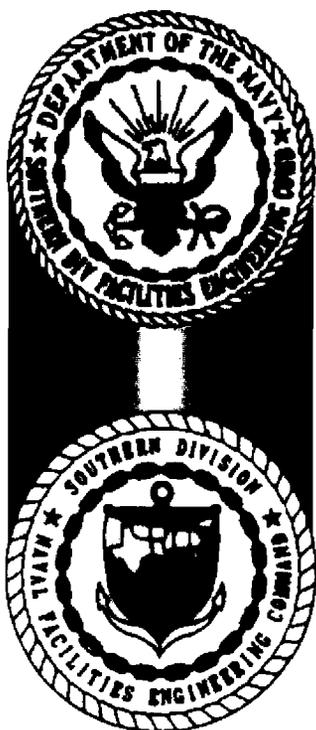


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CORRECTIVE MEASURES STUDY REPORT COMBINED SOLID WASTE MANAGEMENT
UNIT 65 (SWMU 65) ZONE E CNC CHARLESTON SC
12/12/2003
CH2M HILL

CORRECTIVE MEASURES STUDY REPORT

Combined SWMU 65, Zone E



***Charleston Naval Complex
North Charleston, South Carolina***

SUBMITTED TO
***U.S. Navy Southern Division
Naval Facilities Engineering Command***

CH2M Jones

December 2003

Contract N62467-99-C-0960

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Atlanta, GA 30346-1278
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December 12, 2003

Mr. David Scaturo
South Carolina Department of Health and
Environmental Control
Bureau of Land and Waste Management
2600 Bull Street
Columbia, SC 29201

Re: CMS Report (Revision 0) – Combined SWMU 65, Zone E

Dear Mr. Scaturo:

Enclosed please find two copies of the CMS Report (Revision 0) for Combined SWMU 65 in Zone E of the Charleston Naval Complex (CNC). This report has been prepared pursuant to agreements by the CNC BRAC Cleanup Team for completing the RCRA Corrective Action process.

Please contact me at 352/335-5877, ext. 2280, if you have any questions or comments.

Sincerely,

CH2M HILL

A handwritten signature in black ink that reads "Dean Williamson".

Dean Williamson, P.E.

cc: Dann Spariosu/USEPA, w/att
Rob Harrell/Navy, w/att
Gary Foster/CH2M HILL, w/att

CORRECTIVE MEASURES STUDY REPORT

Combined SWMU 65, Zone E



**Charleston Naval Complex
North Charleston, South Carolina**

SUBMITTED TO
**U.S. Navy Southern Division
Naval Facilities Engineering Command**

PREPARED BY
CH2M-Jones

December 2003

Revision 0
Contract N62467-99-C-0960
158814.ZE.EX.19

Certification Page for Corrective Measures Study Report (Revision 0) — Combined SWMU 65, Zone E

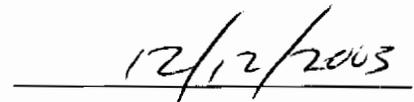
I, Dean Williamson, certify that this report has been prepared under my direct supervision. The data and information are, to the best of my knowledge, accurate and correct, and the report has been prepared in accordance with current standards of practice for engineering.

South Carolina

P.E. No. 21428



Dean Williamson, P.E.



Date

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1 Acronyms and Abbreviations

2	AOC	area of concern
3	BRAC	Base Realignment and Closure Act
4	CA	corrective action
5	CMS	corrective measures study
6	CNC	Charleston Naval Complex
7	COC	chemical of concern
8	COPC	chemical of potential concern
9	CSI	confirmatory sampling investigation
10	DO	dissolved oxygen
11	EnSafe	EnSafe Inc.
12	EPA	U.S. Environmental Protection Agency
13	ft bls	feet below land surface
14	ft msl	feet above mean sea level
15	gpm	gallon per minute
16	HI	hazard index
17	ILCR	Incremental Lifetime Cancer Risk
18	$\mu\text{g}/\text{L}$	microgram per liter
19	LUC	land use control
20	LUCMP	land use control management plan
21	MCL	maximum contaminant level
22	MCS	media cleanup standard
23	NAVBASE	Naval Base
24	NCSS	North Charleston Sanitary Sewer
25	ORP	oxidation reduction potential
26	RAO	remedial action objective
27	RBC	risk-based concentration
28	RCRA	Resource Conservation and Recovery Act
29	RFI	RCRA Facility Investigation

1 **Acronyms and Abbreviations, Continued**

2	RGO	remedial goal option
3	RI	remedial investigation
4	SCDHEC	South Carolina Department of Health and Environmental Control
5	SWMU	solid waste management unit
6	TCE	trichloroethene
7	VOC	volatile organic compound

Section 1.0

1 1.0 Introduction

2 In 1993, Naval Base (NAVBASE) Charleston was added to the list of bases scheduled for
3 closure as part of the Defense Base Realignment and Closure Act (BRAC), which regulates
4 closure and transition of property to the community. The Charleston Naval Complex (CNC)
5 was formed as a result of the dis-establishment of the Charleston Naval Shipyard and
6 NAVBASE on April 1, 1996.

7 Corrective Action (CA) activities are being conducted under the Resource Conservation and
8 Recovery Act (RCRA), with the South Carolina Department of Health and Environmental
9 Control (SCDHEC) as the lead agency for CA activities at the CNC. All RCRA CA activities
10 are performed in accordance with the Final Permit (Permit No. SC0 170 022 560). In April
11 2000, CH2M-Jones was awarded a contract to provide environmental investigation and
12 remediation services at the CNC.

13 A RCRA Facility Investigation (RFI) Report Addendum and Corrective Measures Study
14 (CMS) Work Plan were prepared for Solid Waste Management Unit (SWMU) 65 and Areas
15 of Concern (AOCs) 544 and 546 in Zone E of CNC (CH2M-Jones, 2003). These units were
16 investigated together during the RFI due to their proximity and will be referred to as
17 Combined SWMU 65 in this report. The location of Combined SWMU 65 in Zone E is shown
18 in Figure 1-1. Figure 1-2 shows an aerial photograph of the site. The Combined SWMU 65
19 area is zoned M-2 (for marine industrial land use).

20 The RFI Report Addendum and CMS Work Plan presented the remedial action objectives
21 (RAOs) and media cleanup standards (MCSs) proposed for Combined SWMU 65. This
22 report was reviewed by EPA Region IV on behalf of SCDHEC, and it was approved by EPA
23 in August 2003. This CMS report has been prepared by CH2M-Jones to complete the next
24 stage of the CA process for Combined SWMU 65.

25 1.1 Corrective Measures Study Report Purpose and Scope

26 This CMS report evaluates corrective measure alternatives for antimony, lead,
27 trichloroethene (TCE) and vinyl chloride in shallow groundwater and TCE and vinyl
28 chloride in deep groundwater at Combined SWMU 65. This report consists of: 1) the
29 identification of a set of corrective measure alternatives that are considered to be technically
30 appropriate for addressing contaminated groundwater; 2) an evaluation of the alternatives

1 using standard criteria from EPA RCRA guidance; and 3) the selection of a recommended
2 (preferred) corrective measure alternative for the site.

3 **1.2 Facility Description and Site History**

4 This section of the CMS report presents background information on the facility and site
5 history.

6 **1.2.1 SWMU 65 – Lead Storage Area, Building 221, and South of the Building**

7 SWMU 65 consists of a former lead storage area in which lead blankets and shielding
8 materials were stored on pallets and shelves inside Building 221 and on a paved area south
9 of the building. The majority of the lead was encased in rubber, but some exposed lead was
10 stored beneath a tarp inside the building. This site was also a staging area for scrap lead
11 awaiting disposal. Building 221 was built in 1970 and was used for lead storage and pickling
12 operations until 1985. Building 221 is currently a heavy equipment repair and maintenance
13 shop being used by Metal Trades, Inc., and the area south of the building is used for storage
14 of old metal parts and machinery.

15 As identified in the RCRA Facility Assessment (RFA) documentation (EnSafe Inc.
16 [EnSafe]/Allen & Hoshall, 1995), the materials of concern for SWMU 65 include lead, other
17 heavy metals, and acids.. The CNC RCRA Permit identified SWMU 65 as requiring an RFI.

18 **1.2.2 AOC 544 – Former Pickling Plant, Building 221**

19 AOC 544 is the site of a former pickling plant at Building 221. From 1940 to 1970, the
20 pickling plant consisted of an open-air facility with only the pickling tanks covered by a
21 roof. In 1970, a single-story structure was built to house the pickling operations. The process
22 used a series of chemical baths and water rinses. Until 1974, spent pickling bath solutions
23 were discharged via the storm drainage system into the Cooper River. After 1974, a private
24 contractor disposed of the wastes. Operations were discontinued in 1984 and the process
25 equipment was removed.

26 As identified in the RFA documentation, the materials of concern for AOC 544 include
27 acids, caustics, volatile organic compounds (VOCs), petroleum products, and heavy metals.
28 The CNC RCRA Permit identified AOC 544 as requiring an RFI.

1 **1.2.3 AOC 546 – Former Galvanizing/Pickling Shop, South of Building 221**

2 AOC 546 consists of a former galvanizing/pickling shop that operated within Building 1025
3 from the early 1920s until 1967. Building 1025 was located at two separate areas during its
4 existence. Originally, it was situated adjacent to the southwest corner of Building 6 (at the
5 current location of Building 3) and approximately co-located with SWMU 67 until 1942.
6 During this time, historical engineering drawings referred to it as a galvanizing shed.
7 After it was relocated south of Building 221, it was referred to as a pipe shop/pickling plant.
8 No information was found during the RFA or RFI regarding its operational processes.
9 Currently, both the former and present locations of AOC 546 are covered with pavement or
10 structures. At this time, only a concrete slab exists at the location of Building 1025 south of
11 Building 221, and it is being used as a storage area. The RFI Report Addendum/CMS Work
12 Plan for Combined SWMU 65 (CH2M-Jones, 2003) addressed only the portion of AOC 546
13 that is located next to SWMU 65 and AOC 544. The portion of AOC 546 that is co-located
14 with SWMU 67 was addressed in the RFI Report Addendum/CMS Work Plan for
15 Combined SWMU 67 (CH2M-Jones, 2002).

