for the rest of the calibration curve outlined in Section 13.2.1.

10.4 Potassium Hydrogen Phthalate (KHP): *Spiking Solution* (10,000mg/L equivalent to10,000mg/Kg Carbon, or 1.0 % TOC). Dissolve 2.128g of potassium hydrogen phthalate (primary standard grade) in ASTM Type II water, and dilute to 100mL in a volumetric flask. *Use a separate source or different lot of KHP from that used to prepare the calibration standard.* This stock may be stored up to six months at 4°C. Discard solution if discoloration or any signs of bacterial growth are observed. Use at 1.0 % TOC concentration for solid samples, and at 10,000mg/L for aqueous samples.

10.5 Reporting Limit Standard: An appropriate dilution is made from the stock standard (Section 10.3), which is prepared to confirm the reporting limit for the given matrix (Section 3.2).

10.6 Solid Laboratory Control Sample/Independent Calibration Verification (LCS/ICV):

Standard Reference Material (SRM) NIST 1944, a separate source from the calibration standard that is certified at the concentration of 4.4% TOC for solid samples. For aqueous samples, an ERA QC Standard (ERA Catalog #: 669) containing TOC at varying concentrations (0.9-5.0mg/L) is purchased.

11.0 Sampling Collection, Handling, and Preservation

11.1 Sample collection is not applicable to the WHG laboratory operation.

11.2 Please see the *Sample Management* SOP (G-005) that describes the responsibilities of sample custody including all proper documentation, verification, and tracking procedures following Chain of Custody (COC) protocols, sample receipt procedures using the *Sample Receipt Checklist*, which includes the check for proper sample preservation and cooler temperature verification. SOP G-005 also describes how samples are normally shipped or obtained by the laboratory, precautions to be used in opening sample shipments, and sample storage conditions.

11.3 Internal COC procedures for sample tracking includes the use of sample tracking logbooks. Theses procedures are also described in the *Sample Management* SOP (G-005).

11.4 *Solid samples:* A minimum of 5 grams of sample must be collected in a glass jar. The samples must be refrigerated and maintained at 4°±2°C until drying and analysis. All solid samples (NOT requiring the *Lloyd Kahn* Calibration method) must be analyzed within 28 days from the date of collection. **Note:** If samples require the *Lloyd Kahn* Calibration method, the hold time is 14 days.

11.5 *Aqueous Samples*:

11.5.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.

11.5.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the time between sample collection and the start of analysis should be minimized. Also, samples must be maintained at 4°±2°C and protected from sunlight and atmospheric oxygen. In instances where the analysis cannot be performed within 2 hours from time of sampling, the sample is acidified to pH ≤2 with HCl (preferably in the field, by using pre-preserved

sample containers) and must be analyzed within 7 days from date of collection.

12.0 Quality Control

12.1 Initial Calibration:

12.1.1 Follow the instrument Manufacturers User's Manual for instrument set up and see Section 13.0 for an outline of the initial, daily, calibration procedure.

12.1.2 The correlation coefficient (r) of the initial calibration curve for the *Lloyd Kahn* Calibration method must be ≥0.995. The slope of line should be ±10% of historical curves.

12.1.3 Corrective Action: If the correlation coefficient or slope QC criteria are not met, the standard curve must be re-prepared and re-analyzed until the correlation coefficient and/or slope are acceptable.

12.1.4 *Routine* TOC analyses use K-Factors (3 repeat analyses of a 1.0% TOC standard, Section 10.3) and Blanks, calculated and averaged by the instrument when the calibration is being performed. Follow the instrument Manufacturers User's Manual, page 4-67. Calibration of the instrument using K-Factors and Blanks is performed once per day of analysis.

12.1.5 The K-Factors should reproduce from the mean value within +/-0.15% for carbon. The calculation involves the comparison among the latest K-Factor run, the prior K-Factor run, and the current running average K-Factor. An "out of tolerance" message will be displayed if this criteria is not met.

12.1.6 Corrective Action: If the K-Factors are not reproducible, run several more K-Factors to obtain a working average. If the K-Factors are still not reproducible, the cause may be the Blank value, the sample handling technique, or the weighing procedure. Run a few more Blanks to obtain reproducible Blank values and recalibrate the Microbalance, then re-weigh and re-analyze the K-Factor sample. See the Manufacturers User's Manual SOP, Section 1.1, page 3, for balance calibration instructions.

12.2 Method Blank

12.2.1 A method blank must be analyzed once per every 20 samples or per TOC batch, whichever is more frequent. The Blank consists of 30mg of Filter Aid.

12.2.2 TOC must not be detectable in the method blank at a concentration greater than the reporting limit for the given matrix (Section 3.2).

12.2.3 Corrective Action: Analysis of the method blank and all associated samples must be performed until the blank is in control. Samples cannot be analyzed until an acceptable method blank analysis is obtained. Exceptions may be made with approval of the Section Head, if the samples associated with the out of control method blank are non-detect for TOC, or if sample TOC concentrations are greater than 10X the blank levels. In such cases, the sample results are accepted without corrective action for the high method blank and the client is notified in a project narrative associated with the sample results.

12.3 Laboratory Control Sample (LCS)/Independent Calibration Verification (ICV)

12.3.1 Laboratory control sample (LCS or ICV) must be from a second source or lot number to verify the accuracy of the standard curve. The LCS/ICV is analyzed along with the samples. A LCS/ICV must be analyzed once per every 20 burns or per TOC batch, whichever is more frequent. For *solid* samples, the LCS is the NIST SRM at 4.4% TOC. For *aqueous* samples, the LCS is an ERA QC Standard prepared according to the vendor instructions, and purchased at a known concentration (0.9-5.0mg/L TOC). See Section 10.6 for details.

12.3.2 The acceptable recovery QC limits is 80%-120% for an aqueous LCS/ICV and 75%-125% for the solid LCS/ICV. Both the aqueous and solid recovery limits are continuously monitored and documented in-house through control charts which are updated semi-annually. The WHG SOP *Control Chart Generation* (G-013) provides details explaining how control charts are generated and used for quality control.

12.3.3 Corrective Action: Repeat analysis once to see if an analytical error has occurred. If the LCS/ICV recovery is still out of control, re-calibrate and re-analyze the LCS/ICV and all associated samples. Samples cannot be analyzed until an acceptable LCS/ICV is obtained. Exceptions may be made with approval of the Section Head if the samples associated with the out of control LCS/ICV are also associated with a matrix spike that is in control. This is an acceptable measure of accuracy of the analytical procedures. An explanation of this out of control LCS/ICV recovery must be included in the project narrative to the client and the sample data reported with the acceptable MS results as batch QC.

12.4 Matrix Duplicate (MD)

12.4.1 Duplicate analyses (matrix duplicate) must be performed once per 20 burns (5% frequency).

12.4.2 Acceptable relative percent difference (RPD) of duplicates is ≤ 25% for solid duplicates and ≤ 20% for aqueous duplicates. Acceptance criterion is not applicable to sample concentrations less than 5X the reporting limit. Calculate RPD as follows:

$$\%RPD = \frac{R1 - R2}{\frac{[R1 + R2]}{2}} \times 100$$

The RPD limits are continuously monitored and documented in-house through control charts which are updated semi-annually. The WHG SOP *Control Chart Generation* (G-013) provides details explaining how control charts are generated and used for quality control.

12.4.3 Corrective Action: Repeat analysis once to see if an analytical error has occurred. If the % RPD still exceeds the control limits; include a project narrative with the results to client noting that there may be potential matrix effects on the precision of the TOC results as evidenced by the matrix duplicate RPD exceedance.

12.5 Matrix Spike (MS)

12.5.1 A matrix spike must be performed once per 20 samples (5% frequency). When project specifications dictate, a Matrix Spike Duplicate (MSD) may also need to be performed at the same frequency as the MS. Prepare the MS according to Section 10.4 for the given matrix.

12.5.2 The acceptable recovery QC limits is 80%-120% for an aqueous MS/MSD and 75%-125% for the solid MS/MSD. Calculate the %RPD as in 12.4.2 above when analyzing a MS/MSD pair. The acceptable %RPD is ± 20% for aqueous samples and ±25% for solid samples. Both the aqueous and solid recovery limits and %RPD are continuously monitored and documented in-house through control charts which are updated semi-annually. The WHG SOP *Control Chart Generation* (G-013) provides details explaining how control charts are generated and used for quality control.

12.5.3 Corrective Action: Repeat analysis once to see if an analytical error has occurred.

If the % recovery or %RPD still exceeds the control limits and the LCS is compliant; include a project narrative with the results to client noting that there may be potential matrix effects on the accuracy or precision of the TOC results as evidenced by matrix spike recovery or %RPD outside of QC limits.

12.6 Continuing Calibration Verification (CCV) Check Standard

12.6.1 A CCV must be analyzed at a minimum of every 10 burns and at the close of an analytical sequence. 10µL of the 1.0 % TOC Calibration Solution (Section 10.3) is added to weighed and tared 30mg of Filter Aid (Section 9.9). This standard monitors instrument performance throughout the duration of the analytical run.

12.6.2 The acceptable recovery QC limit for the CCV is 80-120%.

12.6.3 Corrective Action: Repeat analysis once to see if an analytical error occurred. If the CCV still exceeds the control limits, re-calibrate and re-analyze all samples since last acceptable CCV.

12.7 Continuing Calibration Blank (CCB)

12.7.1 A CCB must be analyzed immediately after every CCV. The CCB is 30mg of Filter Aid.

12.7.2 The CCB concentration must not be greater than the reporting limit for the given matrix (Section 3.2).

12.7.3 Corrective Action: Repeat analysis once to see if an analytical error occurred. If the CCB still exceeds the control limits, re-calibrate and/or re-analyze a fresh blank. All samples associated with the out of control CCB must be re-analyzed (since the last acceptable CCB). Exceptions may be made with approval of the Section Head if the samples associated with the out of control method blank are non-detect for TOC or if sample TOC concentrations are greater than 10X the blank levels. In such cases, the sample results are accepted without corrective action for the high CCB and the client is notified in a project narrative associated with the sample results.

13.0 Calibration and Standardization

See the Manufacturers User's Manual, page 5-69, for the default instrument conditions when in the CHN operating mode.

13.1 *Routine* TOC Calibration Method:

13.1.1 The calibration requires 6 initial analyses: **1)** "Primer", a high percentage TOC sample, typically, approximately, 20mg of SRM 1944, **2)** 1st Blank, "B", 30mg of Filter Aid, **3)** 1st K-Factor, "K", 1% TOC standard and 30mg of Filter Aid, **4)** 2nd Blank, "B", **5)** 2nd K-Factor, "K", and **6)** 3rd K-Factor, "K". This is the order in which the samples are loaded into the Autosampler for combustion. All "Blanks" and "K-Factors" are prepared in the same way. Analyze the standards following the procedure in Section 14.2.

13.1.2 Corrective Action: If, at any time during the 6–step process of calibration, one of the K-Factors or Blanks fail, the calibration must be re-prepared and re-analyzed until the instrument accepts all factors as "in tolerance".

13.2 *Lloyd Kahn* Calibration Method: **Note:** The *Routine* instrument calibration procedure (Section 13.1) should be established before the Linear Regression method is used, otherwise, the best results will not be obtained.

13.2.1 Prepare a curve for *Lloyd Kahn* calibration as outlined below. Analyze each point of the calibration curve following Section 14.2. On an Excel spreadsheet, plot *Carbon (mg)* vs. *Instrument Response*, using four standards and a blank covering the analytical range of interest. See Section 10.3 for Calibration Standard preparation.

Blank = 30mg of Filter Aid
Point 1 = 0.1% (1,000mg/Kg) Standard added to 30mg Filter Aid
Point 2 = 0.5% (5,000mg/Kg) Standard added to 30mg Filter Aid
Point 3 = 1.0% (10,000mg/Kg) Standard added to 30mg Filter Aid
Point 4 = 2.0% (20,000mg/Kg) Standard added to 30mg Filter Aid

13.2.2 The correlation coefficient (r) of the initial calibration curve must be ≥0.995. The slope of the line should be ± 10% of historical curves. See Section 12.1 for Corrective Action in the event that the calibration curve does not meet the acceptance criteria. Additionally, see page 5-82 and 5-83 of the Manufacturers User's Manual for proper set-up of this calibration method.

13.3 The Microbalance calibration must be checked every day using 2.0mg - 200mg weights, in the range of daily use, and be accurate within +/1%. If the balance needs to be re-calibrated, see the Manufacturer User's Manual SOP, Section 1.1, page 3, for details.

14.0 Procedure and Data Evaluation

Samples are prioritized by the Section Head for analysis based on hold time and client due date. Section 15.5 outlines the steps for final TOC reporting that will contain the sample analysis final results.

14.1 Pretreatment for Total Organic Carbon:

This procedure is used to remove the inorganic compounds in the sample prior to the determination of Total Organic Carbon. If Total Carbon is to be determined, addition of the phosphoric acid solution is omitted.

14.1.1 Solid Samples:

14.1.1.1 Aliquot 2-5g of pre-dried (103°-105°C) solid sample into an aluminum weigh dish. (This aliquot may be taken from the Percent Solids Determination aliquot, assuming Percent Solids have already been performed).

14.1.1.2 Add Phosphoric Acid Solution (Section 10.2) drop wise to the solid sample in the tin dish and check for effervescence. If effervescence is observed, continue adding drop wise until the effervescence stops to ensure removal of inorganic carbon compounds (carbonate and bicarbonate). Report any excessive effervescence or change in sample consistency to the client in the project narrative.

14.1.1.3 Place the tin dish containing the treated sample into the drying oven at 103°-105°C until dry. Remove the tin and place in a desiccator to cool. The sample is considered dry when the weight change is less than 4%, or 50mg of a previous weight, whichever is less. Samples may need to dry overnight in the oven.

14.1.2 Aqueous Samples:

14.1.2.1 Transfer 10mL of aqueous sample to a beaker and add phosphoric acid solution (Section 10.2) drop wise to reduce the pH $\leq$ 2, then stir vigorously. Because volatile organic carbon will be lost during the stirring of the acidified solution, aqueous organic carbon is reported as total non-purgeable organic carbon.

14.1.2.2 Tin boats must be pre-baked at 180°C for 30 minutes. 1mL of sample is transferred into a large tin boat, using a syringe, and placed into the drying oven at 103°-105°C until dry. Remove the tin and place in a desiccator to cool. The sample is considered dry when the weight change is less than 4%, or 50mg of a previous weight, whichever is less. Samples may need to dry overnight in the oven.

14.2 Weighing Samples and Loading the Instrument:

14.2.1 Removed all pretreated samples from the oven, and allowed to cool in a desiccator. Confirm that a constant weight has been achieved as in Sections 14.1.1.3 and 14.1.2.2. Go directly to Section 14.2.4 for aqueous samples.

14.2.2 The solid samples must be ground using a mortar and pestle into a fine powder, without grinding shells, rocks or other large non-representative material. Carefully pick these materials from the sample with tweezers. Transfer the ground, pre-treated solid sample to a 5.0mL glass vial labeled with the sample ID. Only fill the vial to approximately 2/3 full, the remainder may be discarded.