16 As identified in the Zone E RFI Work Plan (EnSafe/Allen & Hoshall, 1995), the materials of
17 concern for AOC 546 include VOCs, inorganic acids, and heavy metals. The CNC RCRA
18 Permit identified AOC 546 as requiring a confirmatory sampling investigation (CSI).

19 The RFI activities initially conducted by the Navy/EnSafe team were described in the *Zone*
20 *E RFI Report, Revision 0* (EnSafe, 1997). Regulatory review was conducted on this document
21 and draft responses to the comments from SCDHEC were prepared by the Navy/EnSafe
22 team. Remaining issues related to the RFI phase of the CA program were addressed in the
23 RFI Report Addendum/CMS Work Plan (CH2M-Jones, 2003). RFI soil and groundwater
24 sampling locations are shown in Figure 1-3.

25 **1.3 Nature and Extent of COCs At Combined SWMU 65**

26 This section presents a summary of the nature and extent of the chemicals of concern
27 (COCs) at the site. This information is essential to the understanding of the remedial goal
28 options (RGOs), MCSs, and ultimately the evaluation of corrective measure alternatives for
29 Combined SWMU 65. Additional information on the site and hydrogeology in the Zone E
30 area of the CNC is provided in the *Zone E RFI Report, Revision 0* (EnSafe, 1997).

31 Based on the results of the sampling and analysis and evaluation of current contamination
32 levels in the RFI Report Addendum, no soil COCs for the industrial land use scenario were

1 identified for Combined SWMU 65. Antimony, lead, TCE, and vinyl chloride were
2 identified as shallow groundwater COCs and TCE and vinyl chloride were identified as
3 deep groundwater COCs for Combined SWMU 65.

4 **1.3.1 Summary of Hydrogeologic Setting at Combined SWMU 65**

5 Combined SWMU 65 is located in the northeastern portion of Zone E at the CNC, where the
6 surface topography is relatively flat and nearly completely paved. Elevations range between
7 approximately 8 to 10 feet above mean sea level (ft msl). Because the area is highly
8 industrialized, surface water runoff is largely controlled by a system of stormwater sewers
9 that discharge to the Cooper River.

10 **Surface Geology**

11 Due to the extensive surface soil disturbance at CNC during the history of its operations, the
12 soils from land surface to depths of up to approximately 6 feet are typically a mixture of
13 artificial fill and native sediments. The extent of fill material present varies extensively, but
14 in the vicinity of Combined SWMU 65, undifferentiated clay, sand, gravel, dredged
15 material, and construction debris may be present at or near the land surface. In undisturbed
16 areas, surface deposits consist of Quaternary age (Holocene epoch to recent) fine-grained
17 sands and clays typical of a coastal plain environment, repeatedly reworked by marine and
18 river water erosion prior to development by man.

19 **Subsurface Geology**

20 The Zone E RFI report included the installation of soil borings and more than 185
21 monitoring wells, from which geologic information was collected to develop geologic cross
22 sections. The data indicate that Quaternary (Pleistocene to Holocene) and Tertiary age
23 unconsolidated sediments were encountered in the subsurface. The lowermost unit
24 encountered is the Tertiary age Ashley Formation member of the Mid-Tertiary age Cooper
25 Group. Overlying the Ashley Formation are younger upper Tertiary and Quaternary age
26 deposits, which are in turn overlain by the Holocene to recent surface soils.

27 In most of Zone E, the Ashley Formation is encountered in deeper borings, occurring at
28 depths of approximately 16 to 43 feet below land surface (ft bls). However, in northern Zone
29 E, the Ashley Formation dips downward and was not encountered to depths of 75 ft bls

1 during installation of deep borings as part of the RFI. The deeper occurrence of the Ashley
2 Formation in this part of the CNC is probably due to secondary erosion. In the remainder of
3 Zone E, the top of the Ashley Formation is gently rolling and slopes gently downward to the
4 east toward the Cooper River, with measured thickness approaching 40 feet. The Ashley
5 Formation is comprised of brown to olive marine silts with varying amounts of clay,
6 phosphatic sand and microfossils. The Ashley consistency is generally dense to stiff and
7 plastic, with low vertical permeability. The overlying Quaternary age deposits are back
8 barrier and near shore shelf deposits from various past marine transgressions, with
9 subsequent reworking erosion and redeposition. The result is a sequence approximately 15
10 to 85 feet thick at the CNC and comprised mainly of Pleistocene age Wando Formation
11 sands, silts, and clays, with varying amounts of organic matter including peat.

12 In the area where Combined SWMU 65 is located, the bottom of the shallow aquifer system
13 is delineated by Quaternary (dewatered marsh) clay at a depth of approximately -30 ft msl,
14 or approximately 40 bls. The Quaternary clay at Combined SWMU 65 is overlain by
15 interbedded sand, silt and clay layers (including marsh clay), with layers of peat occurring
16 intermittently, and finally by about 5 feet of fill to land surface.

17 Boring logs for wells installed at Combined SWMU 65 are provided in Appendix A.
18 Inspection of these logs indicates that the shallow portion of the surficial aquifer at
19 Combined SWMU 65 consists predominantly of interbedded clay and peat layers, with thin
20 sand and silt layers also present.

21 **Hydrogeology**

22 The shallow aquifer system at Combined SWMU 65 is an unconfined water table aquifer
23 occurring within the Quaternary sediments. The underlying low-permeability Quaternary
24 clay acts as an aquitard for the shallow aquifer system and as a confining unit for deeper
25 geologic units. The Cooper River acts as a regional discharge boundary for the aquifer to the
26 east. The average saturated aquifer thickness in the Combined SWMU 65 area, based on the
27 Zone E RFI Report, is approximately 35 feet.

28 Regionally in Zone E, the shallow groundwater flow direction is east, toward the Cooper
29 River. Because a significant portion of Zone E is along the riverfront, the Cooper River is a

1 major discharge boundary for the shallow aquifer system. Locally at Combined SWMU 65,
2 groundwater flow has been observed to be generally radially outward, with a local
3 groundwater high elevation located in the vicinity of well E065GW003. This outward radial
4 flow pattern was observed during groundwater elevation measurements made during the
5 RFI (see Figure 2-GA in the *Zone E RFI Report, Revision 0*) in 1996, as well as during more
6 recent groundwater elevation measurements as shown in Figure 1-4 (measured in May
7 2002) made by CH2M-Jones. Section 2.3.7 of the *Zone E RFI Report, Revision 0* (EnSafe, 1997)
8 indicates that one shallow monitoring well (E065GW002) indicated a water elevation change
9 of approximately 0.6 ft between measurements made during low tide and high tide,
10 indicating minor tidal influence in this area.

11 The low groundwater elevation trough located west of SWMU 65, as shown in Figure 1-4,
12 may be due to local groundwater drainage into a storm sewer line that runs between
13 Buildings 3 and 56.

14 **1.3.2 COC Distribution in Groundwater**

15 Table 1-1 summarizes all shallow groundwater analyses at the site for the two metal COCs
16 (antimony and lead). As shown in Table 1-1, out of 80 total analyses for COCs, only 10
17 exceedances of the applicable screening criteria (maximum contaminant level [MCL] or
18 Region III tap water risk-based concentration [RBC]) have been observed (approximately
19 12.5 percent), indicating that the number of exceedances is relatively limited.

20 Figure 1-5 shows concentrations of antimony and lead detected in shallow groundwater
21 monitoring wells above the target MCSs (6 micrograms per liter [$\mu\text{g}/\text{L}$] for antimony and 15
22 $\mu\text{g}/\text{L}$ for lead) at Combined SWMU 65. It can be seen in this figure that all but two of the
23 MCS exceedances occurred in well E065GW003. Well E065GW004 had two exceedances of
24 lead above its target MCS of 15 $\mu\text{g}/\text{L}$. No other wells had exceedances of the MCSs for these
25 two COCs.

26 As indicated in Table 1-1, the lead concentrations in well E065GW003 have consistently
27 exceeded the target MCS of 15 $\mu\text{g}/\text{L}$. However, the two exceedances for lead in E065GW004
28 have been interceded by several detections below the MCS at less than 3 $\mu\text{g}/\text{L}$. Antimony
29 exceedances of the MCL have been limited to well E065GW003 and antimony has not
30 consistently been detected above the MCL in this well.

1 The presence of peat and clay layers in the shallow aquifer may be attenuating lead
2 concentrations and limiting the migration of lead in groundwater at the site. Lead is known
3 to be strongly sorbed by clay and peat and the presence of these features at Combined
4 SWMU 65 is limiting lead migration.

5 Figure 1-6 shows concentrations of TCE and vinyl chloride in shallow groundwater above
6 their respective MCSs (5 and 2 $\mu\text{g}/\text{L}$, respectively). As indicated in Figure 1-6, all VOC
7 exceedances in shallow groundwater have occurred in well E065GW003. The extent of VOC
8 contamination in shallow groundwater at the site is limited.

9 Figure 1-7 shows the TCE and vinyl chloride exceedances in deep groundwater. Only two
10 exceedances of the TCE MCL have been observed, at 6 and 8 $\mu\text{g}/\text{L}$. No TCE exceedances
11 have been observed in deep groundwater since 1996. All vinyl chloride exceedances have
12 been no greater than 6 $\mu\text{g}/\text{L}$. Overall, VOC concentrations are relatively low in deep
13 groundwater.

14 **1.4 Overall Approach for Selecting Candidate Corrective** 15 **Measure Alternatives for Combined SWMU 65**

16 Because of the relatively small areal extent of impacted groundwater at Combined SWMU
17 65, the list of practicable remedial alternatives for this site is limited.

18 Remedies that will be considered for the groundwater COCs in this CMS for Combined
19 SWMU 65 are as follows:

- 20 • Monitored Natural Attenuation and land use controls (LUCs);
- 21 • In Situ Stabilization and LUCs; and
- 22 • Groundwater Recovery, Treatment, and Discharge to the Sanitary Sewer and LUCs.

23 **1.5 Report Organization**

24 This CMS report consists of the following sections, including this introductory section:

25 **1.0 Introduction** — Presents the purpose of and background information relating to this
26 CMS report.

27 **2.0 Remedial Goal Objectives and Evaluation Criteria** — Defines the RGOs for Combined
28 SWMU 65, in addition to the criteria used in evaluating the corrective measure alternatives
29 for the site.

- 1 **3.0 Description of Candidate Corrective Measure Alternatives** — Describes each of the
2 candidate corrective measure alternatives for addressing COCs at the site.
- 3 **4.0 Evaluation and Comparison of Corrective Measure Alternatives** — Evaluates each
4 alternative relative to standard criteria, then compares the alternatives and the degree to
5 which they meet or achieve the evaluation criteria.
- 6 **5.0 Recommended Corrective Measure Alternative** — Describes the preferred corrective
7 measure alternative to achieve the MCS and RGOs for COCs based on a comparison of the
8 alternatives.
- 9 **6.0 References** — Lists the references used in this document.
- 10 **Appendix A** contains boring logs for SWMU 65 wells and well sampling forms from the
11 RFI.
- 12 **Appendix B** contains a draft report recently released by the U.S. Environmental Protection
13 Agency (EPA) that provides an overview of metal geochemistry.
- 14 **Appendix C** contains cost estimates developed for the proposed corrective measure
15 alternatives.
- 16 All tables and figures appear at the end of their respective sections.

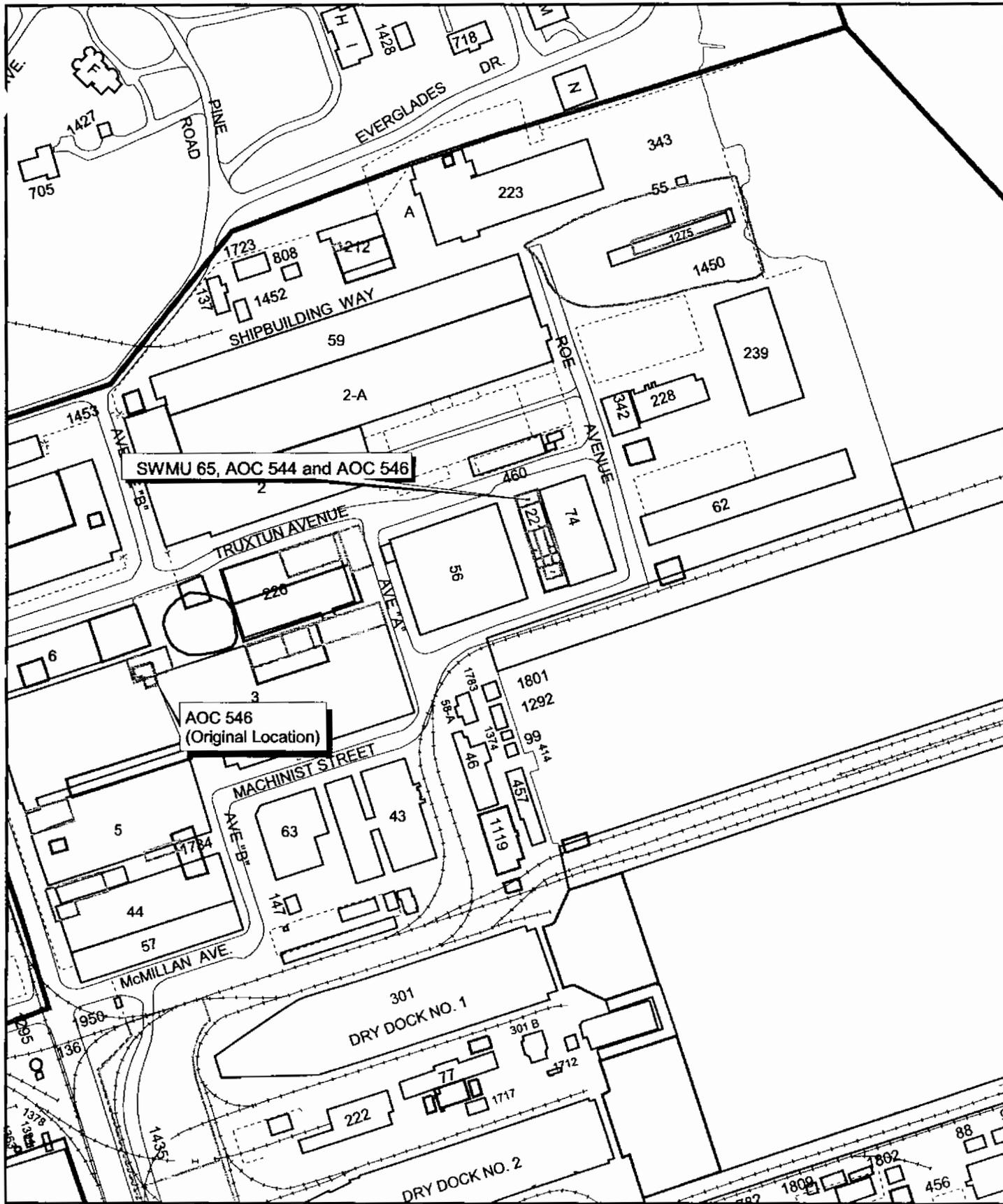
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TABLE 1-1
 Lead and Antimony Results for Groundwater Samples At Combined SWMU 65
 SWMU 65, Charleston Naval Complex

Station	Sample	Chemical	Result	Unit	Qualifier	Date_Col	MCL
E065GW001	065GW00101	Lead	3.00000	µg/L	U	04/17/1996	15
E065GW001	065GW00102	Lead	1.70000	µg/L	U	08/14/1996	15
E065GW001	065GW00103	Lead	1.70000	µg/L	U	12/11/1996	15
E065GW001	065GW00104	Lead	0.90000	µg/L	U	02/26/1997	15
E065GW001	065GW001M2	Lead	1.24000	µg/L	U	09/11/2002	15
E065GW002	065GW00201b	Lead	3.00000	µg/L	U	04/18/1996	15
E065GW002	065GW00202	Lead	1.70000	µg/L	U	08/13/1996	15
E065GW002	065GW00203	Lead	1.70000	µg/L	U	12/11/1996	15
E065GW002	065GW00204	Lead	0.90000	µg/L	U	02/25/1997	15
E065GW002	065GW002M2	Lead	1.57000	µg/L	U	09/11/2002	15
E065GW003	065GW00301b	Lead	1690.00000	µg/L	=	04/18/1996	15
E065GW003	065GW00302	Lead	349.00000	µg/L	=	08/14/1996	15
E065GW003	065GW00303	Lead	224.00000	µg/L	=	12/10/1996	15
E065GW003	065GW00304	Lead	207.00000	µg/L	=	02/26/1997	15
E065GW003	065GW003M2	Lead	683.00000	µg/L	=	09/11/2002	15
E065GW004	065GW00401	Lead	315.00000	µg/L	=	04/17/1996	15
E065GW004	065GW00402	Lead	2.90000	µg/L	J	08/15/1996	15
E065GW004	065GW00403	Lead	1.70000	µg/L	U	12/09/1996	15
E065GW004	065GW00404	Lead	1.30000	µg/L	J	02/25/1997	15
E065GW004	065GW004M2	Lead	25.60000	µg/L	=	09/11/2002	15
E065GW005	065GW00501	Lead	3.60000	µg/L	=	04/17/1996	15
E065GW005	065GW00502	Lead	1.70000	µg/L	U	08/15/1996	15
E065GW005	065GW00503	Lead	1.70000	µg/L	U	12/10/1996	15
E065GW005	065GW00504	Lead	1.70000	µg/L	J	02/25/1997	15
E065GW005	065GW005M2	Lead	1.77000	µg/L	U	09/11/2002	15
E065GW006	065GW00601	Lead	8.90000	µg/L	=	04/19/1996	15
E065GW006	065GW00602	Lead	5.10000	µg/L	=	08/14/1996	15
E065GW006	065GW00603	Lead	4.50000	µg/L	=	12/12/1996	15
E065GW006	065GW00604	Lead	7.60000	µg/L	=	02/26/1997	15
E065GW006	065GW006M2	Lead	2.10000	µg/L	U	09/11/2002	15
E065GW007	065GW00701	Lead	1.70000	µg/L	J	10/30/1996	15
E065GW007	065GW007A2	Lead	1.50000	µg/L	U	03/06/1997	15
E065GW007	065GW007A3	Lead	0.90000	µg/L	U	06/27/1997	15
E065GW007	065GW00704	Lead	0.90000	µg/L	U	10/09/1997	15
E065GW008	065GW00801	Lead	1.70000	µg/L	U	10/30/1996	15
E065GW008	065GW008A2	Lead	0.90000	µg/L	U	03/06/1997	15
E065GW008	065GW008A3	Lead	2.10000	µg/L	U	06/27/1997	15
E065GW008	065GW00804	Lead	0.90000	µg/L	U	10/09/1997	15
E065GW008	065GW008M2	Lead	1.24000	µg/L	U	09/11/2002	15
E065GW009	065GW009M2	Lead	1.24000	µg/L	U	09/11/2002	15

TABLE 1-1
 Lead and Antimony Results for Groundwater Samples At Combined SWMU 65
 SWMU 65, Charleston Naval Complex