14.2.3 Weigh approximately 2-10mg of sample using the Perkin-Elmer Microbalance, Model AD-6, which is linked to the instrument. See the Manufacturer User's Manual SOP, Section 1.2, pages 3-4, for Microbalance and weighing instructions. Samples that are known to be high in TOC may be aliquoted at a lesser weight. Each sample must be weighed in duplicate. *Check the paperwork carefully as often 3 replicate analyses are specified by the client.* Matrix Duplicate and Matrix Spike samples are weighed as separate samples, with their own replicates or triplicates.

14.2.4 Each tin boat must be carefully folded with anti-magnetic tweezers, and placed into its respective holding tray position. See the Manufacturer User's Manual SOP, Section 1.2, page 4, for tin boat folding details. Weights must be recorded in the TOC logbook, along with the sample tray position and Autosampler location. The analyst must be very careful when transferring samples. Documentation of sample consistency is very important. See Section 23.0 for an example logbook page.

14.2.5 A Method Blank, ICV/LCS, CCV/CCB, Matrix Spike, and Matrix Duplicate must be analyzed with each analytical batch at the frequency listed in Section 12.0, Quality Control.

- A **Method Blank, CCB, or Instrument Blank** consists of 30.0mg of Filter Aid.

- A *solid* **ICV/LCS** consists of approximately 3.0-5.0mg of SRM 1944, with a true value of 4.4% TOC. An *aqueous* **ICV/LCS** consists of 1mL of ERA QC Standard, with a certified value of 0.9-5.0mg/L. See Section 10.6 for details.

- A *solid* **Matrix Spike** sample is spiked with 10µL of *Spiking Solution*, at a 1.0 % TOC true value. An *aqueous* **Matrix Spike** sample is spiked with 10µL of *Spiking Solution*, at a 10,000mg/L concentration for a true value of 100mg/L. See Section 10.4 for details. The weight or volume recorded is the sample weight or volume, prior to spiking.

- A **Matrix Duplicate** sample is weighed to represent its sample in consistency, and weight.

- A **CCV** is approximately 10.0mg of tared Filter Aid weighed and spiked with 10µL of *Calibration Solution*, with a 1% TOC true value. (See Section 10.3). The weight recorded is the Calibration Solution, only. (10µL of solution should weigh approximately 10mg).

14.2.6 Daily Instrument Sequence:

On the accompanying computer, or "PC", Perkin Elmer software has been loaded to collect and save sample and standard analysis data. Create a file to store the data from each day's analytical sequence by clicking on the PE 2400 icon, go to "new" and "save" the file "as" the name of the date of the analysis (*i.e.,* 060503.chn). Data from each standard or sample analysis will be automatically stored in this file for future reference.

- **Instrument "Primer"** (~20.0mg of SRM 1944, with true value of 4.4% TOC)

- **Blank 1** (30.0mg of Filter Aid)

- **K-Factor 1** (10µl of *Calibration Solution*, Section 10.3, into tared Filter Aid) The weight recorded is the Calibration Solution, only.

- **Blank 2** (30.0mg of Filter Aid)

- **K-Factor 2** (10µl of *Calibration Solution*, Section 10.3, into tared Filter Aid) The weight recorded is the Calibration Solution, only.

- **K-Factor 3** (10µl of *Calibration Solution*, Section 10.3, into tared Filter Aid) The weight recorded is the Calibration Solution, only.

14.2.7 The first set of batch QC samples, the ICV/LCS and Method Blank, are prepared to run immediately following the third K-Factor, given the instrument is "in tolerance". Field samples follow these QC samples, with a CCV/CCB analyzed every 10 "burns", and at the end of the analytical sequence.

14.2.8 If following the *Lloyd Kahn* Calibration method, it is suggested by the Manufacturer to follow the third K-Factor analysis with a Blank, and the four additional standard points from Section 13.2.1, to create the calibration curve for Linear Regression analysis. Follow the *Lloyd Kahn* Calibration with the first set of batch QC samples, the ICV/LCS and Method Blank, followed by field samples with a CCV/CCB analyzed every 10 "burns", and at the end of the analytical sequence.

14.3 Multiple Sample Instrument Loading:

14.3.1 Adjust the Autosampler tray to begin sampling at auto-slot #1 and carefully transfer the folded tins containing the samples to the correct auto-slot, using tweezers. All Instrument Calibration Standards (Blanks, K-Factors and/or *Lloyd Kahn* Calibration Standards) should be loaded first. Immediately following will be the first batch QC samples, the ICV/LCS and Method Blank for the run, followed by field samples. Rotate the Autosampler in a *counter clockwise* manner.

14.3.2 A maximum of 60 tins can be held on the Autosampler at one time. The instrument only allows for 100 total samples (including calibration/blank samples) to be programmed for any given run.

14.3.3 Select the *Auto Run* option on the keypad on the instrument. The following menu appears:

AUTO RUN NO. 1
1B 2K 3S

where: B = Blank
K = K-Factor
S = Sample

14.3.4 Assuming the *Instrument Standardization* occupies auto-slots 1-6, Enter "3" for Sample, then select "Enter". Enter the weight of the "Primer" Standard (position 1) and select "Enter".

14.3.5 You should now be prompted for AUTO RUN NO. 2 as in 14.3.3, except now there is a function "4NP" which allows the analyst to stop/erase everything by selecting this feature. Enter "1" for the Blank. The weight will not be asked for.

14.3.6 Enter "2" for the first K-Factor, then select "Enter". Enter the weight of your K-Factor (the standard weight should be ~ 10mg). Select "Enter".

14.3.7 Enter "1" for the second Blank, then "Enter".

14.3.8 Enter "2" for the second K-Factor, then "Enter". Enter the weight, then "Enter".

14.3.9 Enter "2" for the third K-Factor, then "Enter". Enter the weight, then "Enter".

14.3.10 All remaining sample weights will be added by entering "3" for Sample, and then by entering the sample weight. Continue adding all information to the run sequence, using the keypad. When entering sample identification, and letters are necessary, refer to the Manufacturer's User's Manual, page 3-4, for instructions for converting numbers to letters.

14.3.11 When all sequence information is entered and complete, select "Start". The analyses will begin. The computer will continue to display the "AUTO RUN" menu during sample analysis.

14.3.12 Standard and sample data prints out as it is collected on the line printer, and is also collected on the linked computer using the PE 2400 software. The data on the computer is saved in a file named as the date of the analysis (*i.e.,* 060503.chn) for future reference, as noted in 14.2.6.

14.3.13 When all analyses are complete, refer to the Manufacturers User's Manual SOP, Section 3.1, page 7, for instructions to "Shut Down" the instrument.

14.4 Evaluate all batch QC samples first, to confirm or exclude the need for re-analyses. The ICV/LCS, Method Blank, CCB/CCV samples must meet the acceptance criteria in Section 12.0. Follow the corrective action for any QC failures.

14.5 Evaluate the field samples next. If duplicate or triplicate "burns" of the same sample

appear inconsistent, or vary by more than 50%, re-weigh a sample aliquot similar to the initial weight used, and re-analyze the sample. If inconsistencies persist, report this observation in the project narrative to the client.

15.0 Calculations and Reporting

15.1 Procedures for data and record management for TOC analysis must adhere to the Quality Systems Manual, other subordinate documents covering record keeping, and the *Document Control* SOP, G-016. All records shall be stored in such a manner as to be safe and accessible for at least 10 years.

15.2 The relevant TOC laboratory notebooks must follow the specifications in the *Laboratory Notebook Usage* SOP, G-009, and all record keeping and document control practices.

15.3 Sample results for TOC are directly reported from the instrument printout, for solid samples as a percentage of TOC, and as mg/L of TOC, for aqueous samples.

15.4 The following calculations are applied by the instrument when determining the percentage of Total Organic Carbon:

Carbon Blank (CB): Used to make all other determinations, namely, K-Factor and weight percent calculations. When run alternately with samples, the instrument averages the blank values.

Carbon Blank (CB) = Carbon Read – Nitrogen Read

Carbon K-Factor (C KF): K-Factor, or detector calibration factor, is determined when a known standard is analyzed to calibrate the analyzer in terms of micrograms of carbon. This calibration factor is then used to determine unknowns.

C KF = ((CR – NR) – CB x 100) / (SW x C Theory Wt. %)

where: CR = Carbon Read
NR = Nitrogen Read
CB = Carbon Blank
SW= Sample Weight (mg)
C Theory Wt % = 1% (based on the concentration of the K-Factor standard)

Carbon Weight Percent:

Carbon Weight Percent = ((CR – NR) – CB) x 100) / (SW x C KF)

where: CR = Carbon Read
NR = Nitrogen Read
CB = Carbon Blank
SW = Sample Weight (mg)
C KF = Carbon K-Factor

Example Calculation of Percent TOC from the instrument, converted to mg of TOC:

If, the result from the instrument is 1.083% and the sample weight is 10.76mg:

1.083% = 100 x [**X** / 10.76mg] (to solve for **X,** divide each side by 100)
0.01083 = **X** / 10.76mg (multiply each side by 10.76mg)
0.116mg = **X**

15.5 The following procedures must be followed for reporting of TOC results:

- Go to the next page in the bound TOC logbook. See Section 23.0 for an example.
- Enter the analyst initials, date, sample ID #'s, sample weights (solids), or volumes (aqueous), of all Standards, QC samples and field samples, onto the logbook. Include the standard, LCS and MS IDs and concentrations.
- Perform sample pretreatment and analysis as per this SOP. Retain all computer printouts for the standard and sample analyses of this sequence.
- Print the sequence from the computer and review it to make sure that no weight or sample ID transcription errors were made.
- Calculate the recoveries for the QC samples (IVC/LCS, CCV, MS and RPD between the duplicate samples) and ensure the Method Blank and CCB meet the criteria. Remember any "QC Failures" require corrective action. See Section 19.0, below, or 12.0.
- After reviewing the final logbook entries, make a copy of the logbook page for secondary review.
- Go to the LIMS and "batch" and "associated" the set of QC samples and field samples that were just analyzed.
- Enter the Final Results into the LIMS report sheet and check for transcription errors.
- Transfer, all associated sample paperwork, to the Section Head for the second

level review and approval.

16.0 Method Performance

16.1 Initial Demonstration of Proficiency (IDP) is determined by every new analyst during training, and before actual sample analysis. The IDP consists of the preparation and/or analysis of four replicate samples spiked at approximately 10X the TOC MDL. This process ensures the competency of the individual analysts

16.1.1 The following information needs to be supplied to the QA Manager for reporting and acceptance of TOC IDP: The *Training Checklist* must be completed by the trainer and the analyst, and supplied with all of the supporting raw data including, calibration standards, and method blanks in order to reconstruct and validate these analyses. The QA Manager will enter the information on to the individual employee spreadsheet. The following information is entered: preparation or analysis date, method name or number, blank ID, the four replicate file IDs, mean recovery, standard deviation and a comparison against the control limits, for precision and accuracy. The aqueous limits are 80%-120%, and the soil limits are 75%-125%.

16.1.2 If any parameter does not meet the control limits, the QA Manager will notify the Section Head and the analyst. The analyst must repeat the IDP until all criteria are met.

16.1.3 Upon successful completion of the IDP, *The IDP Certification Statement* form will be completed by the analyst, and signed-off by the Laboratory Director and the QA Manager. All of the above information will be retained in the employee-training file kept by the QA Manager.

17.0 Pollution Prevention

See Section 21.0, Waste Management for a discussion on Pollution Prevention.

18.0 Data Assessment and Acceptance Criteria

All TOC results are reportable without qualification if analytical holding times are met, preservation (including pH and cooler temperatures) are met, all QC criteria defined in the table below are met, and matrix interference was not suspected during analysis of the TOC samples. If any of the below QC parameters are not met, all associated samples must be evaluated for re-analysis.

QC Parameter	Acceptance Criteria
Initial Calibration Curve, *Lloyd Kahn*	r ≥ 0.995 and slope ± 10% the historical curves
Initial Standardization (K-Factor)	±0.15% from average of previous K-Factors
Method Blank	< reporting limit for matrix
Laboratory Control Sample	80-120% R for aqueous, 75-125% R for solid
Matrix Duplicate	20%RPD aqueous, 25%RPD solid, for results <5x reporting limit
Matrix Spike	80-120% R for aqueous, 75-125% R for solid
Matrix Spike Duplicate if requested	80-120%R/20%RPD for aqueous, 75-125%R/25%RPD for solid
Continuing Calibration Verification	80-120% of True Value
Continuing Calibration Blank	< reporting limit for matrix

19.0 Corrective Actions for Non-Compliant Data

Section 12.0, Quality Control, defines the corrective actions that must be taken in instances where QC outliers exist. If the corrective actions have been followed and the data is still unacceptable, reference Section 20.0, Contingencies for Handling Unacceptable Data, for guidance on reporting.

20.0 Contingencies for Handling Unacceptable Data

Section 18.0 outlines sample batch QC acceptance criteria. If non-compliant TOC results are to be reported, the Section Head and/or the Laboratory Director, and the QA Manager must approve the reporting of these results. The laboratory Project Manager shall be notified, and may chose to relay the non-compliance to the client, for approval, or other corrective action, such as re-sampling and re-analysis. The analyst or Section Head performing the secondary review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

21.0 Waste Management

The Woods Hole Group *Hazardous Waste and Sample Disposal* SOP (G-006), must be referenced for disposal of used standards, solvents, acids, reagents or other chemicals.

21.1 Once satisfactory TOC results have been generated, the sample containers must be logged back into *Internal Tracking Logbook* and returned to the appropriate sample refrigerator and held for 30 days.

21.2 All waste generated must be transferred to the waste disposal area. Dispose all solid samples in solid waste container. Aqueous samples must be poured into a 55-gallon drum marked acidic/non-chlorinated waste.

22.0 References

References in addition to the Total Organic Carbon and analytical test methods listed in Section 1.0. Identification of Test Methods, used to create this SOP, include the following:

22.1 EPA/600/R-96/027, *Guidance for the Preparation of Standard Operating Procedures (SOPs) for Quality Related Documents*, 1996.