Station	Sample	Chemical	Result	Unit	Qualifier	Date_Col	MCL
E065GW001	065GW00101	Antimony	4.00000	µg/L	U	04/17/1996	6
E065GW001	065GW00102	Antimony	2.10000	µg/L	U	08/14/1996	6
E065GW001	065GW00103	Antimony	2.50000	µg/L	U	12/11/1996	6
E065GW001	065GW00104	Antimony	2.30000	µg/L	U	02/26/1997	6
E065GW001	065GW001M2	Antimony	4.79000	µg/L	U	09/11/2002	6
E065GW002	065GW00201b	Antimony	4.00000	µg/L	U	04/18/1996	6
E065GW002	065GW00202	Antimony	2.10000	µg/L	U	08/13/1996	6
E065GW002	065GW00203	Antimony	2.80000	µg/L	U	12/11/1996	6
E065GW002	065GW00204	Antimony	2.60000	µg/L	U	02/25/1997	6
E065GW002	065GW002M2	Antimony	4.79000	µg/L	U	09/11/2002	6
E065GW003	065GW00301b	Antimony	42.00000	µg/L	J	04/18/1996	6
E065GW003	065GW00302	Antimony	24.20000	µg/L	U	08/14/1996	6
E065GW003	065GW00303	Antimony	13.90000	µg/L	U	12/10/1996	6
E065GW003	065GW00304	Antimony	17.90000	µg/L	J	02/26/1997	6
E065GW003	065GW003M2	Antimony	30.70000	µg/L	J	09/11/2002	6
E065GW004	065GW00401	Antimony	4.00000	µg/L	U	04/17/1996	6
E065GW004	065GW00402	Antimony	4.20000	µg/L	U	08/15/1996	6
E065GW004	065GW00403	Antimony	2.90000	µg/L	U	12/09/1996	6
E065GW004	065GW00404	Antimony	3.10000	µg/L	U	02/25/1997	6
E065GW004	065GW004M2	Antimony	4.79000	µg/L	U	09/11/2002	6
E065GW005	065GW00501	Antimony	4.50000	µg/L	J	04/17/1996	6
E065GW005	065GW00502	Antimony	2.10000	µg/L	U	08/15/1996	6
E065GW005	065GW00503	Antimony	2.10000	µg/L	U	12/10/1996	6
E065GW005	065GW00504	Antimony	3.20000	µg/L	U	02/25/1997	6
E065GW005	065GW005M2	Antimony	4.79000	µg/L	U	09/11/2002	6
E065GW006	065GW00601	Antimony	4.00000	µg/L	U	04/19/1996	6
E065GW006	065GW00602	Antimony	2.10000	µg/L	U	08/14/1996	6
E065GW006	065GW00603	Antimony	2.90000	µg/L	U	12/12/1996	6
E065GW006	065GW00604	Antimony	1.60000	µg/L	U	02/26/1997	6
E065GW006	065GW006M2	Antimony	4.79000	µg/L	U	09/11/2002	6
E065GW007	065GW00701	Antimony	2.10000	µg/L	U	10/30/1996	6
E065GW007	065GW007A2	Antimony	1.70000	µg/L	U	03/06/1997	6
E065GW007	065GW007A3	Antimony	2.10000	µg/L	U	06/27/1997	6
E065GW007	065GW00704	Antimony	1.60000	µg/L	U	10/09/1997	6
E065GW008	065GW00801	Antimony	2.10000	µg/L	U	10/30/1996	6
E065GW008	065GW008A2	Antimony	1.60000	µg/L	U	03/06/1997	6
E065GW008	065GW008A3	Antimony	1.60000	µg/L	UJ	06/27/1997	6
E065GW008	065GW00804	Antimony	1.60000	µg/L	U	10/09/1997	6
E065GW008	065GW008M2	Antimony	4.79000	µg/L	U	09/11/2002	6
E065GW009	065GW009M2	Antimony	4.79000	µg/L	U	09/11/2002	6



- Railroads
- Roads - Lines
- AOC Boundary
- SWMU Boundary
- Buildings
- Zone Boundary

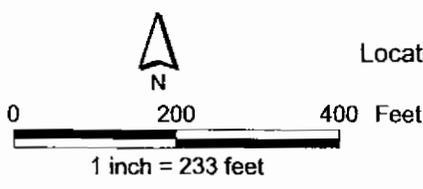
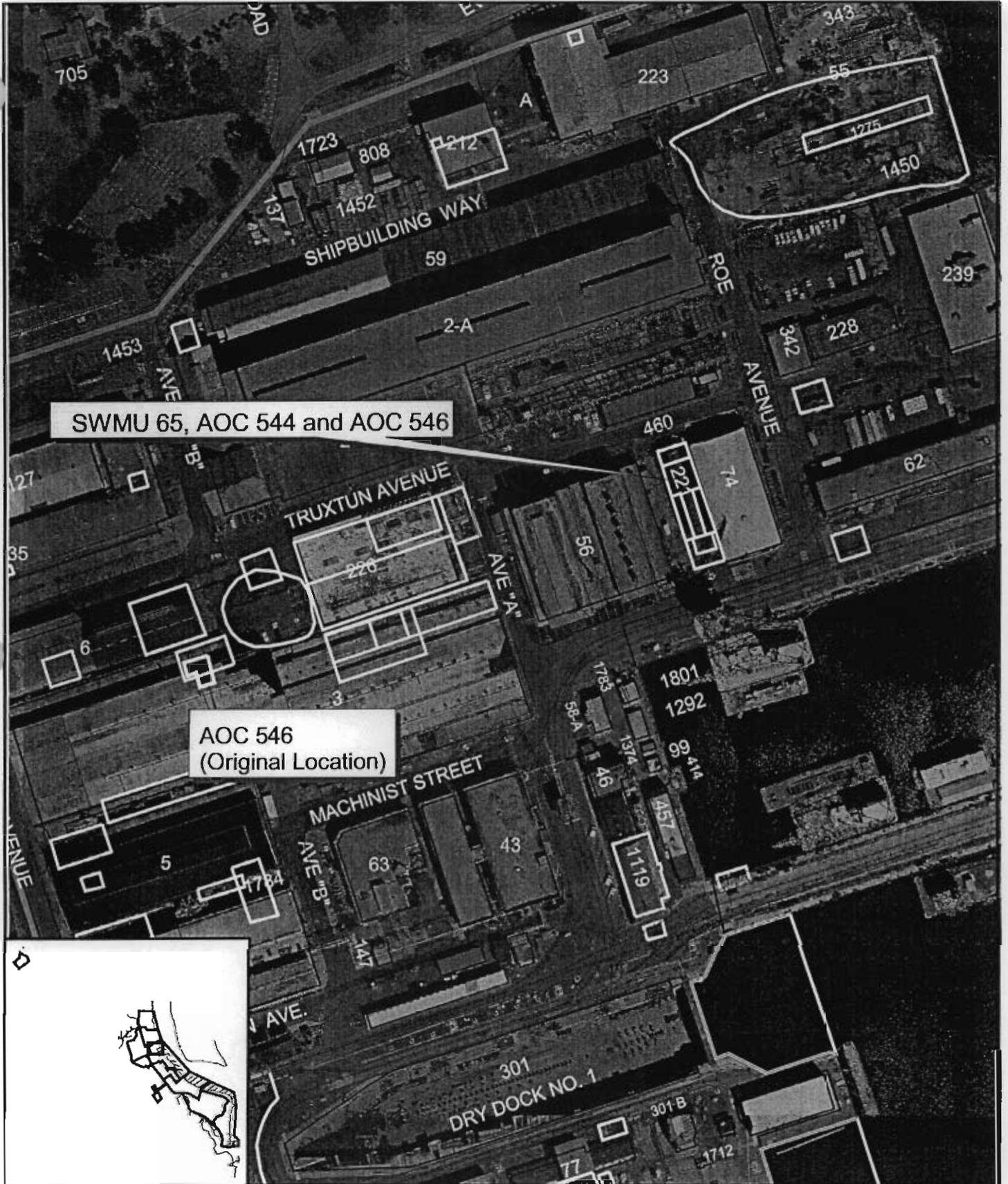


Figure 1-1
 Location of Combined SWMU 65 in Zone E
 Charleston Naval Complex



SWMU 65, AOC 544 and AOC 546

AOC 546
(Original Location)

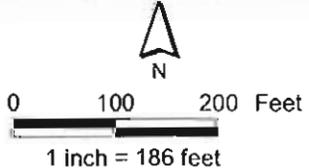
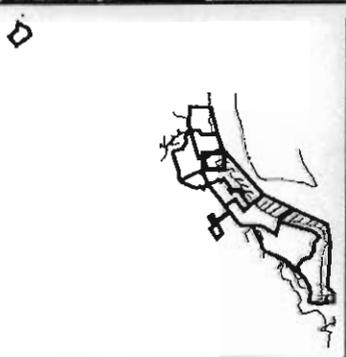