22.2 EPA, 40CFR, Part 136, Appendix B, 7/1997.

22.3 National Environmental Laboratory Accreditation Conference (NELAC) Standard, Chapter 5, 7/1999.

22.4 Smith, Roy-Keith, *Handbook of Environmental Analysis,* 4th Edition, 1999.

23.0 Tables, Diagrams, Flowcharts and Data Validation

TOTAL ORGANIC CARBON
415.1 / 9060 (mod.) / Lloyd Kahn

Date: _____ Standard ID: _____ MS ID: _____
Analyst: _____ 2° Review: _____ LCS ID: _____

ETR	SAMPLE	QC D/MS	TRAY LOCATION	AUTO SLOT	WEIGHT
Conditioning Std					
Blank					
K Factor					
Blank					
K Factor					
K Factor					
LCS					
Blank					
CCV					
CCB					

ETR	SAMPLE	QC D/MS	TRAY LOCATION	AUTO SLOT	WEIGHT
CCV					
CCB					
CCV					
CCB					

Page: _____

APPENDIX D

PAH FORENSICS QUALITY ASSURANCE PROJECT PLAN

WORK/QUALITY ASSURANCE PROJECT PLAN
FORENSIC SEDIMENT SAMPLE ANALYSIS
PORTSMOUTH NAVAL SHIPYARD
KITTERY, MAINE

August 2005

prepared for

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TABLE OF CONTENTS

1. General Information 2
2. Technical Approach 3
3. Sample Collection and Laboratory Subcontractor 4
4. Sample Preparation 5
5. Sample Analysis 8
6. Hydrocarbon Interpretation and Reporting 14
7. References 15

1. GENERAL INFORMATION

Project Name:	Portsmouth Naval Shipyard		
Project Number:	112GN1292-0000.9701 (Tetra Tech NUS, Inc.)		
Client:	Tetra Tech NUS, Inc. 600 Clark Avenue, Suite 3 King of Prussia, PA 19406-1433		
QAPP Effective Date:	August, 2005		
Revision Number:	1.0		
Project Manager:	Aaron Bernhardt		
Prepared by:	Elizabeth Porta	Date:	07/11/2005
Reviewed by:	Stephen Emsbo-Mattingly	Date:	07/12/2005
Laboratory Due Date:	Net 30 days from sample receipt		
Final Report:	Net 30 days from receipt of the final laboratory deliverable		

2. TECHNICAL APPROACH

Pursuant to the Tetra Tech NUS, Inc. Statement of Work (SOW), Woods Hole Group Environmental Laboratories (WHG) will identify sources of petroleum contamination in samples from Portsmouth Naval Shipyard (PNS), Kittery Maine, in selected monitoring stations.

It is our understanding that Tetra Tech NUS, Inc. will arrange for the collection of the forensic samples. Based on the SOW (Attachment A, Subcontract No. 1001227, 01/04/2005), we understand that samples will be collected as follows:

- MS-01 (sediments)
- Site 34 (ash)
- MS-12 (sediments)
- Offshore Monitoring Program reference stations (sediments)
- Catch basin or outfall (sediments)
- Microscopy (sediments)

The field samples will be analyzed by specialized forensic analytical methods that have been used successfully in the past to determine the origins of PAHs in sediments (Emsbo-Mattingly et al., 2002; Stout et al., 2002; Stout et al., 2003; Stout et al., 2004). These methods include:

- High Resolution Hydrocarbon Fingerprints
- Alkylated PAHs
- Biomarkers
- Total Organic Carbon (TOC)

Based on the available chemistry and historical data, NewFields will determine the likely origin(s) of PAHs in these samples. Although not yet identified, historical activities around the site indicated that potential origins of PAHs might be the result of sources from upland Installation Restoration sites, boat maintenance activities, former/continuing ship fueling operations and urban runoff. Consequently, the sampling program will emphasize these PAH sources. The conclusion of this investigation will attempt to answer four primary questions:

- Is the ash associated at Site 34 the source of the PAHs in the sediment at monitoring station MS-01, and if not, what are the potential sources of PAHs in the sediment in this area?
- Are there particles in the sediment (i.e., ash, coal, etc.) that could be contributing to the elevated levels of PAHs in the sediment at MS-01?
- Is Building 178 (located next to MS-12) the source of PAHs in the sediment at MS-12, and if not, what are the potential sources of PAHs in the sediment in this area?
- Are there particles in the sediment (i.e., ash, coal, metal debris, etc.) that could be contributing to elevated levels of PAHs and/or lead in the sediment?

3. SAMPLE COLLECTION AND LABORATORY SUBCONTRACTOR

Sediment samples will be collected in hydrocarbon free 8-oz clear wide mouth jars – 4-oz jars are also acceptable. Tetra Tech NUS, Inc. will provide the required sampling containers, coolers, and chain of custody records.

The samples will be chilled immediately after collection. The samples will be wrapped in a sufficient quantity of bubble wrap to prevent sample container breakage. The shipping cooler will be packed with ice that is double-bagged in zip-lock freezer bags for next day shipment.

The sample delivery address is:

Ms. Liz Porta
Woods Hole Group Analytical Laboratories
375 Paramount Drive, Suite 2
Raynham, MA 02767
Tel: 508-822-9300
Fax: 508-822-3288
Email: eporta@whgrp.com

The field team will fax copies of the COCs to Liz Porta within 24 hours of sample release to the courier. Saturday delivery is subject to availability by the laboratory and must be confirmed at least 48 hours prior to shipment.

4. SAMPLE PREPARATION

The analytical laboratory will handle each sample according to the provisions in Table 1. The sediment samples will be serially extracted using EPA 3550, modified for a shaker table as per NOAA methods for the Status and Trends program (Peven and Uhler, 1998; WHG SOP OP-013). The nominal sample size will be 30 g wet weight. Excess water will be removed by centrifuge and decanting until the each sample is greater than 50% solid. Thereafter, a 5-g aliquot will be dried to determine the percent solid content (WHG SOP W-001).

After the percent solid content is determined, approximately 0.5 g of the dried sample will be ground, acidified with phosphoric acid, re-dried, and analyzed for total organic content (TOC). This procedure will be repeated a second time in order to generate replicate independent burns for each sample. The average of the two replicate samples will be the TOC concentration for the forensic interpretation.

Table 1. Summary of Analytical Parameters.

Matrix	Parameter/ Reference Method	Laboratory SOP	Container/Storage	Holding Time
Sediment	High Resolution Hydrocarbon Fingerprint (EPA 8015)	TPH-8100 Rev 1.1 07/15/1999	4oz/8oz Wide Mouth Glass Store Below 6°C	Extraction: 14 d from collection Analysis: 40 d from preparation
Sediment	Alkylated PAHs (EPA 8270)	O-008 Rev 2.0 07/25/2002	4oz/8oz Wide Mouth Glass Store Below 6°C	Extraction: 14 d from collection Analysis: 40 d from preparation
Sediment	Biomarkers (EPA 8270)	O-008 Rev 2.0 07/25/2002	4oz/8oz Wide Mouth Glass Store Below 6°C	Extraction: 14 d from collection Analysis: 40 d from preparation
Sediment	Total Organic Carbon (TOC) (EPA 9060)	W-028 Rev 2.0 1/22/2003	4oz/8oz Wide Mouth Glass Store Below 6°C	Analysis: 28 d from collection

After physically separating the free water from the sample, the remaining moisture will be removed by mixing with sodium sulfate until the sample flows like sand. The resulting sample (nominal 30g, wet weight) will be spiked with surrogate (Table 2) and serially extracted three times (6 hrs for 1st extraction, 2 hrs for 2nd extraction and 30 minutes for 3rd) with 100-mL dichloromethane (DCM). Three extracts will be combined into an Erlenmeyer flask after filtering through a powder funnel containing glass wool plug and sodium sulfate. The sample extract will be concentrated to 1 mL using Kuderna Danish apparatus and nitrogen blow down. The sample extract will be treated with activated copper to remove sulfur. The extract will then be quantitatively transferred a 4 mL vial with a Teflon lined septa. During this process, the final volume will be adjusted to 1.8 mL with DCM.

The concentrated extract will be split into two portions with the following volumes: 0.9 mL for analysis by GC/FID plus PAHs and 0.9 mL for fractionation. Section 5 details the analytical procedure for the GC/FID and PAH methods. The remaining 0.9 mL sample extract will be solvent exchanged to hexane and fractionated on a 5 g silica gel column. The aliphatic fraction will be concentrated to 0.9 mL and transferred to the GC/MS laboratory for biomarker analysis.

Table 2. Quality Control Spiking Schedule for Extracted Samples

Mixture	Applicability	Content in DCM Solvent	Spike Volume
FID Surrogate	All Field and QC Samples	o-Terphenyl 500 ng/µL Tetracosane-d50 500 ng/µL	100 µL
PAH Surrogate	All Field and QC Samples	2-Methylnaphthylene-d10 10 ng/µL Pyrene-d10 10 ng/uL Benzo(b)fluoranthene-d12 10 ng/µL	100 µL
Biomarker Surrogate	All Field and QC Samples	5(β)H-Cholane 10 ng/µL	100 µL
FID Analyte Spike	LCS and MS Samples	Selected n-C_9 to n-C_{36} Normal Alkanes 500 ng/µL	100 µL
PAH Analyte Spike	LCS and MS Samples	Priority Pollutant PAH 10 ng/µL	100 µL

Each sample batch will have several QC parameters with which to assess data quality. An analytical batch is defined as 20 or fewer samples prepared or analyzed per day. The associated QC parameters are described in Table 3 for extracted samples and Table 4 for TOC samples. All of the batch QC samples will be analyzed by all methods regardless of the applicable performance criteria. Corrective actions are listed in the approximate order of execution. The WHG Project Manager can adjust the corrective actions based on the needs of the interpretation.

Field samples will be stored for 6 months after the laboratory report is delivered to NewFields for forensic interpretation. Analyzed samples and extracts can be discarded after the holding time. Laboratory records will be archived for a minimum of 5 years.

Table 3. Sample Preparation QC Parameters for Extracted Samples

QC Parameter/Purpose	Data Quality Objective (DQO)	Corrective Action
Surrogate Recovery/ Accuracy measured as the sample specific extraction efficiency	50% - 130% Recovery	Review Integration Evaluate Coelution Potential Review with Project Manager Re-Extract and Analyze to Demonstrate Matrix Effect
Procedural Blank/ Accuracy relative to bias from background conditions in the lab	Less than sample equivalent of low calibration standard 5x less than detected analyte concentration in field samples	Review Integration Evaluate Ret Time Shift Review with Project Manager Re-Extract and Analyze Batch if within calibration range and 5x sample concentration Flag sample hits within 5x the blank concentration
Laboratory Control Sample/ Accuracy for Target Analytes	50% - 130% Recovery For FID and PAH Analytes	Review Integration Evaluate Ret Time Shift Review with Project Manager Re-Extract and Analyze Batch
Duplicate/ Precision for target analytes	Less than 30% RPD	Review Integration Evaluate Coelution Potential Review with Project Manager Flag outliers within the calibration range
Matrix Spike/ Accuracy for target analytes in native sample matrix	50% - 150% recovery for 90% of the analytes spiked >5 times native sample	Review Integration Evaluate Coelution Potential Review with Project Manager Flag outliers within the calibration range

Table 4. QC Parameters for TOC Samples

QC Parameter/Purpose	Data Quality Objective (DQO)	Corrective Action
Procedural Blank/ Accuracy relative to bias from background conditions in the lab	Less than sample equivalent of low calibration standard 5x less than detected analyte concentration in field samples	Review Instrument Data Review with Project Manager Re-Analyze Batch if within calibration range and 5x sample concentration Flag sample hits within 5x the blank concentration
Duplicate/ Precision for target analytes	Less than 20% RPD	Review Instrument Data Review with Project Manager Flag duplicate outlier within the calibration range
Standard Reference Material/ Accuracy for target analyte	50% - 130% Recovery	Review Instrument Data Review with Project Manager Re-Analyze Batch

5. SAMPLE ANALYSIS

The concentrated sample extracts will be spiked with internal standard at a rate of 100 µL of internal standard mix for every 900 µL of sample extract (Table 5). Whenever possible, the internal standard will be added to the extract in the sample preparation laboratory immediately after concentration. The resulting mixture yields a 1.0 mL working extract volume for the respective analytical laboratories with a 1:2 split of the final extract volume; i.e., a 2.0 mL final extract volume with a 1.0 mL split for FID/PAH and a 1.0 mL split for biomarkers. The analyst will remove 150 µL of working extract for each analysis using a 250 µL gas tight syringe and transfer to a low volume insert equipped with an aluminum crimp cap. The remaining extract will be stored in a 2 mL screw cap vial with a Teflon® liner.

High resolution hydrocarbon fingerprints will be generated from a concentrated sample extract using a gas chromatograph equipped with a flame ionization detector (GC/FID, EPA Method 8015B modified). The resulting chromatogram will focus on the hydrocarbon elution range from nonane (n-C_9) to tetracontane (n-C_{40}). This range includes many possible hydrocarbon source materials (i.e., #2, #4, and #6 fuels, coal tars, asphalt residues, and others). The concentration of total extractable hydrocarbon material (TEM) will be calculated for each sample.

Table 5. Internal Standard Spiking Schedule.

Mixture	Applicability	Content in DCM Solvent	Spike Volume
FID Internal Standard	All Field and QC Samples	5a-Androstane 500 ng/µL	100 µL
PAH Internal Standard	All Field and QC Samples	Acenaphthene-d10 5 ng/µL Chrysene-d12 5 ng/uL	100 µL
Biomarker Internal Standard	All Field and QC Samples	Acenaphthene-d10 5 ng/µL Chrysene-d12 5 ng/uL	100 µL

Based on the results of the GC/FID analyses, a subset of samples will be identified for further analysis of PAHs and Biomarkers. A second aliquot of the concentrated extract will be analyzed for selected PAH isomers and alkylated groups (Table 6) on a gas chromatograph equipped with a mass spectrometer operated in selected ion monitoring mode (GC/MS/SIM, EPA Method 8270B modified). This method replaces the SPCC, CCC, and retention time check criteria with pattern recognition techniques and independent reference sample evaluation criteria. These data will help differentiate petroleum and combustion derived PAH sources.

The fractionated extract will be analyzed for selected biomarkers (Table 7) and associated biomarker fingerprints on a gas chromatograph equipped with a mass spectrometer operated in selected ion monitoring mode (GC/MS/SIM, EPA Method 8270B modified). These biomarker patterns help identify and match petroleums based on the petroleum formation from which the materials ultimately originated.

Finally, total organic carbon (TOC) will be measured using EPA Method 9060. This method will help identify the presence of large molecular weight organics that do not chromatograph well (e.g., asphaltines).

Analytical quality control (QC) parameters will be associated with every analytical instrument sequence (Table 8). Corrective actions are listed in the approximate order of execution. The WHG Project Manager can adjust the corrective actions based on the needs of the interpretation.

The laboratory data will include hardcopy and electronic data deliverables (EDD). The hardcopy will include the sample preparation and analytical records. The scale of the high resolution hydrocarbon fingerprints (GC/FID) will start immediately after the solvent peak and extend to the end of the run with the vertical axis scaled to the tallest non-QC peak. The scale of the biomarker fingerprints will vary based on the retention times of reference peaks from the crude oil reference sample. The biomarker fingerprints will include triterpanes (m/z 191) stacked on top of steranes (m/z 217), normal alkanes (m/z 85) stacked on top of alkylcyclohexanes (m/z 83), and sesquiterpanes (m/z 123) without association. The EDD will be required for all quantitative results. These data will be formatted for NewFields, in Excel, with samples in columns and analytes in rows. These data will also be provided to Tetra Tech NUS, Inc. in the electronic format described in Attachment B of the SOW.

Target analyte qualifiers will be applied to concentrations with associated QC outliers. The qualifiers must be defined in the hardcopy and electronic data deliverables. Some suggested qualifiers are presented in Table 9.

Table 6. Primary PAH Analytes.

PAH Analyte	Abbreviation	Ring Number
Naphthalene	NO	2
C1-Naphthalenes	N1	2
C2-Naphthalenes	N2	2
C3-Naphthalenes	N3	2
C4-Naphthalenes	N4	2
Biphenyl	B	2
Acenaphthylene	AY	3
Acenaphthene	AE	3
Dibenzofuran	DF	3
Fluorene	FO	3
C1-Fluorenes	F1	3
C2-Fluorenes	F2	3
C3-Fluorenes	F3	3
Dibenzothiophene	DBT0	3
C1-Dibenzothiophenes	DBT1	3
C2-Dibenzothiophenes	DBT2	3
C3-Dibenzothiophenes	DBT3	3
C4-Dibenzothiophenes	DBT4	3
Anthracene	A0	3
Phenanthrene	P0	3
C1-Phenanthrenes/Anthracenes	PA1	3
C2-Phenanthrenes/Anthracenes	PA2	3
C3-Phenanthrenes/Anthracenes	PA3	3
C4-Phenanthrenes/Anthracenes	PA4	3
Fluoranthene	FL0	4
Pyrene	PY0	4
C1-Fluoranthenes/Pyrenes	FP1	4
C2-Fluoranthenes/Pyrenes	FP2	4
C3-Fluoranthenes/Pyrenes	FP3	4
C0-Benzo(b)naphthothiophene	BNT0	4
C1-Benzo(b)naphthothiophene	BNT1	4
C2-Benzo(b)naphthothiophene	BNT2	4
C3-Benzo(b)naphthothiophene	BNT3	4
C4-Benzo(b)naphthothiophene	BNT4	4
Benzo(a)anthracene	BA0	4
Chrysene	C0	4
C1-Chrysenes	BC1	4
C2-Chrysenes	BC2	4
C3-Chrysenes	BC3	4
C4-Chrysenes	BC4	4
Benzo(b)fluoranthene	BB	5
Benzo(k)fluoranthene	BJK	5
Benzo(e)pyrene	BEP	5
Benzo(a)pyrene	BAP	5
Perylene	PER	5
Indeno(1,2,3-c,d)pyrene	IND	6
Dibenz(a,h)anthracene	DA	5
Benzo(g,h,i)perylene	GHI	6

Table 7. Primary Biomarker Analytes.

Abbrev	Terpanes
T4	C23 Tricyclic Terpane
T5	C24 Tricyclic Terpane
T6	C25 Tricyclic Terpane
T6a	C24 Tetracyclic Terpane
T6b	C26 Tricyclic Terpane-22S
T6c	C26 Tricyclic Terpane-22R
T7	C28 Tricyclic Terpane-22S
T8	C28 Tricyclic Terpane-22R
T9	C29 Tricyclic Terpane-22S
T10	C29 Tricyclic Terpane-22R
T11	18a-22,29,30-Trisnorneohopane-TS
T12	17a(H)-22,29,30-Trisnorhopane-TM
T14a	17a/b,21b/a 28,30-Bisnorhopane
T14b	17a(H),21b(H)-25-Norhopane
T15	30-Norhopane
T16	18a(H)-30-Norneohopane-C29Ts
X	17a(H)-Diahopane
T17	30-Normoretane
T18	18a(H)&18b(H)-Oleananes
T19	Hopane
T20	Moretane
T21	30-Homohopane-22S
T22	30-Homohopane-22R
T26	30,31-Bishomohopane-22S
T27	30,31-Bishomohopane-22R
T30	30,31-Trishomohopane-22S
T31	30,31-Trishomohopane-22R
T32	Tetrakishomohopane-22S
T33	Tetrakishomohopane-22R
T34	Pentakishomohopane-22S
T35	Pentakishomohopane-22R

Abbrev	Steranes
S4	13b(H),17a(H)-20S-Diacholestane
S5	13b(H),17a(H)-20R-Diacholestane
S8	13b,17a-20S-Methyldiacholestane
S12	14a(H),17a(H)-20S-Cholestane
S17	14a(H),17a(H)-20R-Cholestane
S18	13b,17a-20R-Ethyldiacholestane
S19	13a,17b-20S-Ethyldiacholestane
S20	14a,17a-20S-Methylcholestane
S24	14a,17a-20R-Methylcholestane
S25	14a(H),17a(H)-20S-Ethylcholestane
S28	14a(H),17a(H)-20R-Ethylcholestane
S14	14b(H),17b(H)-20R-Cholestane
S15	14b(H),17b(H)-20S-Cholestane
S22	14b,17b-20R-Methylcholestane
S23	14b,17b-20S-Methylcholestane
S26	14b(H),17b(H)-20R-Ethylcholestane
S27	14b(H),17b(H)-20S-Ethylcholestane

Table 8. Analytical QC Parameters for GC Methods

QC Parameter/Frequency/Purpose	Data Quality Objective (DQO)	Corrective Action
Tune for GC/MS/ Run before every ICal/ Instrumental reproducibility relative to established performance standard	m/z 69: Base peak > 100,000 counts m/z 219: 30% - 60% base peak counts m/z 502: 2% - 8% base peak counts	Re-Run Tune Clean Source Review with Project Manager
Initial Calibration (ICal)/ Run after major maintenance/ Precision for target analytes over calibration range	%RSD < 25% for 90% of analytes %RSD < 35% for all analytes	Review Integrations Re-Tune and Re-Run ICal Instrument Maintenance Clean Source Review with Project Manager
Continuing Calibration (CCal)/ Run every 10 samples/ Precision of target analytes throughout the analytical sequence	%D < 25% for 90% of analytes %D < 35% for all analytes	Review Integrations Re-Run CCal Instrument Maintenance Clean Source Review with Project Manager
Crude Oil Reference Sample (RS)/ Run after ICal/ Accuracy for target analytes	± 35% Difference for analytes with reference values within the calibration range	Review Integrations Re-Analyze RS Review with Project Manager Re-Analyze Batch
Internal Standard/ Evaluate in every field and QC sample/ Accuracy of analytical procedure for each sample	50% to 200% of area counts From the middle ICal standard	Review Integrations Re-Analyze Review with Project Manager

Table 9. Suggested Data Qualifiers.

Qualifier	Use
U	Analyte not detected, sample specific MDL will be reported
B	Analyte detected in sample < 5X detected in the blank
J	Analyte detected between RL and ND (< 3X S/N)
E	Estimated concentration
NA	Not Applicable
D	Secondary dilution performed
D1	Tertiary dilution performed
[a]	Value outside of QC Limits
§	Surrogate value outside of acceptable range

6. HYDROCARBON INTERPRETATION AND REPORTING

NewFields will analyze the data to determine chemical "fingerprints", and interpret the potential similarities between site sediments, ash samples and reference station sediments. Other factors, such as deterioration, aging and sample locations will be considered. As necessary, this analysis will draw upon reference materials analyzed as part of past forensic investigations for the Navy. This comparison may also include multivariate analysis of the PAH data (e.g., principal component analysis).

The data interpretation will require the receipt of several documents from Tetra Tech NUS, Inc. These will include past environmental reports from the site, a detailed site history, regional land use history, and electronic map with sampling locations and property boundaries.

At the conclusion of the study NewFields will provide a draft written report summarizing the data and the forensic interpretation. This report will include descriptions of the samples, the tabulated data, and the chromatographic fingerprints.

NewFields will deliver the forensic interpretation report approximately 30 days after it receives the laboratory data. NewFields will store the supporting data for two years after the submission of the final deliverable for the project.

The final report to Tetra Tech NUS, Inc. will include the data analyses and forensic interpretation, and will adhere to the format described in the cited SOW, Attachments A and B.

REFERENCES

Emsbo-Mattingly, S.D. (2002) Environmental Forensic Investigation of Petroleum Types and Sources from the Former Fire Training Area at the Naval Computer and Telecommunications Station in Cutler, Maine – Final Report. Prepared for Northern Division, Naval Facilities Engineering Command, Lester, PA.

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Stout, S.A., Uhler, A.D., McCarthy, K.J. and Emsbo-Mattingly, S.D. (2002) Chemical Fingerprinting of Hydrocarbons. In: Introduction to Environmental Forensics, (B. Murphy and R. Morrison, Eds.), Academic Press.

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Stout, S.A., Uhler, A.D., and Emsbo-Mattingly, S.D. (2004) Comparative Evaluation of Background Anthropogenic Hydrocarbons in Surficial Sediments from Nine Urban Waterways. Environ. Sci. Technol. 38(11): 2987-2994.

APPENDIX E

RESPONSES TO COMMENTS, CONFERENCE CALL NOTES, AND MEETING MINUTES RELATED TO THE QAPP

GENERAL RESPONSES TO COMMENTS
DRAFT ADDITIONAL SCRUTINY QUALITY ASSURANCE PROJECT PLAN FOR OU4
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

The draft Additional Scrutiny Quality Assurance Project Plan (QAPP) for Operable Unit (OU) 4 was presented at the April 12, 2005 Restoration Advisory Board (RAB) meeting. During the regulatory/RAB review period for the draft QAPP, a technical conference call was held on May 5, 2005 to discuss comments and/or questions on the draft QAPP. The notes from the conference call, provided to the conference call participants on May 19, 2005, are attached to these responses to comments. A site visit and technical meeting was held on June 14, 2005 to observe the proposed sampling locations and discuss the MEDEP comments on the draft QAPP. The minutes are attached to these responses. Revisions to the QAPP will be made based on the RAB meeting, conference call, and technical meeting. Specific revisions discussed at the technical meeting are provided in the meeting minutes. Other revisions not specified in the responses to specific comments are:

- The text on page 1-1 will be revised as follows: "The objective of the additional scrutiny is to assess existing data and ~~to recommend collection of any~~ ***to collect and assess*** additional data ~~that may be required~~ at monitoring stations where concentration trend lines...."
- Figures 1-7 and 4-5 will be corrected to change "Berth 6" to "Berth 4." Also, the samples shown under Building 238 will be repositioned to reflect the correction made to figures in the Site 10 QAPP (March 2005 revisions).
- The date and source of the aerial photography will be added to all applicable figures.
- Text will be added to clarify that Round 8 sampling will also be the start for re-establishing the trend lines for MS-05 and MS-09, which is why sampling at the interim offshore monitoring locations is not presented in this QAPP. The following text revisions will be made:
    - Page 1-1: "As discussed in the June 2004 Technical Memorandum for Additonal Scrutiny at Monitoring Stations MS-05, MS-08, and MS-09 (included in Appendix B), ~~the only additional scrutiny for MS-08 at this time is to conduct sediment sampling to re-establish the trend line.~~ ***additional scrutiny for MS-05, MS-08, and MS-09 includes sediment sampling to re-establish the trend line.*** This sampling will be conducted as part of Round 8 of the interim offshore monitoring program, which is scheduled for August 2005. Therefore, sampling **to re-establish the trend line at MS-05, MS-08, and MS-09** ~~as part of additional scrutiny for MS-08~~ is not discussed further in this QAPP. ***Re-establishing the trend line is the only additional scrutiny activity for MS-08; therefore, MS-08 is not discussed further in this QAPP. Additional scrutiny sampling proposed at MS-05 and MS-09 is presented in this QAPP.***"
    - Section 2.3, page 2-9 and Section 2.4, page 2-12. Add "(Round 8 of the interim offshore monitoring program will be used to re-start the trend line)" after the second sentence.
- Text will be added explaining why the inside of Building 178 is not an IRP source. The following text will be added to the first paragraph of Section 1.7.3.2 (Non-IRP Sources): "The operations inside Building 178 is not considered an IRP source because it is a release from within a building which is not eligible for ER,N funds."

Other general revisions:

- Appendix E will be added to the QAPP for responses to comments, conference call notes, and meeting minutes related to the QAPP. The November 30, 2004 correspondence with enclosure for the Navy's teleconference with NOAA and USFWS regarding prioritization of the additional scrutiny, conference call notes from May 5, 2005, and meeting minutes from June 14, 2005 will be included along with these responses to comments..
- The Navy memorandum on the MS-11 site walk/shoreline observation will be included in Appendix A-3 (supporting information on MS-11) and a reference will be added to the text (on 1-18). The memorandum is attached.
- The following text will be added to the end of Section 3.5.2 to help ensure that potential issues that occur at the analytical laboratory are addressed when they occur so the appropriate corrective actions may occur:
    - The Department of Defense (DoD) has developed specific corrective actions for laboratory analyses when the analyses do not meet specified quality control (QC) criteria. The applicable actions are specified in Appendix D and in Tables B-1 through B-10 of the Appendix DOD-B of the DoD Quality Systems Manual for Environmental Laboratories-Version 2 Final (DoD, June 2002).

      The laboratory is expected to make reasonable efforts to prevent the release of qualified data. The laboratory must contact the Project Manager or his designee when it is evident that data quality will be compromised. This may occur, for example, when an analytical run yielded data of substandard quality but insufficient sample remains for re-analysis. Another example is when spiking concentrations are not sufficient to at least double the native analyte concentration in the sample. Flagging data with qualifier flags as described in Appendix DOD-B without an attempt to restore an analytical system to an "in-control" condition will generally not be acceptable."

      DoD, June 2002. Department of Defense Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Final Version 2, June, 2002.
- Section 4.4 will be changed as follows (text in bold and italics will be added): "Each ***sediment*** sample location will be identified and mapped using a Global Positioning System (GPS) accurate to within 1 meter. All locations/coordinates will be recorded in the field notebook. In addition, a known survey benchmark will be surveyed using the GPS equipment as a control point. Base datum will be identified and recorded. Location information will be converted to the state plane system [North American Datum (NAD) 83] for consistency in past and future mapping efforts. ***The soil sample locations will be measured from known landmarks or estimated from the aerial photograph.***

RESPONSES TO MEDEP COMMENTS DATED MAY 19, 2005
DRAFT ADDITIONAL SCRUTINY QUALITY ASSURANCE PROJECT PLAN FOR OU4
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

General Comments

1. **Comment:** The MEDEP recognizes that sources in the estuary other than the Shipyard can potentially influence contaminant concentrations in sediments adjacent to the Shipyard. However, we believe that contamination in these sediments is attributable primarily to the Shipyard. Therefore, while the Navy's policy is to prove that the source is indeed from the yard (in order to obtain funding) the State's position is that the burden of proof is upon the Navy to show that the contamination is *not* from the yard.

   We believe that the proposed additional scrutiny should help to answer that question.

   Response: The Navy agrees that the additional scrutiny activities will help with understanding the potential sources for the contamination detected in the sediment at the interim offshore monitoring stations. The Navy will evaluate the data and present the results in the Additional Scrutiny report, which will be provided to the regulators and RAB for review (see planned schedule in Section 3.0 of the QAPP). Also see Discussion Item 1 in the June 14, 2005 technical meeting minutes.

Specific Comments

2. **Comment:** <u>1.3.3 Summary of Interim Offshore Monitoring Program, p. 1-5</u>

   This section should mention that the ER-M was used to evaluate lead.

   Response: The following text will be added after the first paragraph on page-5 (discussing the PRGs): "[Lead was not identified as a limiting COC, so a PRG was not developed. Lead is a primary COC for several on-shore sites; therefore the Effects-Range Median (ER-M) value (Long et al., 1995) was used for screening sediment lead data.]"

3. **Comment:** <u>1.4.2 Summary of Interim Offshore Monitoring Program Data, p. 1-8</u>

   Partial sentence at top of page: Has the Navy determined an explanation for the wide variation between the original and duplicate 4, 4'-DDT samples?