Figure 1-2
Site Location
Combined SWMU 65, Zone E
Charleston Naval Complex

NOTE: Original figure created in color

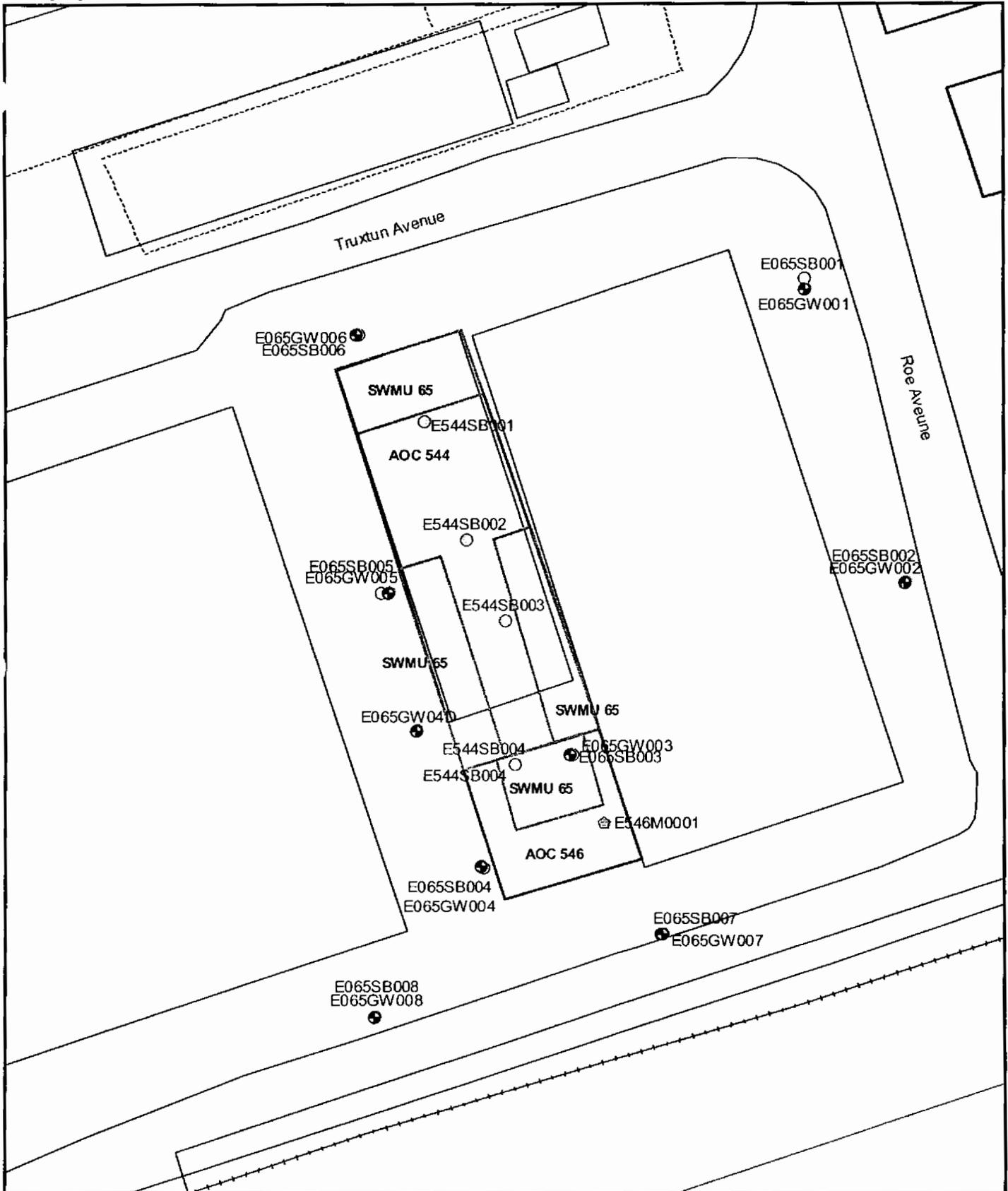
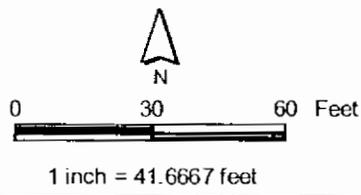
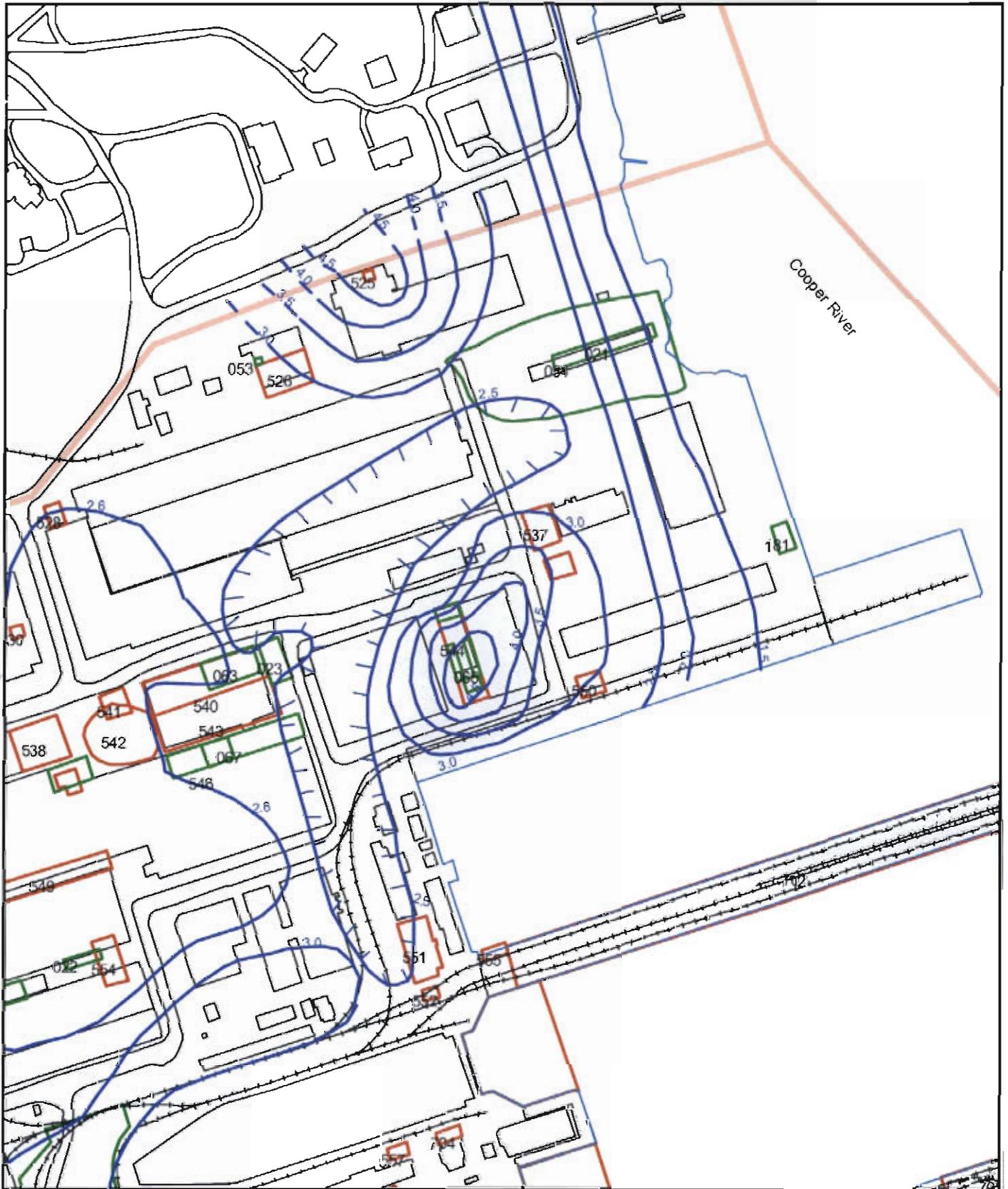


Figure 1-3
RFI Sampling Locations
Combined SWMU 65, Zone E
Charleston Naval Complex

- Groundwater Monitoring Well
- ⊕ Sediment Sampling Location
- Soil Boring Location
- - - Fence
- ≡ Railroads
- ≡ Roads
- ▭ AOC Boundary
- ▭ SWMU Boundary
- ▭ Buildings



CH2MHILL



- Known Shallow Groundwater Contour (5/14/02)
- Inferred Shallow Groundwater Contour (5/14/02)
- Fence
- Railroads
- Roads
- Groundwater Well
- AOC Boundary
- SWMU Boundary
- Buildings
- Zone Boundary

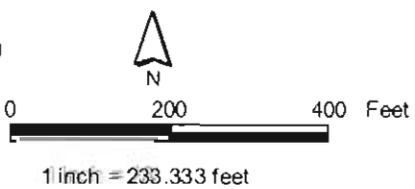
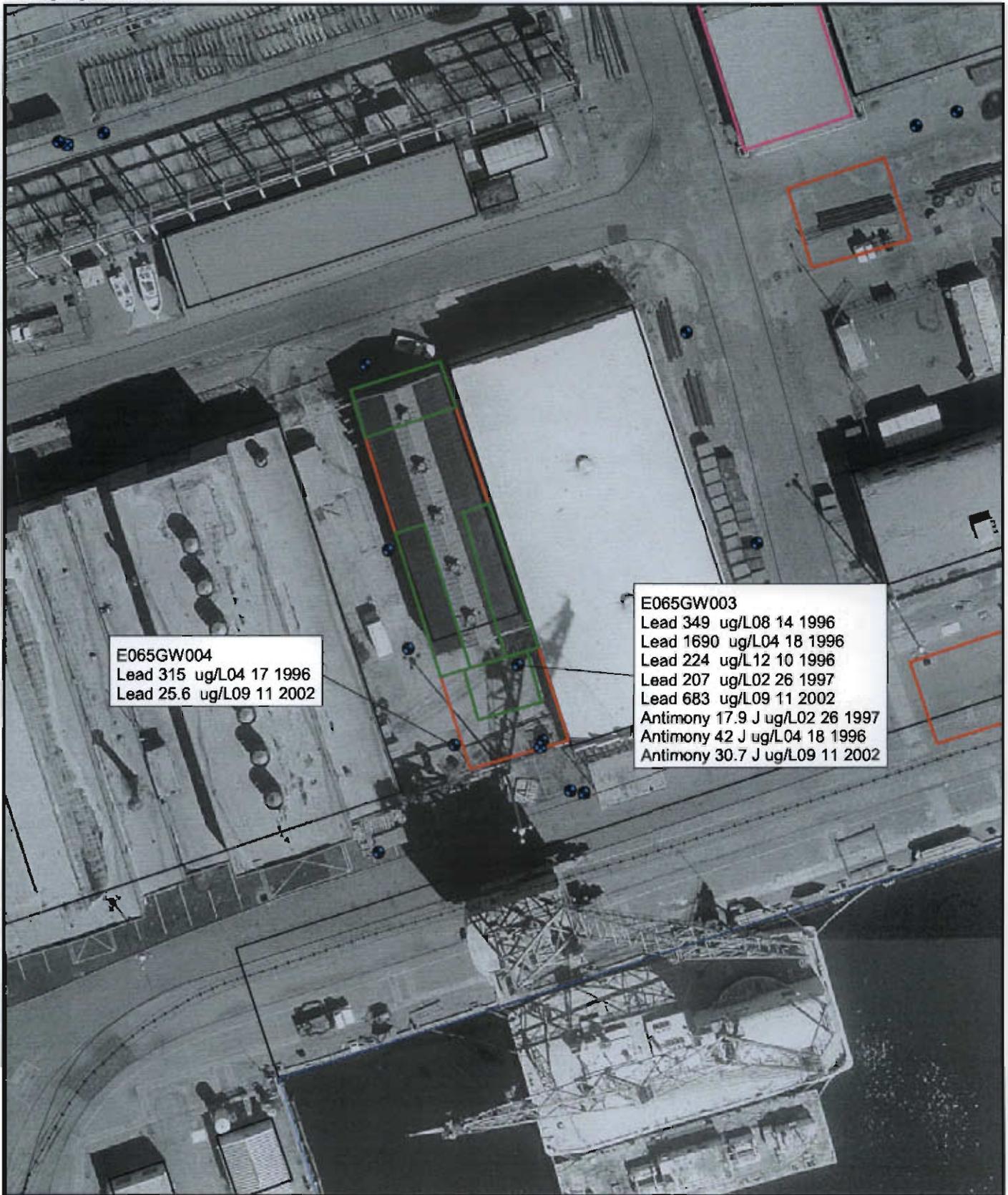