   Response: As part of the additional scrutiny activities, the Navy will evaluate the potential cause of the difference between the original and duplicate for the 4,4'-DDT samples (see pages 2-2 through 2-9 related to the DQOs for MS-01). The table below provides the DDD, DDE, and DDT concentrations in the original and duplicate samples collected from MS-01 during Round 6 (taken from Table 3-2, page 1, from the Round 6 Data Package, March 2003). As can be seen in the table, the concentrations between the original and duplicate are more similar (within an order of magnitude) for the other chemicals and the concentrations are more similar to the original 4,4'-DDT concentration than it's duplicate result. As noted in the QAPP text, the offshore area at MS-01 is rocky and multiple attempts are necessary to collect sufficient volume of sediment for analysis. The heterogeneous

nature of the sediment may be the reason for the large difference between original sample and duplicate DDT concentrations. Please also see Discussion Item in the June 14, 2005 technical meeting minutes.

Parameter	302A (ug/kg)	302A-DUP (ug/kg)
2,4'-DDD	9.89	12
2,4'-DDE	0.47	0.35
2,4'-DDT	4.97	42J
4,4'-DDD	27.81	105J
4,4'-DDE	5.57	34J
4,4'-DDT	22.64	1613J

4. **Comment:** 1.4.3.1 IRP Sources, p. 1-8

"Tar...is not in contact with groundwater...therefore it is not a source of contamination to the offshore."

Given that the tar pit has never been observed it is premature to make such a conclusive statement. Likewise, although groundwater was not observed in any of the wells during the 2003 Site Screening Investigation this does not mean that such a low water table has always been the case.

Response: The text will be revised to clarify that it is not a likely source. Please see Discussion Item 2 in the June 14, 2005 technical meeting minutes.

5. **Comment:** 1.4.3.1 IRP Sources, p. 1-9

a) "...information from the Initial Assessment Study (Weston, June 1983) indicates that pesticide management at PNS from the 1960s to the present was carefully managed..."

Please change "the present" to "1983" as the IAS contains information only as recent as 1983.

b) "Pesticides stored in the building included..."

Was DDT or any pesticide containing DDT known to be stored in the building?

Response: The text will be revised to read as follows: "However, information from the Initial Assessment Study (Weston, June 1983) indicates that pesticide management at PNS since the 1960s was carefully managed..."

There is no specific information available that indicates that DDT or a pesticide containing DDT was stored in Building 62.

6. **Comment:** 1.4.3.2 Non-IRP Sources (MS-01), p. 1-10

"The pesticides in soil are considered a non-IRP source to the offshore."

Regardless of what program is responsible, CERCLA requires the Navy to address contamination resulting in unacceptable risk.

Response: No text revision is required. Please see Discussion Item 1 in the June 14, 2005 technical meeting minutes.

7. **Comment:** 1.5.3.1 IRP Sources (MS-05), p. 1-14

"The layout of OU3 is shown on Figure 1-5. This figure reflects the new boundary of the landfill..."

Figure 1-5 should be recent enough to show the new Jamaica Cove wetlands. MEDEP can provide a high resolution aerial photo taken in 2004 to the Navy, if necessary.

Response: Figure 1-2 reflects the configuration of the new shoreline after construction of the Jamaica Cove wetlands.

Please see Discussion Item 3 in the June 14, 2005 technical meeting minutes. The aerial photography will be reviewed to determine whether it can be used in place of the existing aerial photography on the site figures for the Additional Scrutiny Report. A more recent aerial photograph that reflects more current conditions at OU3 will be included in Appendix A-2 of the QAPP, and cited in the text.

8. **Comment:** 1.5.4 Non-PNS Sources of Contamination (MS-05 and MS-09), p. 1-15

a) Clark Cove is a semi-enclosed basin. Therefore, it would seem that non-PNS sources of contamination there would be less prevalent than at other PNS offshore locations. This should be mentioned in the text.

b) "...metals and PAHs related to boat traffic, especially in Clark Cove, where numerous boats are docked and often refueled, may be a significant source of metals and PAHs in Clark Cove."

Boats that are docked and refueled in Clark Cove are non-IR sources but are certainly PNS sources of contamination. Therefore this statement should be removed from this subsection (or the subsection retitled).

Response: Please see Discussion Item 4 in the June 14, 2005 technical meeting minutes.

9. **Comment:** 1.7.3.2 Non-IRP Sources (MS-12), p. 1-22

This section includes discussion of Building 178. As noted in the post-meeting note in the minutes for the May 5, 2005 conference call, "The issue is whether a release from within Building 178 is eligible for ER-N funds. If Building 178 is found to be a primary source causing risk in the sediment, the Navy will need to address the release through some funding source."

While the Navy acknowledges their responsibility in such a situation we do not believe that CERCLA or the National Contingency Plan make a differentiation between releases inside a building and releases outside a building. Please cite the section(s) of these statutes that would support the Navy's policy.

Response: Please see the Navy's general response for text revision to this section based on the May 5, 2005 conference call. Please also see Discussion Item 1 in the June 14, 2005 technical meeting minutes.

10. **Comment:** 2.2.3 Decision Inputs (MS-01), p. 2-5

"Sample duplicate...data from sediment collected as MS-01 during previous sampling rounds to determine whether elevated detections are anomalies and not representative of station conditions."

Are there holding time issues for sampling sediments collected in 2003?

Also, given the relatively high Coefficients of Variation for MS-01 how will duplicate samples indicate whether elevated detections are anomalies?

Response: Re-analysis of samples previously collected is not planned (and the samples were not retained at the laboratory). The evaluation of the duplicate data will be qualitative in nature and will include reviewing duplicate data for other chemicals and data from other rounds to determine whether the elevated detection appears to be an anomaly or whether it truly represents conditions at the station. The coefficient of variation data will not be used in this evaluation.

11. **Comment:** 2.2.6 Sampling Design and Rationale (MS-01), p. 2-8, 1st bullet

"Whether the PAH source signature of sediment in the catch basin matches the source signature of the offshore sediment, indicating that this sediment is a potential source of PAHs to the offshore area."

If there are multiple sources of PAHs to the estuary why would the catch basin sediment signature match the offshore sediment signature? It seems this would be the case only if the catch basin sediments were the only, or predominant, source of the offshore sediments.

Response: The text will be clarified. Please see Discussion Item 5 in the June 14, 2005 technical meeting minutes.

12. **Comment:** 2.2.6 Sampling Design and Rationale (MS-01), p. 2-8

"Two surface soil samples will be collected from Site 34 in areas where exposed ash is present. One sample will be collected in the vegetated area..."

Please clarify "exposed ash". There should not be any exposed ash at Site 34. Furthermore, if you're collecting samples where ash is exposed how can they be soil samples?

Response: As discussed in Section 1.4.3.1, and observed during the June 14, 2005 site visit, the ash material at Site 34 is actually ash mixed with varying amounts of soil. The sentence will be revised as follows for clarity: "Two surface soil samples will be collected from Site 34 in areas where **the potential for ash/soil erosion is the greatest** ~~exposed ash is present~~." The locations where the samples will be collected were identified during the June 14, 2005 site visit at PNS.

13. **Comment:** 2.2.6 Sampling Design and Rationale (MS-01), p. 2-9

One intertidal sediment sample will be collected...The purpose of this sample is to determine the extent of pesticides and PAHs in the intertidal area...

How can one sample determine extent? You must bound the area by at least two samples (assuming it's a relatively narrow area).

Response: Please see Discussion Item 6 in the June 14, 2005 technical meeting minutes. The Additional Scrutiny data will be evaluated in conjunction with the previously collected sediment data (see Appendix A for figures showing the data for previously collected samples) to determine extent of contamination. Table 4-2 in the Additional Scrutiny QAPP provides a summary of the samples to be collected and analyses to be conducted as part of the Additional Scrutiny.

14. **Comment:** 2.2.6 Sampling Design and Rationale (MS-01), p. 2-9

"The soil sample with ash will be used as a 'reference sample' for comparison to the sediment sample."

It is unclear what sort of reference the soil sample with ash will provide. Relative mass of ash in the sample? PAH concentration? Please clarify.

Response: The text will be clarified. Please see Discussion Item 6 in the June 14, 2005 technical meeting minutes.

15. **Comment:** 2.6.5 Decision Statements (MS-12), p. 2-18

This section mentions "current IRP source" several times. The word 'current' should be removed as contamination in the sediment may be a result of a previously unknown IRP source.

Response: No text revisions are necessary. Please see Discussion Item 8 in the June 14, 2005 technical meeting minutes.

16. **Comment:** 4.2 Sediment/Catch Basin Sampling, p. 4-1

Please clarify that catch basin sediment is intended to represent current conditions, rather than an accumulation of historic sediments that are not completely flushed from the basin after rain events.

Response: Please see Discussion Item 9 in the June 14, 2005 technical meeting minutes. Also, the following text will be added to the end of the fourth bullet (as the third sub-bullet) in Section 2.6.3:

- "Elevated levels of lead and/or PAHs in sediment collected from catch basins that ultimately discharge to the offshore area. Sediment from these catch basins represent current sources of contamination to the offshore area."

17. **Comment:** MS-12, p.4-4

Please add brief discussion of the catch basin samples to this section.

Response: The following text will be added to the end of Section 4.2, Subsection MS-12:

"Sediment, if available, will be collected from two catch basins (as described above) for PAH and/or lead analysis.

- Sediment samples will be collected at CB-01 and CB-02 to determine whether lead-contaminated soil is entering the storm water system through cracks (if present) and ultimately discharging to the offshore area. The sediment samples from both catch basins will be analyzed for lead. The sediment sample collected at CB-01 will also be analyzed for PAHs to determine whether elevated levels of PAHs are entering the storm water system via surface runoff and ultimately discharging to the offshore area at MS-12. The sediment sample from CB-01 will not be analyzed for PAH forensics."

The following changes also will be made to the QAPP:

- The following seventh bullet in Section 2.6.3 "The presence of lead in sediment in storm water catch basins" will be deleted.
- The following text will be added as the fourth bullet in Section 2.6.4: "Sediment from catch basins at Site 10 that ultimately discharge to the offshore area."
- The following paragraph will be added to the end of Section 2.6.6: "Sediment will be collected from two catch basins, if an adequate volume of sediment is available. The sediment in one catch basin will be analyzed for PAHs to determine whether elevated levels of PAHs are discharging to the offshore area. Sediment from both catch basins will be analyzed for lead to determine whether soil containing lead is entering the stormwater system through cracks (if present) and ultimately discharging to the offshore area."

18. **Comment:** Table 4-2, p. 3 of 4, reference samples

a) "This sample will be collected at reference station RS...to determine the PAH levels and signature from sediment related to PNS."

Please change this to "sediment not related to PNS."

b) Please justify the selection of the specific locations, e.g. RS-02, Loc. 4 to represent reference conditions. It appears that the locations chosen represent some of the higher concentrations found at the reference stations. Most of the PAH results are above the 90% confidence interval shown in the trend plots. Also, why were no locations from RS-04 chosen? This station has the lowest PAH levels of any reference station and are just as valid as results from the other stations.

Response: The text will be revised. Please see Discussion Item 10 in the June 14, 2005 technical meeting minutes.

19. **Comment:** Appendix D, PAH Forensics QAPP, 4. Sample Preparation

a) This section needs to include a discussion of criteria for duplicates. Table 3 mentions "Less than 30% RPD" but the text should state this.
b) Please indicate the sample size for dichloromethane extraction.
c) Table 3, DQO, second row: "Less than 5x detected analyte concentration in field samples." We assume this should be "5x less than detected analyte concentration..." Please clarify. This wording occurs in Table 4 as well.
d) Table 4, DQO, second row: "Less than 30% RPD" should be changed to "Less than 20% RPD".
e) Table 4, Corrective Action, second row: "Flag duplicate outlier within the calibration range." The Navy should not only flag a duplicate outlier but also discuss how the outlier could affect the data and how the data can be used.

Response: The responses to the above comments are listed below:

a) The basis for adding the "less than 30% RPD" to the text is not clear. However, the "less than 30% RPD" objective will just be used by the laboratory conducting the analysis to determine whether corrective actions need to be taken. It will not be used as the criteria for determining whether the data are usable. Section 5.4.2 and 6.3.1.1 of the main portion of the Additional Scrutiny QAPP discusses how the duplicate data will be used and evaluated.
b) The sample size for the dichloromethane extraction is presented in the first paragraph of Section 4 and is 30 grams. This sample size will also be added to some of the subsequent paragraphs in that section.
c) The referenced text in Tables 3 and 4 will be revised as suggested.
d) Please provide the basis for suggesting that the text in the second row of Table 4, "Less than 30% RPD", should be changed to "Less than 20% RPD". The Navy believes that the 30% RPD is acceptable for duplicate samples for total organic carbon analysis.
e) Section 5.4.2 and 6.3.1.1 of the main portion of the Additional Scrutiny QAPP discusses how the duplicate data will be used and evaluated.

DEPARTMENT OF THE NAVY
ENGINEERING FIELD ACTIVITY, NORTHEAST
NAVAL FACILITIES ENGINEERING COMMAND
10 INDUSTRIAL HIGHWAY
MAIL STOP, #82
LESTER, PA 19113-2090

IN REPLY REFER TO

5090
Code EV23/FE
November 30, 2004

Mr. Matthew Audet
U.S. Environmental Protection Agency, Region I
1 Congress Street
Suite 1100
Mail Code HBT
Boston, MA 02114-2023

Mr. Iver McLeod
Maine Department of Environmental Protection
State House Station 17
Augusta, ME 04333-0017

Dear Mr. Audet /Mr. McLeod:

SUBJECT: OPERABLE UNIT 4, ADDITIONAL SCRUTINY; INSTALLATION RESTORATION PROGRAM FOR PORTSMOUTH NAVAL SHIPYARD

Enclosed is a copy of the Navy's Telephone Conversation Report on a telephone conversation with NOAA and USFWS regarding prioritization of the additional scrutiny under Operable Unit 4.

The Navy's intent is to perform the additional scrutiny at each of the monitoring stations (MS-1, MS-5, MS-8, MS-9, MS-11, and MS-12) as part of the round 8 sampling in August 2005. However, should funding of all work become an issue, the Navy is providing attached telephone conversation report for information for the USEPA, MEDEP, and the Navy to consider along with advice from the community in determining prioritization of the additional scrutiny under Operable Unit 4.

If additional information is required please contact Mr. Fred Evans at (610) 595-0567 extension 159.

Sincerely,

Frederick J. Evans

FREDERICK J. EVANS
Remedial Project Manager
By direction of the
Commanding Officer

5090
Code EV23/FE
November 30, 2004

Copy to:
Mr. Jeff Clifford
Mr. Jack McKenna
Ms. Carolyn Lepage
PNS (Code 106.3R)
TtNUS (D. Cohen)
NOAA (K. Finkelstein)
USFWS (K. Munney)
Mr. Onil Roy (w/out encl)
Dr. Roger Wells (w/out encl)
PNS Code 100PAO (w/out encl)
CNRNE (A. Stackpole) (w/out encl)
MEDMR (D. Card) (via email)
NHFG (Dr. C. McBane) (via email)
Mr. Doug Bogen (via email)
Mr. Peter Britz (via email)
Mr. Alan Davis (via email)
Ms. Michele Dionne (via email)
Mr. James Horrigan (via email)
Ms. Mary Marshall (via email)
Ms. Diana McNabb (via email)
NEHC (A. Lunsford) (w/out encl)

TELEPHONE CONVERSATION REPORTING FORM

Recorded By: Aaron Bernhardt		***Telephone Number:*** 412-921-8433	
Call: To __ From __	***Name:*** Ken Finkelstein (NOAA) Ken Munney (FWS) Jason Speicher (Navy-EFANE)	***Telephone Number:*** Meeting Place	
Company: NORTHDIV		***Date:*** 11-09-04	***Time:*** 10:00 AM
Internal copies: *Bernhardt, Cohen*			
Client/Project: Portsmouth Naval Shipyard, Kittery Maine			***Job Number: 2833***
Subject: Additional Scrutiny memo for PNS			

Discussion Record:

Ken F. and Ken M. reviewed the memo for the proposed additional scrutiny at MS-1, MS-11, and MS-12 but did not have any specific comments. Overall, they indicated that the approach was fine.