Figure 1-4
 Shallow Groundwater Contours
 Combined SWMU 65, Zone E
 Charleston Naval Complex

NOTE: Aerial Photo Date is 1997
NOTE: Original figure created in color



E065GW004
Lead 315 ug/L04 17 1996
Lead 25.6 ug/L09 11 2002

E065GW003
Lead 349 ug/L08 14 1996
Lead 1690 ug/L04 18 1996
Lead 224 ug/L12 10 1996
Lead 207 ug/L02 26 1997
Lead 683 ug/L09 11 2002
Antimony 17.9 J ug/L02 26 1997
Antimony 42 J ug/L04 18 1996
Antimony 30.7 J ug/L09 11 2002

- Abandoned
- Active

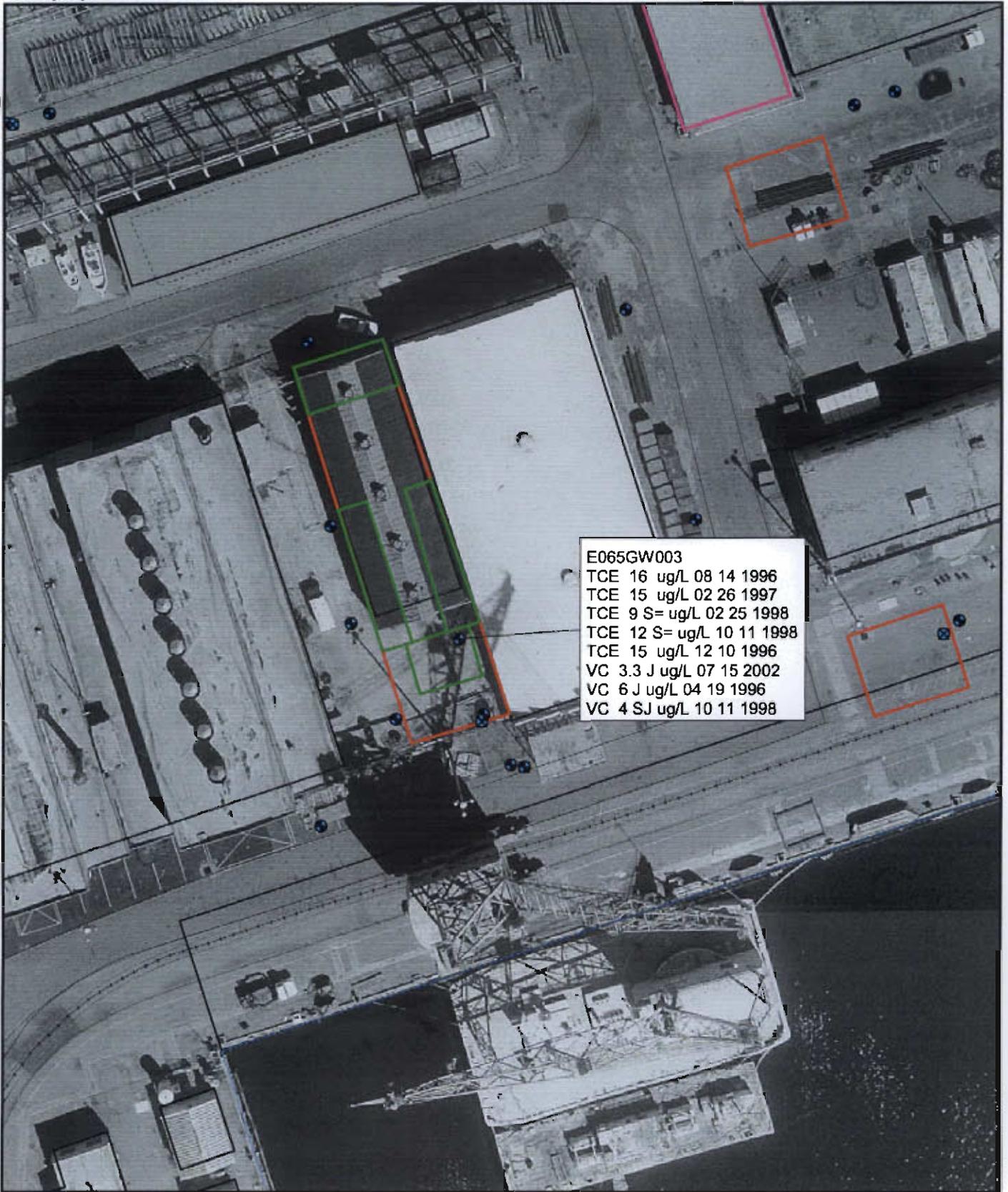


Shallow Groundwater Exceedances of Antimony and Lead
Combined SWMU 65
Charleston Naval Complex

0 40 80 Feet

1 inch = 58.5097 feet

NOTE: Aerial Photo Date is 1997
NOTE: Original figure created in color



- Abandoned
- Active



0 50 100 Feet

1 inch = 58.9167 feet

Figure 1-6
VOC Exceedances in Shallow Groundwater
Combined SWMU 65, Zone E
Charleston Naval Complex

NOTE: Aerial Photo Date is 1997
NOTE: Original figure created in color



- ⊗ Abandoned
- Active



0 60 120 Feet



1 inch = 75.2637 feet

Figure 1-7
VOC Exceedances in Deep Groundwater
Combined SWMU 65, Zone E
Charleston Naval Complex

Section 2.0

2.0 Remedial Goal Objectives and Evaluation Criteria

2.1 Remedial Action Objectives

RAOs are medium-specific goals that protect human health and the environment by preventing or reducing exposures under current and future land use conditions. The RAO identified for the subsurface soil at Combined SWMU 65 is to achieve concentrations of COCs that are protective of groundwater (prevent leaching of COCs at concentrations that cause concentrations of COCs in groundwater to exceed their target MCSs. The RAO for groundwater is to prevent ingestion of groundwater containing COCs at unacceptable levels and to restore the aquifer to its beneficial use to the extent practicable.

2.2 Media Cleanup Standards

Throughout the process of remediating a hazardous waste site, a risk manager uses a progression of increasingly acceptable site-specific media levels in considering remedial alternatives. Under the RCRA program, RGOs and MCSs are developed at the end of the risk assessment in the RFI/Remedial Investigation (RI) programs, before completion of the CMS.

RGOs can be based on a variety of criteria, such as specific incremental lifetime cancer risk (ILCR) levels (e.g., 1E-04, 1E-05, or 1E-06), Hazard Index (HI) levels (e.g., 0.1, 1.0, 3.0), or site background concentrations. For a particular RGO, specific MCSs can be determined as target concentration values. Achieving these MCSs is accepted as demonstrating that RGOs and RAOs have been achieved. Achieving these goals should promote the protection of human health and the environment, while achieving compliance with applicable state and federal standards.

The exposure medium of concern for Combined SWMU 65 is shallow groundwater containing antimony, lead, TCE, and vinyl chloride and deep groundwater containing TCE and vinyl chloride.

For the chemicals identified as COCs in shallow groundwater, the following MCSs were previously proposed in the CMS Work Plan:

COC	Proposed MCS
Shallow Groundwater	
Antimony	MCL for antimony - 6 $\mu\text{g/L}$
Lead	Drinking water Target Treatment Level for lead - 15 $\mu\text{g/L}$
TCE	MCL for TCE - 5 $\mu\text{g/L}$
Vinyl chloride	MCL for vinyl chloride - 2 $\mu\text{g/L}$
Deep Groundwater	
TCE	MCL for TCE - 5 $\mu\text{g/L}$
Vinyl chloride	MCL for vinyl chloride - 2 $\mu\text{g/L}$

1

2 **2.3 Evaluation Criteria**

3 According to the EPA RCRA CA guidance, corrective measure alternatives should be
4 evaluated using the following five criteria:

- 5 1. Protection of human health and the environment.
- 6 2. Attainment of MCSs.
- 7 3. The control of the source of releases to minimize future releases that may pose a threat
8 to human health and the environment.
- 9 4. Compliance with applicable standards for the management of wastes generated by
10 remedial activities.
- 11 5. Other factors, including (a) long-term reliability and effectiveness; (b) reduction in
12 toxicity, mobility, or volume of wastes; (c) short-term effectiveness; (d)
13 implementability; and (e) cost.