Jason said that the goal was to prepare one work plan for additional scrutiny at MS-1, MS-5, MS-8, MS-9, MS-11, and MS-12, and then implement the plan in phases, if adequate funding was not received to complete all the work at one time. Therefore, we discussed the priority of the sites, based on the availability of funding. There was general agreement that the priority of the sites were as follows:

1. MS-1 and MS-12: Equal importance
2. MS-11: Important because possible continuing source of erosion and because of OU2 FS
3. MS-9: Now that OU3 activities are completed, would like to reestablish trend but also want to determine how large an area was impacted. Ken M. said that there were high suspended loads in the area during the OU3 activities
4. MS-8: The intertidal area was excavated so chemical concentrations are expected to be low
5. MS-5: This station has the lowest priority because only one location was elevated and only during the last two rounds

Id as regarding number of samples and/or sampling approach for additional scrutiny at each monitoring station was discussed. Discussions were as follows:

- MS-1: Collection of six sediment samples total, including the three interim monitoring locations.
- MS-5: As discussed in the June 18th tech memo, collection of the three interim monitoring locations to reestablish trends now that OU3 activities are complete and collection of up to 15 additional sediment samples adjacent to location 1 at MS-5. Samples at location 1 would be collected in a ring pattern (3 rings total) and would be analyzed for lead, copper, and nickel based on the strategy discussed in the June 18th tech memo.
- MS-8: As discussed in the June 18th memo, collection of the three interim monitoring locations to reestablish trends now that OU3 activities are complete.
- MS-9: As discussed in the June 18th memo, collection of the three interim monitoring locations to reestablish trends now that OU3 activities are complete and the collection of three additional samples within the station to determine extent.
- MS-11: Collection of three soil and/or sediment samples to be collected from apparent erosion areas abutting Sites 6 and/or 29, and to analyze for copper, nickel, and lead.
- MS-12: Collection of eight sediment samples within and adjacent to MS-12. Locations for samples would be chosen based upon past MS-12 interim monitoring locations and proximity to Site 10 and Building 178. As discussed below it was mentioned that at least one or more of the samples should be collected as close as possible to Building 178 or inside door if possible.

It was also reiterated that additional scrutiny needed at MS-3 and MS-4 was being addressed by current Site 32 remedial investigation activities.

We discussed that based on the schedule of the work plan it is likely that we would not get out there until August 2005, which would coincide with the RD 8 OU4 offshore sampling event. Also, by combining the additional scrutiny sampling with the Round 8 sampling we would be able to save on mobilization costs.

Ken F. and Ken M. were ok with that schedule. However, it was mentioned between participants that schedule and milestones needed to be discussed by the RPMs to determine what was both acceptable and achievable.

Jason discussed the approach for the PAH fingerprinting which included initial analysis of the samples for total petroleum hydrocarbons (TPH). The TPH chromatograms would then be reviewed to determin which samples would be selected for advanced chemical fingerprinting.

We also discussed some potential sampling at MS-12 including inside the building. Ken M. said that based on the size of the building, more than one sediment sample should probably be collected from inside the building to evaluate the potential for a large source area. Jason said that an EBS report was done for the building but there was not a lot of useful information in it. Aaron suggested having Marty take some photographs of the inside of the building to determine if there were sediment deposits that could be sampled. It was also recommended to obtain and review the building specifications for potential areas that could be sampled. This information could be included in the work plan.

Ken M. Asked if Matt Audet and Iver McLeod were aware of this call and Jason said that they were. Jason also said that he would have Fred relay the proposed sampling schedule as discussed above to the regulators for their concurrence. Finally, there was discussion about the need for a technical meeting in late December or early January prior to submitting the work plan to get FWS and NOAA input. Both Ken M. and Ken F. thought it was a good idea depending on their schedule. Jason indicated that he would call them when the time got closer to check their schedule and see if there was a need to meet or have a conference call with them.

NOTES FROM TECHNICAL CONFERENCE CALL ON THE DRAFT ADDITIONAL SCRUTINY QUALITY ASSURANCE PROJECT PLAN
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE
MAY 5, 2005

Participants: Matt Audet, Aaron Bernhardt, Debbie Cohen, Fred Evans, Ken Finkelstein, Amanda Kittelson, Iver McLeod, Marty Raymond, and Jason Speicher

Objective: Discuss and address any questions or concerns during the review of the draft QAPP, before comments are due, to help resolve issues and expedite finalization of the QAPP. Comments are due May 19, 2005 and the majority of sampling activities are planned for August 2005.

Discussion:

General Comment:

- Ken Finkelstein had a general comment that the QAPP indicates that additional work will be conducted based on the additional scrutiny investigation. He questioned when a decision for the stations would be made and what the additional work would consist of. The Navy indicated that they need the information to support whatever action would come next. It is difficult to predict all the different outcomes; however, the Navy would look at actions needed for source control, additional evaluation of risk, and/or removal action. So, the Navy cannot indicate a specific decision for each monitoring station before collecting the data.
- Ken Finkelstein asked whether everyone agreed that MS-01 and MS-12 are the most concern. Jason Speicher said the Navy agreed and these two stations also have the most sampling/evaluation activities planned as part of additional scrutiny.
- Matt Audet asked whether the purpose of the additional scrutiny was to determine whether ongoing releases are the cause of the potential increasing concentration trends or is it to draw a connection for historical releases to the offshore? The Navy indicated that it is really to look at ongoing releases to see whether an onshore site has a current release. Fred Evans indicated that the Navy did a risk assessment for the offshore before the start of the interim offshore monitoring program but wanted to understand whether concentrations were decreasing because various source control actions had been conducted at PNS. The Navy expects to see stable or decreasing trends if source control has been conducted. Based on discussion at the April RAB and technical meetings, additional discussion among the Navy, USEPA, and MEDEP will be required to determine how to address past releases (also see the discussion under MS-01).

MS-01 (Offshore of Site 34):

- Iver McLeod had a chemist review the forensics work plan and does not have a comment on the planned work; however, he is concerned with how the results will be used to make a decision for PAHs in the offshore sediment. He questioned whether the Navy would assume that PAHs in the offshore are not from Site 34 if the forensics does not show a match between the PAH patterns in the ash and offshore sediment. The Navy wants to determine whether Site 34 is a current primary source to the offshore. Fred Evans mentioned that the Navy is already looking at a removal action for the ash as part of the onshore evaluation. Iver McLeod indicated a concern for past releases

and whether the Navy is trying to prove whether concentrations are from past releases. Fred Evans indicated that the Navy needs to make sure that an IRP source is the primary source to the offshore before the Navy can justify using Navy money on any cleanup. If the Navy is the primary source, then the Navy needs to address the contamination. Especially given the ubiquitous nature of certain chemicals in the Pistcataqua River, it would be difficult to clean up contamination in the offshore if an IRP site is not the primary source. Jason Speicher indicated that if the Navy is not able to make a definitive conclusion based on the results of the additional scrutiny, further discussion will be needed. Also, Jason Speicher said he would provide additional information on the forensics evaluation. [Post call note: Fred Evans emailed the forensics evaluation that Jason Speicher discussed during the call.]

- Iver McLeod asked some questions about the purpose of the catch basin samples. It was clarified that the catch basin samples were to represent sediment concentrations from storm water run off that was not associated with Site 34. One of the things that will be done is to compare the DDT concentrations in the catch basis samples to the DDT concentrations found in the catch basin sediment from the wash pad. These samples are intended as reference samples. Table 4-2 provides a summary of the planned samples, analyses, and rationale.

MS-05/MS-09 (Offshore of OU3):

- Iver McLeod indicated that the text indicates that the concentration trend lines were disrupted by the construction activities and that the Navy needs to re-establish the trend lines. However, the decision rules only discuss evaluation of extent of contamination. Aaron Bernhardt mentioned that page 1-1 (scope and objectives) discusses that Round 8 samples are for re-establishing the trend lines for MS-08 while the samples taken as part of the additional scrutiny are for determining the extent of contamination. This is the same for re-establishing the trend lines for MS-05 and MS-09. Text will be added to clarify that Round 8 sampling will also be the start for re-establishing the trend lines for MS-05 and MS-09, which is why sampling at those locations is not presented in this QAPP.

MS-11 (Offshore of OU2 which includes Sites 6 and 29):

- Aaron Bernhardt mentioned that that soil sampling as part of the additional scrutiny is expected to occur in early June. Fred Evans said that the removal action (shoreline stabilization) will be conducted and the Navy is in the early planning stages.
- Iver McLeod wondered if the answers to the decision rule questions (on pages 2-16 and 2-17) are already known to be "yes," is this decision rule needed. Aaron Bernhardt explained that the sampling is being used to justify and document the planned shoreline removal action, even though the Navy is very confident of the answers to the questions.

MS-12 (Offshore of Site 10 and Building 178):

- The regulators mentioned previous comments on the potential for lead at Site 10 to be the source of metals contamination at MS-11. Based on the erosion observed along the OU2 shoreline, the Navy believes that the source of the metals at MS-11 is from OU2 erosion and not likely form Site 10. Matt clarified that USEPA is not saying there is a connection between Site 10 and MS-11, but the potential for there to be a connection should not be discounted until after the Navy conducts the additional scrutiny investigation for MS-11 and MS-12. The results of the investigation will likely make the question of a Site 10/MS-11 connection moot; however, that can be discussed after the investigation is conducted.

- Iver McLeod indicated that there was some discussion at the June RAB about the inside of buildings (Building 178) not being an IRP source. It is not clear from the QAPP text why the inside of the building is not an IRP source. FS indicated that it was based on current Navy policy. The text will be revised to clarify why the inside of Building 178 is not an IRP source. [Post Meeting Note: The issue is whether a release from within Building 178 is eligible for ER-N funds. If Building 178 is found to be a primary source causing risk in the sediment, the Navy will need to address the release through some funding source.]

Additional Scrutiny Quality Assurance Project Plan for Operable Unit 4 (OU4)Technical Meeting
Kittery Outlet Inn, Kittery, ME
June 14, 2005

Meeting Attendees:

- Matt Audet (USEPA)
- Iver McLeod (MEDEP)
- Fred Evans and Jason Speicher (EFANE)
- Ken Munney (USFWS) (arrived ~1 p.m., end of first discussion item, comment 6)
- Ken Finkelstein (NOAA)
- Marty Raymond and Ken Plaisted (PNS Environmental)
- Aaron Bernhardt and Rebekah Young (TtNUS)

Aaron Bernhardt began the meeting explaining that the purpose of the meeting was to understand and resolve concerns indicated in MEDEP comments dated May 19, 2005 on the OU4 draft Additional Scrutiny QAPP so that the Navy can move forward with the investigation.

Items for Discussion:

1. Difference between actions taken for IRP and Non-IRP sources (MEDEP Comment Nos. 1, 3, 6, and 9)

The Navy explained that PNS sources are not necessarily IRP sources. The Navy also explained that there needs to be a release outside a building to qualify for funding under the Navy's IR program. For example, while parking lot run-off (i.e., storm water runoff) is related to PNS, it is not considered a CERCLA release and cannot be addressed using IRP funding. Storm water outfalls at PNS are covered under the Shipyard's storm water permits. [Post meeting note: Please see Section 8.5, Activities Eligible for ER,N Funding, of the Navy/Marine Corps Installation Restoration Manual dated February 1997 regarding the requirements for ER,N funding.]

For the PAHs and lead contamination at MS-12, the Navy would not consider remediating contaminated sediment when sources of contamination can not be linked to an existing IRP site(s). The purpose of the additional scrutiny QAPP and eventual field work is to assist the Navy in determining whether existing chemical concentrations found in sediment can be linked to an existing IRP site(s). Although the trend line for PAHs at MS-12 appears to be increasing; the increase is really only occurring at the intertidal location. The PAH concentration trend lines at the subtidal locations are relatively flat. The Navy is proposing collecting samples as part of the additional scrutiny investigation to determine the source of the PAHs. The results would be used to determine whether there is an IRP source(s) for the contamination.

It was mentioned that dredging had occurred in the area at MS-12 in 2000 or 2001 to make room for a boat being launched from Building 178. The dredging disturbed the sediment and may have caused an increase in chemical concentrations at all three locations at MS-12. The assumption of the offshore program is that concentration trend lines should decrease over time because the estuary as a whole has fewer sources of contamination. However, the time required for the chemical concentrations to decrease is not known. The sedimentation rate is a few cm/year, therefore, because the sediment samples are collected from the top 10 cm, disturbed sediment is still being sampled. Also, there may be less sedimentation in the intertidal

area because this area may be more disturbed from tidal action. [Post-meeting note: The dredging apparently was conducted in the summer of 2000, between the Round 2 and Round 3 sampling events. The dredging was more in the intertidal area than subtidal area. Concentrations of lead and copper (and possible nickel and some PAHs) increased after Round 2, with the increase most apparent at the intertidal location (Location 1).]

Ken Finkelstein indicated that although he believes that the high PAHs are coming from PNS, he expects most of the samples to be collected as part of the additional scrutiny to also have high PAH concentrations and he believes the solution should be simple. The Navy indicated that if an IR site is not the source, it will be difficult to determine which program would pay for clean-up.

During discussions regarding MS-12, it was noted that it is difficult to see some of the sampling locations (e.g., 10A and 10B) on the figure. In particular, the offshore sampling locations with black sample labels are difficult to see. The sample labels on the figures will be modified, as necessary (i.e., changed to white) to make them easier to see.

Regarding MEDEP Comment No. 3 (variation between the original and duplicate sample results for DDT), Aaron Bernhardt explained that the substrate is very rocky at MS-01, which is likely because the channel narrows in that area resulting in increased water velocity that scours the bottom of the channel. During sampling it was often necessary to relocate the boat many times to obtain a successful grab because the rocks would prevent the sampler from completely closing. The sediment at MS-01 is also heterogeneous and similar differences between the sample and its duplicate were observed for PAHs during other rounds. The heterogeneous nature of the sediment may be the reason for the large difference between original sample and duplicate DDT concentrations.

Regarding MEDEP Comment No 6 (related to addressing pesticides in soil under CERCLA), the Navy indicated that DDT in media is not considered a CERCLA release when used following legal application procedures. However, other releases of DDT (i.e., spills, disposal, etc.) may be considered a CERCLA release. Concentrations of DDT at Site 34 are similar to concentrations in other areas across the shipyard and the Navy does not consider the levels in the soil to be from a CERCLA release. Risk management needs to consider how to handle contributions to overall site risk from non-CERCLA releases and background contributions. In answer to whether an offshore PRG had been developed for DDT, Fred Evans explained that the protocol for developing a PRG for DDT was established; however a PRG was not recommended because DDT has not been linked to any onshore sites and there was uncertainty with the dose response.