14 Each of these criteria is defined in more detail below:

- 15 1. **Protection of human health and the environment.** The alternatives will be evaluated on
16 the basis of their ability to protect human health and the environment. The ability of an
17 alternative to achieve this criterion may or may not be independent of its ability to
18 achieve the other criteria. For example, an alternative may be protective of human
19 health, but may not be able to attain the MCSs if the MCSs were not developed based on
20 human health protection factors.
- 21 2. **Attainment of MCSs.** The alternatives will be evaluated on the basis of their ability to
22 achieve the MCS defined in this CMS. Another aspect of this criterion is the time frame

1 required to achieve the MCS. Estimates of the time frame for the alternatives to achieve
2 RGOs will be provided.

3 3. **The control the source of releases.** This criterion deals with the control of releases of
4 contamination from the source (the area in which the contamination originated) and the
5 prevention of future migration to uncontaminated areas.

6 4. **Compliance with applicable standards for management of wastes.** This criterion deals
7 with the management of wastes derived from implementing the alternatives (i.e.,
8 treatment or disposal of residuals from groundwater treatment processes). Corrective
9 measure alternatives will be designed to comply with all standards for management of
10 wastes. Consequently, this criterion will not be explicitly included in the detailed
11 evaluation presented in the CMS, but such compliance would be incorporated into the
12 cost estimates for which this criterion is relevant.

13 5. **Other factors.** Five other factors are to be considered if an alternative is found to meet
14 the four criteria described above. These other factors are as follows:

15 a. Long-term reliability and effectiveness

16 Corrective measure alternatives will be evaluated on the basis of their reliability, and
17 the potential impact should the alternative fail. In other words, a qualitative
18 assessment will be made as to the chance of the alternative's failing and the
19 consequences of that failure.

20 b. Reduction in the toxicity, mobility, or volume of wastes

21 Alternatives with technologies that reduce the toxicity, mobility, or volume of the
22 contamination will be generally favored over those that do not. Consequently, a
23 qualitative assessment of this factor will be performed for each alternative.

24 c. Short-term effectiveness

25 Alternatives will be evaluated on the basis of the risk they create during the
26 implementation of the remedy. Factors that may be considered include fire,
27 explosion, and exposure of workers to hazardous substances.

28 d. Implementability

29 The alternatives will be evaluated for their implementability by considering any
30 difficulties associated with conducting the alternatives (such as the construction
31 disturbances they may create), operation of the alternatives, and the availability of
32 equipment and resources to implement the technologies comprising the alternatives.

1 e. Cost

2 A net present value of each alternative will be developed. These cost estimates will
3 be used for the relative evaluation of the alternatives, not to bid or budget the work.
4 The estimates will be based on information available at the time of the CMS and on a
5 conceptual design of the alternative. They will be "order-of-magnitude" estimates
6 with a generally expected accuracy of -50 percent to +100 percent for the scope of
7 action described for each alternative. The estimates will be categorized into capital
8 costs and operations and maintenance costs for each alternative.

1 **3.0 Description of Candidate Corrective** 2 **Measure Alternatives**

3 **3.1 Introduction**

4 Currently available groundwater remedial technologies were screened for applicability to
5 the contaminants and physical conditions present at Combined SWMU 65, with only the
6 most viable technologies known for addressing the COCs present at the site selected for
7 alternatives analysis.

8 Three remedies will be considered for the groundwater COCs in the CMS for Combined
9 SWMU 65:

- 10 • Monitored Natural Attenuation and LUCs;
- 11 • In Situ Stabilization and LUCs; and
- 12 • Groundwater Recovery, Treatment, and Discharge to the Sanitary Sewer and LUCs.

13 The sections below describe each alternative in more detail.

14 **3.2 Alternative 1: Monitored Natural Attenuation and LUCs**

15 **3.2.1 Description of Alternative**

16 Alternative 1 would rely on natural attenuation processes, such as adsorption, ion exchange,
17 precipitation, dispersion, and dilution, to reduce concentrations of antimony and lead in
18 groundwater over time. Similarly, natural attenuation processes, such as biodegradation,
19 adsorption, volatilization, dispersion, and dilution, would act to reduce concentrations of
20 TCE and vinyl chloride in shallow and deep groundwater.

21 This alternative is considered feasible for the site because the extent of groundwater
22 contamination is limited in size, groundwater concentrations of COCs are relatively low,
23 and there are no ongoing sources of release for the COCs.

24 Groundwater samples from only two shallow wells at the site have exhibited concentrations
25 of lead above the target MCS; samples from only one shallow well have exhibited
26 concentrations of antimony above their respective MCSs, and samples from only one
27 shallow and one deep well have exhibited TCE and vinyl chloride concentrations above

1 their respective MCSs. To date, there is little to no evidence that migration of any COCs
2 from the vicinity of these wells is occurring. Because no sources of release of these chemicals
3 remain, it is expected that over time, concentrations of all COCs in all wells exhibiting
4 exceedances will decline to below the target MCSs.

5 During the period while natural attenuation processes are actively decreasing the
6 groundwater COC concentrations, periodic groundwater monitoring would be conducted
7 to track the rate at which concentrations are decreasing. LUCs, which would preclude uses
8 of groundwater that may cause inadvertent exposure to COCs, would be applied until all
9 groundwater COCs achieve their MCSs.

10 **3.2.2 Key Uncertainties**

11 The only significant uncertainty regarding Alternative 1 is the length of time that may be
12 required for the natural attenuation processes to achieve a reduction in COC concentrations
13 to below the MCSs. For some COCs, such as the VOCs in the shallow and deep well, it may
14 take only a few years until concentrations are consistently below the MCS. For antimony
15 and lead, the expected time to achieve the MCSs is more difficult to estimate, but is likely to
16 be on the order of no more than 10 to 15 years; it is also possible that concentrations of lead
17 and antimony may attenuate to less than their MCSs in less than 10 years.

18 **3.2.3 Other Considerations**

19 LUCs restricting the use of groundwater at the site will be necessary during the period until
20 MCLs are achieved. The LUCs will also address restricting the site use to industrial only.

21 **3.3 Alternative 2: In Situ Stabilization and LUCs**

22 **3.3.1 Description of Alternative**

23 Alternative 2 would use in situ stabilization to accelerate the reduction of lead and
24 antimony concentrations in groundwater. Dissolved concentrations of heavy metals in
25 groundwater are typically significantly influenced by a wide variety of geochemical factors,
26 such as the types of minerals present in the aquifer, pH, and the presence or absence of
27 other anions, such as sulfides, phosphates, and carbonates. A complete discussion of the
28 geochemistry of these two metals is beyond the scope of this CMS, but a useful draft
29 summary report on the environmental chemistry of metals recently released by EPA is
30 included as Appendix B. A brief summary of relevant factors regarding the geochemistry of
31 lead and antimony is presented below.

1 **Lead Geochemistry** - Lead is considered a relatively immobile heavy metal in soil and
2 groundwater systems, largely due to its propensity to adsorb to or be sequestered by
3 organic matter, clays, and iron and manganese oxides. Lead in groundwater typically does
4 not migrate significantly through the aquifer. The most common form of lead in
5 groundwater systems at a pH up to 7 is as a divalent cation (Pb^{+2}). Its oxidation state is not
6 significantly influenced by oxidation-reduction potential (ORP) conditions. At a pH above 7,
7 it is typically present as lead carbonate ($PbCO_3$) or complexed with a hydroxyl ion ($PbOH^+$).
8 An Eh-pH phase diagram for lead in water is shown in Figure 23 of the draft report in
9 Appendix B.

10 **Antimony Geochemistry** - Antimony is considered a near metal or metalloid element.
11 Located beneath arsenic on the standard periodic table, it exhibits several similarities to
12 arsenic in its geochemical behavior. Antimony is an ORP-sensitive element and its oxidation
13 state will change depending on the ORP conditions. Like arsenic, it forms oxyanions in
14 aqueous solutions. In oxic water, antimony is typically found in the +5 oxidation state (in
15 the form of the oxyanion antimonate), but can be reduced to the +3 oxidation state (as the
16 oxyanion antimonite) at lower ORP levels. These oxyanions exhibit negative charges and
17 generally behave quite differently geochemically than metals that form cations, such as lead.
18 Antimony is strongly adsorbed to iron and manganese oxides at neutral to low pH but may
19 be more mobile at elevated pH. Antimony generally forms weak complexes, except with
20 sulfide, at low ORP conditions. A phase diagram for antimony is shown in Figure 32 of the
21 draft report provided in Appendix B.

22 Alternative 2 would involve injection into the aquifer of a liquid solution containing a
23 chemical that would react with and promote precipitation or adsorption of the dissolved
24 lead and antimony in the vicinity of well E065GW003 and, potentially, well E065GW004.
25 The purpose of the injection would be to promote and enhance the precipitation/adsorption
26 of the metal COCs such that their dissolved phase concentrations decrease towards or below
27 their respective MCS. This injection process would essentially accelerate the natural
28 precipitation processes already acting to decrease lead and antimony concentrations at the
29 site.

30 Bench-scale testing might be required to select the best-suited reagent for injection, or a
31 reagent that is considered likely to be effective could be selected based on a geochemical
32 evaluation. After the selected reagent is injected, the groundwater would be monitored to
33 assess the effectiveness of the stabilization process. Monitoring would continue until all
34 COCs were below their respective target MCS.

1 The other COCs (TCE and vinyl chloride) would be allowed to naturally attenuate, as
2 described in Alternative 1. Natural attenuation processes are expected to be adequate for
3 TCE and vinyl chloride in both shallow and deep groundwater, given the low
4 concentrations of these VOCs.