2. <u>Rewording of tar pit discussion in Section 1.4.3.1 (MEDEP Comment No. 4)</u>

Regarding the discussion of the tar pit, Iver McLeod indicated that the text should be changed because the tar pit may have been a source of contamination in the past, and that the Navy can not conclusively say that the tar pit was definitely not a source of contamination to the offshore. No changes are needed in the sampling design to address MEDEP's concern. The Navy agreed to revise the text to indicate that the tar pit is not believed to have been a source of contamination to the offshore. The Navy will e-mail the proposed text revisions to MEDEP for their concurrence to expedite finalization of the QAPP. [Post meeting note: The third paragraph in Section 1.4.3.1 will be replaced with the following text]:

"Potential environmental concerns associated with Site 34 operations are associated with the generation of ash and tar and management of pesticides. Tar was generated and contained in a pit within Building 62 (from 1870s to early 1900s). Based on physical properties of tar and site geology and hydrogeology observed during the 2003 and 2004 investigations, it is unlikely that tar would migrate to groundwater and to the offshore. Tar typically has a high viscosity and a low solubility with water and does not tend to migrate through soil to groundwater. Also, the tar is under the building and is not in contact with surface water runoff. Immediately below the upper disturbed layers (observed to several feet below ground surface throughout Site 34) is a dense, silty clay to clayey silt layer that overlies bedrock and groundwater was not observed in the overburden material at Site 34. Because tar is not likely a source of contamination to the offshore, tar associated with Site 34 operations is not discussed further in this QAPP."

3. Use of high resolution aerial photos (MEDEP Comment No. 7)

Iver McLeod indicated that MEDEP has 2004 photos from their GIS server that the Navy could obtain. The contact person at MEDEP is Michael Smith (207-287-4292) from MEDEP GIS. The Navy does not need to use the new aerial photos for the final Additional Scrutiny QAPP, but should use them in the report with the results of the sampling. The Navy will include an updated aerial figure showing the Jamaica Cove area in the appendix of the QAPP.

4. Non-PNS sources of contamination in Clark Cove, including docked boats (MEDEP Comment No. 8)

Regarding 8a), although Clark Cove is a semi-enclosed cove, non-PNS sources of contaminants can enter with the nine to ten-foot tide. Known PNS sources in the Cove are the landfill (which is controlled), storm water runoff, and boat traffic. The landfill is the only known IRP site in the area. Fred Evans indicated that they must try to differentiate between IRP and non-IRP and not necessarily PNS and non-PNS. Regarding 8b), Ken Plasted indicated that all boats in Clark Cove are privately owned, but if a private boat leaks, PNS conducts the spill response. Iver McLeod indicated that he is fine with statement as is so it does not need changed in the QAPP.

5. Purpose of catch basin samples (Comment MEDEP No. 11)

Iver McLeod indicated that "multiple sources of PAHs" in his comment refers to multiple catch basins. Jason Speicher explained that the signatures of all catch basins at PNS are expected to be "ambient signatures" and that they act as a surrogate signature for others across PNS (for example, catch basins from parking lots across PNS). For clarity, the text will be reworded as follows: "... indicating that ~~this~~ sediment ***from catch basins are*** ~~is a~~ potential sources ..." because the intent is not to link the PAHs in the offshore sediment to one particular catch basin. The Navy will forward the background document that explains "ambient" signatures. [Post-meeting note: The document was provided in an e-mail from Fred Evans dated June 17, 2005.]

6. Explain how extent will be determined using historic data (MEDEP Comment No. 13)

Aaron Bernhardt explained that the data from samples collected as part of the additional scrutiny investigation will be combined with the data from the historical samples to determine

the extent of contamination. The Navy does not expect the outermost samples to have elevated concentrations (especially for SD-07). However, the data will be evaluated to determine the next step in the process should the contamination not be bounded and if the contamination is determined to be related to an IRP source

7. Purpose of soil/ash sample as a reference for the microscopic analysis (MEDEP Comment No. 14)

The Navy explained that ash is used as a reference for comparison based on the physical characteristics of the sediment (i.e., grain size, presence of ash, coal, etc.). The text will be clarified to explain that the reference will be used for a physical comparison; not a comparison of the chemical concentrations. [Post-meeting note: The last sentence in the last paragraph in Section 2.2.6 will be changed as follows:] "The soil sample with ash will be used as a "reference" sample for comparing the physical characteristics (i.e., grain size, presence of ash, coal, etc.) between the soil sample and the sediment sample."

8. Current versus historic sources at MS-12 (MEDEP Comment No. 15)

There are different decisions for current and historic sources. The decisions are identical except that source control is included in the decision for current sources. Iver McLeod said that the decision statements do not need to be revised.

9. Cleanout of catch basins that are proposed for sampling (MEDEP Comment No. 16)

Iver McLeod asked whether sediment builds up in the catch basins and if so, if there is a record of how much sediment is in the catch basins and how often they are cleaned out. Aaron Bernhardt indicated that he had an appointment to speak with Jeff Hoyt (PNS public works) the following day to determine how often catch basins are cleaned out. Jason Speicher indicated that the sediment would be indicative of more recent sources based on the cleaning program. Post meeting note: Based on information provided by Jeff Hoyt, the following changes will be made to the QAPP (note that the rationale will also be changed in Table 4-2 to reflect these changes, as necessary):

- CB-01 at MS-01 (see Figure 4-1) will be moved to catch basin 45-27 (see Figure A-8 in Appendix A-1 of the QAPP). The reason is that CB-01 is only accessible via an underground tunnel so it would not be easily sampled. Catch-basin 45-29A was considered as a back-up but it was last cleaned in 2003 and no sediment was reported to be present in the catch basin. Catch basin 45-27 was last cleaned out in 2004, at which time it had 2 inches of sediment. It is scheduled to be cleaned out again in 2005. Catch basin 45-26 will be sampled if sediment is not available at 45-27. It was last cleaned out in 2004, at which time it had 4 inches of sediment. It is also scheduled to be cleaned out again in 2005.
- CB-02 at MS-01 (see Figure 4-1) will be moved to catch basin 45-22A (see Figure A-8 in Appendix A-1 of the QAPP). The reason is that CB-02 was cleaned out this past May or June because of sedimentation associated with construction of the parking garage. Catch basin 45-22A was last cleaned out in 2004, at which time it had 2 inches of sediment. It is scheduled to be cleaned out again in 2005. This area drains a residential area, including a large grass covered area.

Jeff Hoyt also provided the following information, which does not affect the QAPP but which may be used to evaluate the data in the Additional Scrutiny Report:

- The catch basin in the small wash pad on the south side of Building 62 was last cleaned out in 2000.
- CB-01 at MS-11 (see Figure 4-4) has not been cleaned out since at least 2004.
- CB-01 and CB-02 at MS-12 (see Figure 4-5) have not been cleaned out since at least 2001.

10. Selection of reference samples (MEDEP Comment No. 18)

a) The text will be revised to "...reference station RS to compare to PAHs levels and signature from sediment not related to PNS."
b) The rationale for the selection of the reference stations is provided in the DQOs. The specific discussion is provided on page 2-9. The intent of the samples is PAH forensics analysis of sediment that is indicative of urban runoff. Reference stations RS-02 and RS-03 have the greatest likelihood of exhibiting a pattern of urban runoff because of there location in more urban areas compared to reference stations RS-01 ad RS-04. The evaluation of the PAH data does not involve comparing the PAH ***concentrations*** between the site samples and reference samples, rather it involves comparing the PAH ***signatures*** between the site samples and reference samples. PAH concentrations would not be used to eliminate PAHs as chemicals of concern at MS-01 and MS-12.

Other discussion

Matt Audet indicated that the USEPA does not expect to have significant comments on the draft Additional Scrutiny QAPP, however, he is still in the process of reviewing the document.

Regulators will be notified at least one week before sampling. FWS and NOAA would like to observe the sampling at MS-1 and MS-12. The Navy will schedule a day that they can go out and observe the sampling (probably Monday 8/22 or Tuesday 8/23). Aaron Bernhardt will determine whether the sampling boat is large enough for everyone to go out on it. Otherwise, they can probably observe from shore (i.e., from Site 10 for MS-12). The sampling event is expected to take approximately 5 to 6 days. Aaron Bernhardt reminded everyone that the Navy is changing from NOAA methods to USEPA analytical methods; metals for the Round 8 sediment samples will be analyzed using NOAA methods. Additional scrutiny samples will be analyzed using USEPA methods. Aaron Bernhardt indicated that the soil and catch basin samples at MS-11 were collected in late May, 2005.

Ken Munney says he has not reviewed the QAPP in detail but it looks good to him so far; he is anxious for sampling to begin.

RESPONSES TO MEDEP FOLLOW-UP COMMENTS DATED AUGUST 5, 2005
DRAFT ADDITIONAL SCRUTINY QUALITY ASSURANCE PROJECT PLAN FOR OU4
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

1. **Comment:** General Response to Comment

"The following text will be added [explaining why the inside of Building 178 is not an IRP source]...'The operations inside Building 178 is not considered an IRP source because it is a release from within a building which is not eligible for ER,N funds.'"

The post meeting note in the minutes for the June 14, 2005 technical meeting state, "Please see Section 8.5, Activities Eligible for ER, N Funding, of the Navy/Marine Corps Installation Restoration Manual dated February 1997 regarding the requirements for ER, N funding."

Section 8.5.2 of that document, Activities Not Eligible for ER, N Funding, states, "The following activities are not eligible for DERP funding...Cleanups within buildings (e.g., PCB contaminated floor cleanups, etc.)."

This section does not state that releases from within a building are not eligible, only that cleanups within buildings are not eligible. Clearly, in discussing OU4 we are not discussing a cleanup within a building. Therefore, the MEDEP maintains that should it be determined that Building 178 is the source of the PAHs at MS-12 then it is clearly an IRP source eligible for ER, N Funding.

Response: Further discussion will be needed within the Navy if Building 178 is determined to be a source. However, the Navy does not believe the discussion will affect the sampling activities. The text will be revised to read as follows:

"[The Navy does not currently consider the operations inside Building 178 to be an IRP source because it would be a release from within a building, which is not eligible for Environmental Restoration, Navy (ER,N) funds. However, further evaluation will be performed to determine whether a release from within a building is eligible for ER,N funds when appropriate.]"

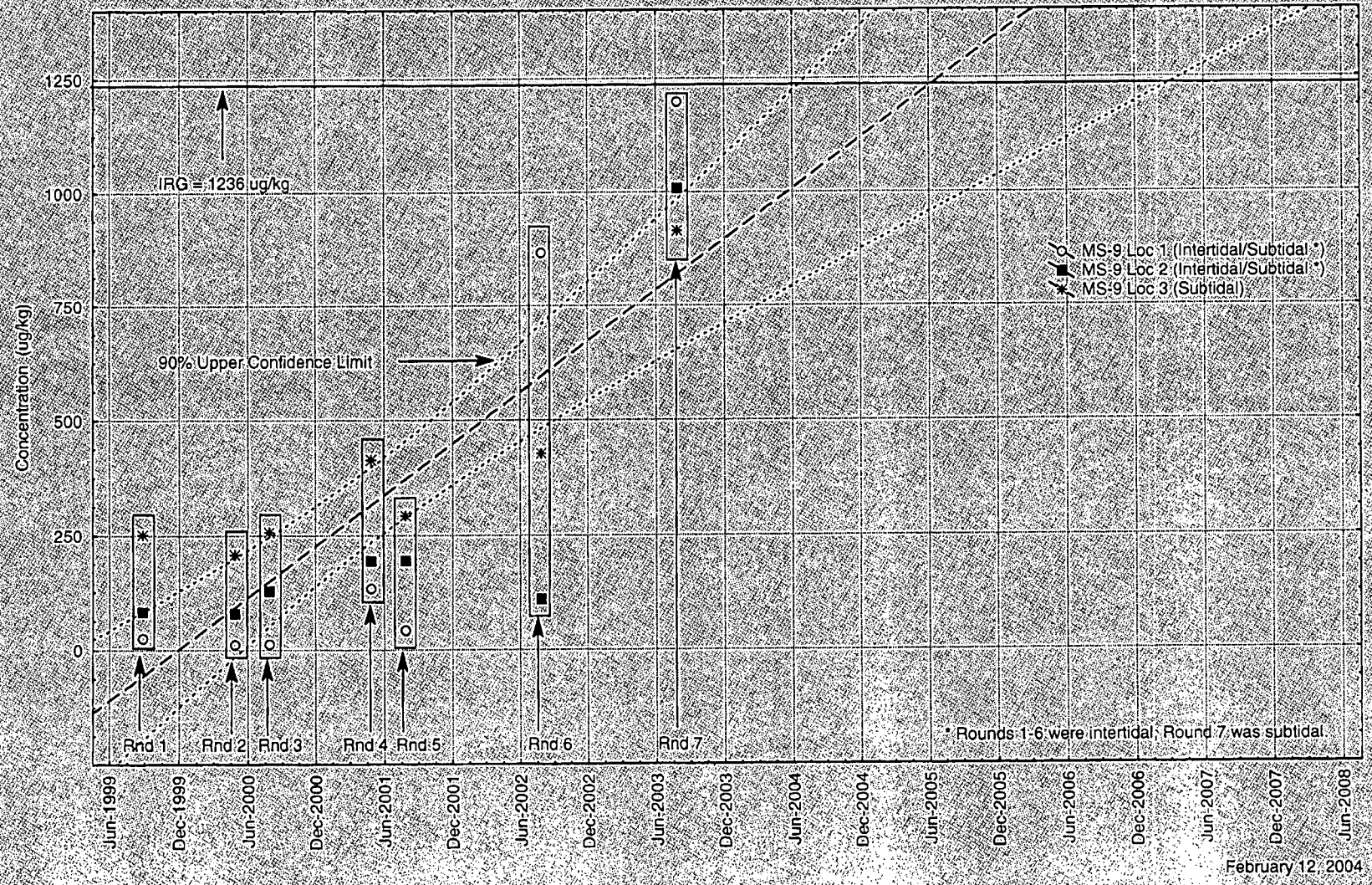
2. **Comment:** Shoreline Evaluation at MS-11, Site 6 (DRMO) Shoreline

"In the short term maintenance consisting of repositioning in the displaced surface stones is required."

Please discuss when this work will occur.

Response: A schedule for conducting the maintenance work along the Site 6 shoreline has not been determined at this time.

Monitoring Station 9 - Sediment
Anthracene Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine

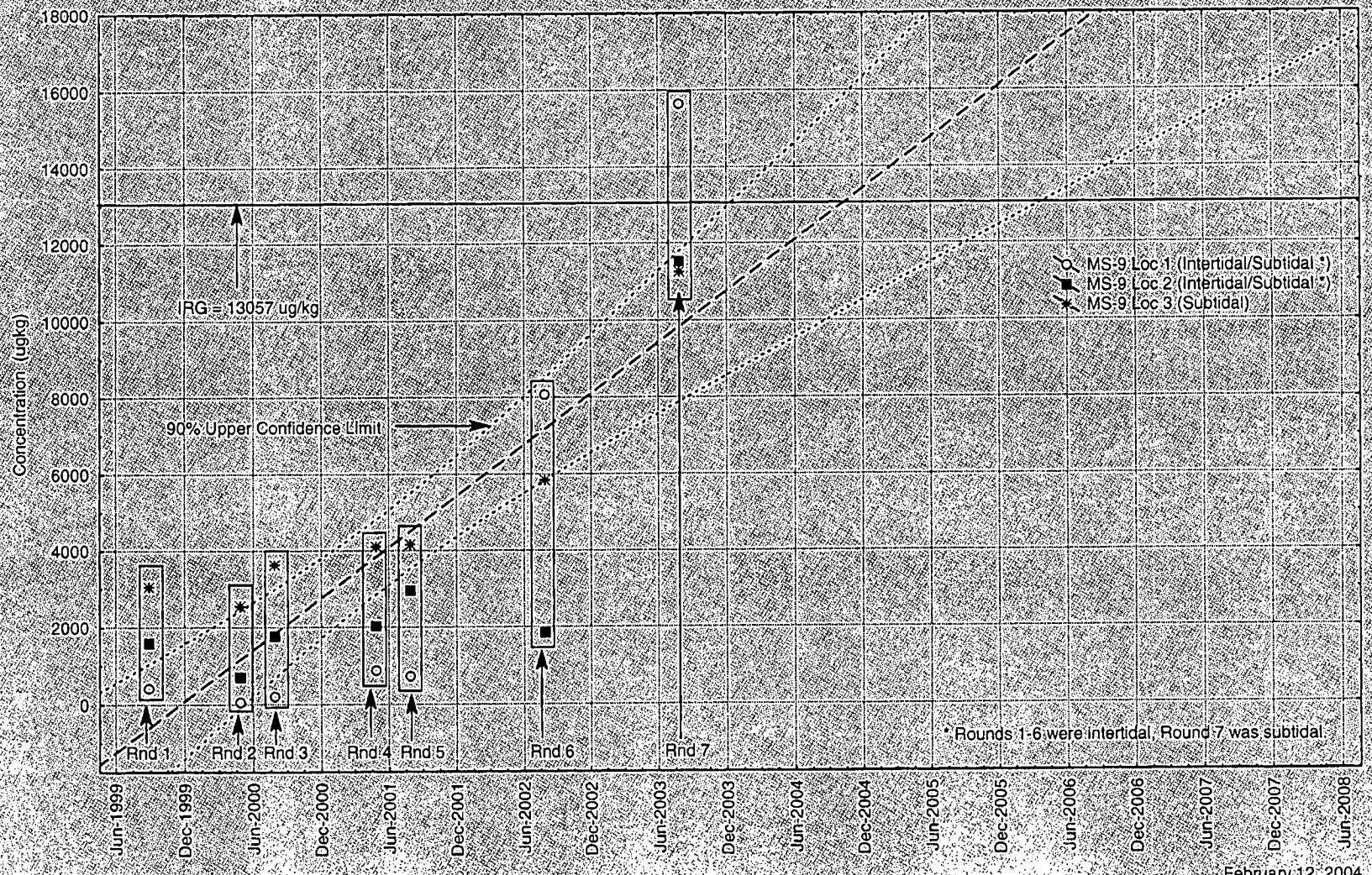


February 12, 2004

Monitoring Station 9 - Sediment
Fluorene Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine

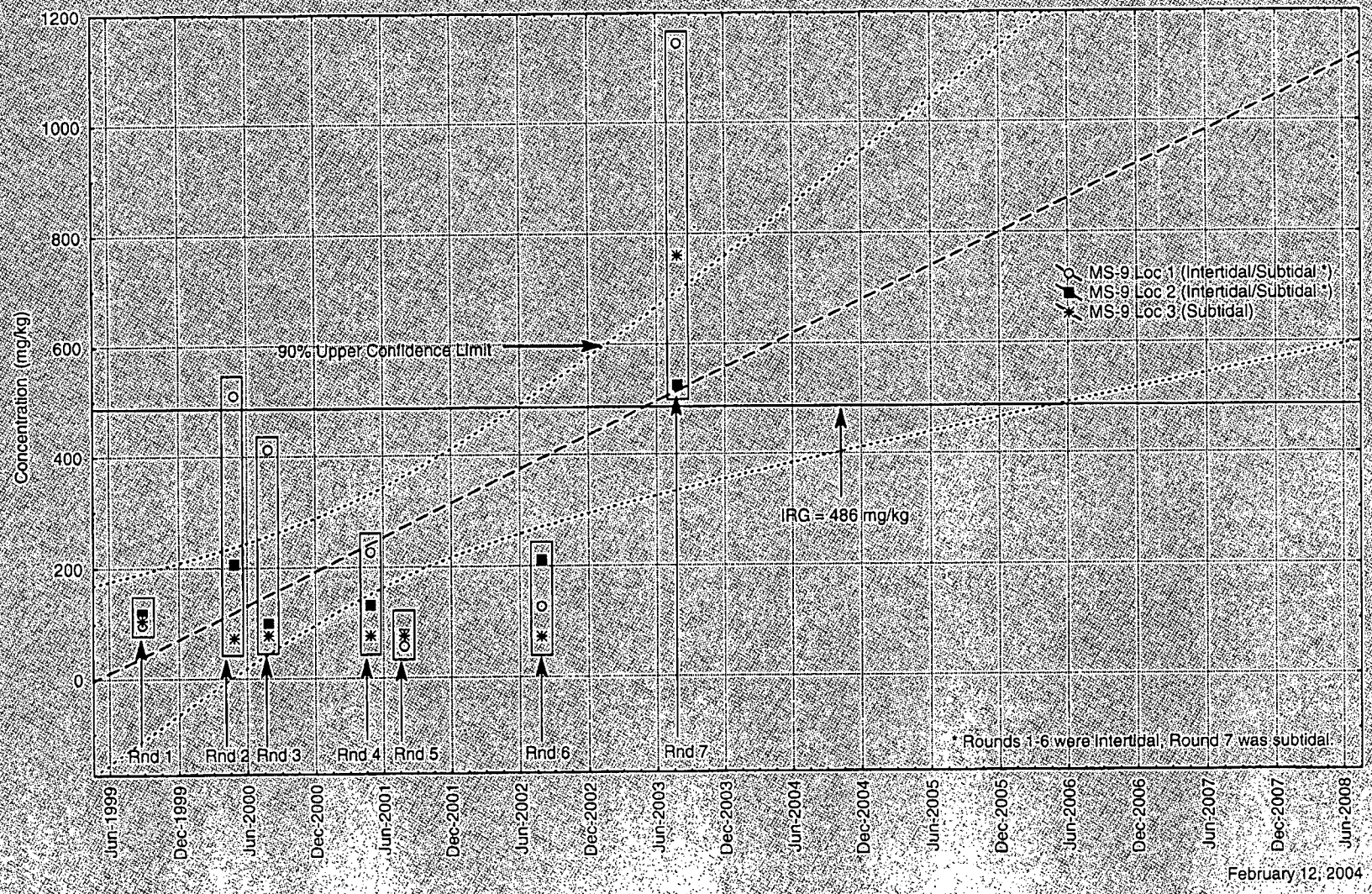
February 12, 2004

Monitoring Station 9 - Sediment
High Molecular Weight PAH Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine

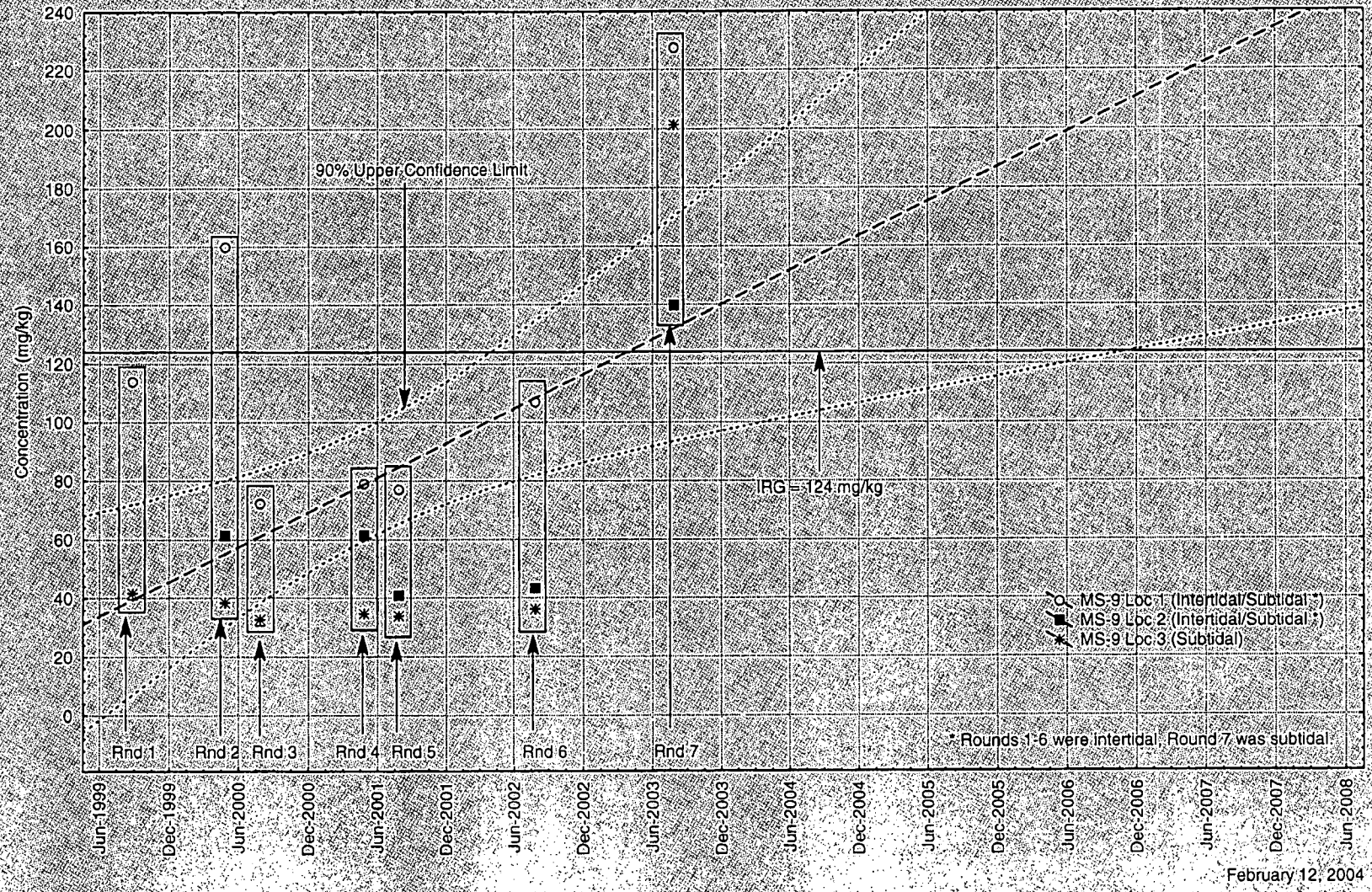


February 12, 2004

Monitoring Station 9 - Sediment
Copper Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine

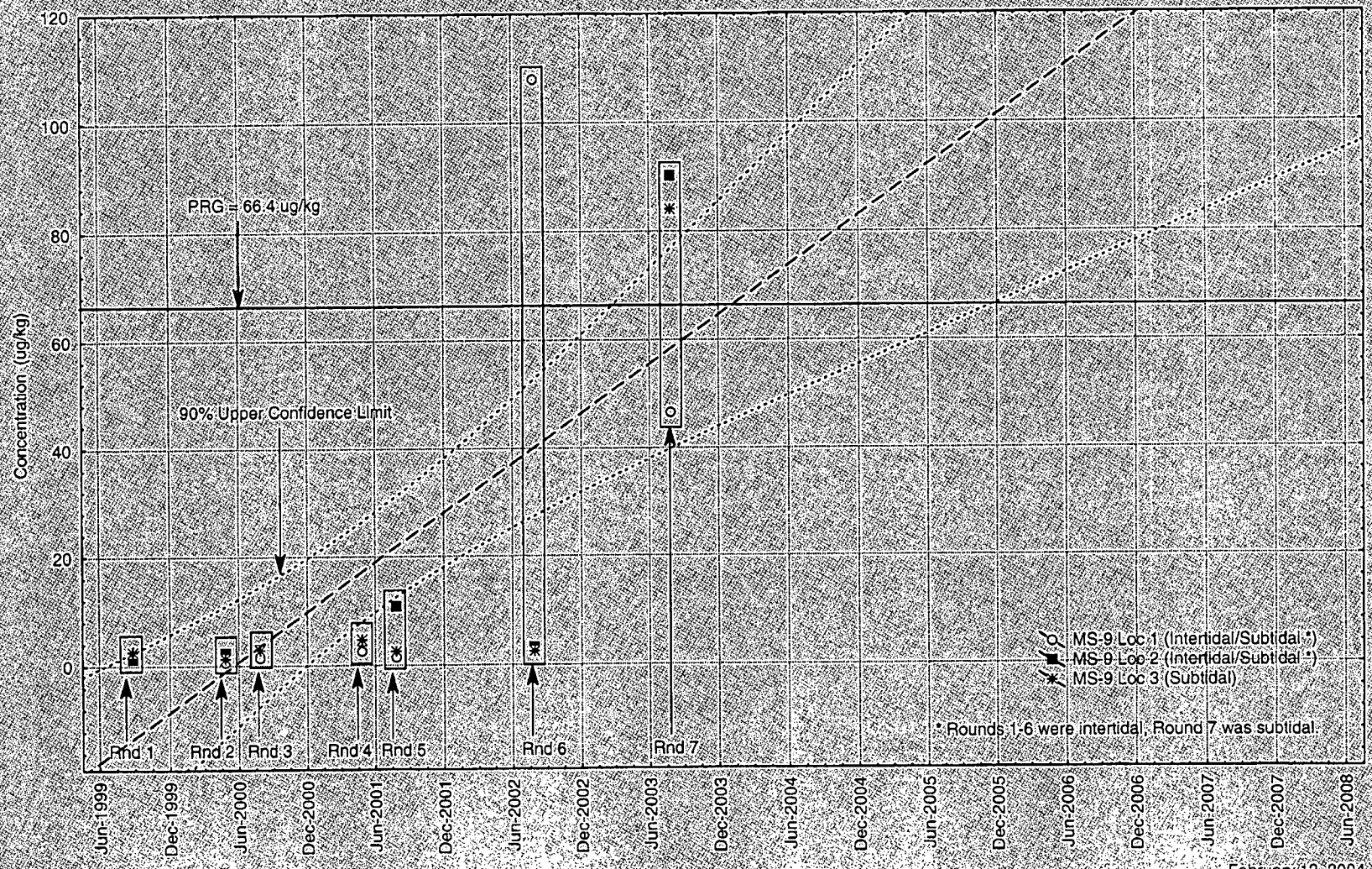


February 12, 2004



February 12, 2004

Monitoring Station 9 - Sediment
4,4'-DDT Results by Round
Rounds 1 through 7 Interim Offshore Monitoring Program Report
Portsmouth Naval Shipyard, Kittery, Maine



February 12, 2004