5 **3.3.2 Key Uncertainties**

6 Some uncertainty exists regarding which chemical reagent would be best suited for in situ
7 stabilization of lead and antimony. Review of the groundwater sampling forms for SWMU
8 65 (see Appendix A) indicate that the pH of groundwater samples collected from well
9 E065GW003 are elevated compared to other Combined SWMU 65 wells, with groundwater
10 from well E065GW003 exhibiting a pH in the range of 9 to 9.5. This elevated pH may be
11 contributing to or causing the elevated concentrations of lead and antimony observed in this
12 well. It is possible that simply lowering the pH of the groundwater in the vicinity of this
13 well to a near neutral pH by injection of a dilute acidic solution could restore the attenuative
14 capacity of the soil and result in lower dissolved concentrations of the two metals COCs.
15 Other potentially effective chemical agents that could be injected include polysulfide (for
16 lead). Some bench-scale testing may be required to determine the chemical additive that
17 would be best suited for this application.

18 An additional uncertainty is the permeability of the aquifer and whether it is adequate to
19 accept the dosage of reagent that would be required. If the aquifer formation has a very low
20 permeability, injection may be impracticable.

21 **3.3.3 Other Considerations**

22 As with the other alternative considered, LUCs restricting the use of groundwater at the site
23 will be necessary during the period until MCLs are achieved. The LUCs will also address
24 restricting the site use to industrial only.

25 **3.4 Alternative 3: Groundwater Recovery, Treatment, and** 26 **Discharge to the Sanitary Sewer and LUCs**

27 **3.4.1 Description of Alternative**

28 This alternative would involve recovering impacted groundwater in the vicinity of well
29 E065GW003, treating the groundwater if necessary to meet applicable wastewater discharge
30 requirements, and discharging the groundwater to the North Charleston Sanitary Sewer
31 (NCSS) system. This alternative is typically referred to as pump and treat.

1 Because of the limited extent of COC-impacted groundwater, it is assumed that a single
2 recovery well installed near well E065GW003 would be adequate for this approach. The
3 recovery well would be screened in the shallow aquifer. Deep groundwater, which contains
4 only low levels of VOCs, would not be actively recovered. Natural attenuation processes are
5 expected to be adequate to address the VOCs in the deep aquifer. It is expected that the
6 groundwater recovery rate for a single well in this area would be relatively low, below 5
7 gallons per minute (gpm), possibly in the range of 1 to 3 gpm.

8 It is possible that the groundwater may not require pretreatment prior to discharge to the
9 sanitary sewer. The discharge limits for the NCSS for antimony and lead are 2,000 and 300
10 $\mu\text{g}/\text{L}$, respectively. Since antimony has not been previously detected at a concentration
11 greater than 42 $\mu\text{g}/\text{L}$, no pretreatment of the groundwater to remove antimony would be
12 required. Pretreatment for lead may be required, based on previously measured
13 groundwater lead concentrations greater than 300 $\mu\text{g}/\text{L}$. However, because the
14 groundwater recovery rate is expected to be low, it may be feasible to regulate the discharge
15 of lead to the NCSS on a mass discharge basis (such as a specific number of pounds per
16 day), which may allow for discharge of the groundwater to the NCSS without treatment. In
17 addition, experience with many other pump and treat systems has shown that
18 concentrations of contaminants in actively pumping wells is typically significantly less than
19 those concentrations measured in monitoring wells. Thus, it is possible that the lead
20 concentrations in recovered groundwater would decrease to below the 300 $\mu\text{g}/\text{L}$ pre-
21 treatment level and, thus, treatment may not be required for this alternative.

22 **3.4.2 Key Uncertainties**

23 Several uncertainties exist regarding Alternative 3. A key uncertainty is whether the aquifer
24 yield is adequate to allow this alternative to be effectively implemented. A short-term
25 aquifer pumping test may be required to better assess the viability of this approach. The
26 aquifer at some locations of the CNC has been found to have inadequate yield (well below 1
27 gpm) to allow this type of remedial approach.

28 The degree of treatment that may be required is also not clear, although as indicated above,
29 treatment may not be required. An additional uncertainty is the length of time that pumping
30 of the aquifer would be required prior to concluding that an adequate amount of
31 groundwater had been removed, such that MCSs for the key COCs have been achieved.

1 **3.4.3 Other Considerations**

- 2 As with the other alternative considered, LUCs restricting the use of groundwater at the site
3 will be necessary during the period until MCLs are achieved. The LUCs will also address
4 restricting the site use to industrial only.

4.0 Evaluation and Comparison of Corrective Measure Alternatives

The three corrective measure alternatives were evaluated relative to the evaluative criteria previously described in Section 2.0 and then subjected to a comparative evaluation. A cost estimate for each alternative was also developed; the assumptions and unit costs used for these estimates are included in Appendix C.

4.1 Alternative 1 – Monitored Natural Attenuation and LUCs

The assumptions for Alternative 1 include the following:

- A base-wide LUC management plan (LUCMP) will be developed for the CNC. The plan will allow for restrictions on the use of groundwater at Combined SWMU 65 and other areas, and it will be developed outside the scope of this CMS.
- Groundwater monitoring will be performed for up to 10 years. Samples will be collected from up to four existing monitoring wells, including the wells that have had past MCL exceedances, on an annual basis. The samples will be analyzed for metal COCs, (filtered and unfiltered) and VOCs. Standard field parameters (dissolved oxygen [DO], ORP, turbidity, temperature) will be also monitored.

4.1.1 Protection of Human Health and the Environment

Alternative 1 is effective at protecting human health because it uses LUCs to prevent ingestion of and direct contact with groundwater until all groundwater COCs are below the MCLs.

4.1.2 Attain MCS

Alternative 1 is expected to eventually attain the MCS.

4.1.3 Control the Source of Releases

There are no ongoing sources of releases at Combined SWMU 65; therefore, this issue is not applicable.

1 **4.1.4 Compliance with Applicable Standards for the Management of Generated**
2 **Wastes**

3 Alternative 1 does not generate any wastes that require special management. The primary
4 generated waste would be purge water from monitoring wells, which is easily managed to
5 applicable standards.

6 **4.1.5 Other Factors (a) Long-term Reliability and Effectiveness**

7 Alternative 1 has adequate long-term reliability and effectiveness.

8 **4.1.6 Other Factors (b) Reduction in the Toxicity, Mobility, or Volume of Wastes**

9 Alternative 1 relies on natural attenuation processes to reduce the toxicity, mobility, and
10 volume of the contaminated groundwater.

11 **4.1.7 Other Factors (c) Short-term Effectiveness**

12 Through the implementation of LUCs, Alternative 1 has short-term effectiveness in
13 preventing ingestion of, or contact with, the contaminated groundwater. No significant
14 short-term risks would be created using this alternative.

15 **4.1.8 Other Factors (d) Implementability**

16 Alternative 1 is easily implemented since it requires only the implementation of LUCs and
17 an appropriate monitoring well program.

18 **4.1.9 Other Factors (e) Cost**

19 Alternative 1 is the least costly to implement. Using the assumptions described earlier, the
20 total present value of this alternative is \$63,000.

21 **4.2 Alternative 2: Alternative 2: In Situ Stabilization and LUCs**

22 The following assumptions for Alternative 2 were made:

- 23 • A base-wide LUCMP will be developed for the CNC. The plan will allow for restrictions
24 on the use of groundwater at Combined SWMU 65 and other areas, and it will be
25 developed outside the scope of this CMS.
- 26 • A limited bench-scale evaluation would be conducted to identify a reagent likely to be
27 effective in situ. Injection of the reagent would require installation of one new injection

1 well within 10 feet of well E065GW003. For the purpose of this evaluation, it is assumed
2 that a commonly used and relatively non-toxic reagent, such as ferrous sulfate, would be
3 suitable for this application.

- 4 • Groundwater monitoring would continue for up to 5 years after the reagent injection,
5 after which all COCs are assumed to be below their respective MCS. Samples will be
6 collected from up to four existing monitoring wells, including the wells that have had
7 past MCL exceedances, on an annual basis. The samples will be analyzed for metal
8 COCs, (filtered and unfiltered) and VOCs. Standard field parameters (DO, ORP,
9 turbidity, temperature) will be also monitored.

10 **4.2.1 Protection of Human Health and the Environment**

11 Alternative 2 is effective at protecting human health and the environment because it uses
12 LUCs to prevent ingestion of and direct contact with groundwater during the time period
13 when groundwater COC concentrations are greater than the MCS.

14 **4.2.2 Attain MCS**

15 Alternative 2 is likely to eventually achieve the MCS. The duration to achieve the MCSs is
16 expected to be less than that required by Alternative 1.

17 **4.2.3 Control the Source of Releases**

18 There are no ongoing sources of releases at Combined SWMU 65; therefore, this issue is not
19 applicable.

20 **4.2.4 Compliance with Applicable Standards for the Management of Generated 21 Wastes**

22 Alternative 2 does not generate any wastes that require special management. Purge water
23 and drill cuttings generated as part of this alternative can be handled using conventional
24 disposal methods.

25 **4.2.5 Other Factors (a) Long-term Reliability and Effectiveness**

26 Alternative 2 has long-term reliability because of the implementation of LUCs, the in situ
27 stabilization of the metal COCs, and natural attenuation of the VOCs.

1 **4.2.6 Other Factors (b) Reduction in the Toxicity, Mobility, or Volume of Wastes**

2 Alternative 2 reduces the toxicity, mobility, and volume of the contaminated groundwater
3 via in situ treatment and natural attenuation.

4 **4.2.7 Other Factors (c) Short-term Effectiveness**

5 Because of the implementation of LUCs, this alternative will have short-term effectiveness in
6 preventing ingestion of, or contact with, the contaminated groundwater. No unmanageable
7 hazards would be created during its implementation.

8 **4.2.8 Other Factors (d) Implementability**

9 This alternative can be implemented with conventional equipment and standard
10 procedures, provided that the aquifer has adequate permeability.

11 **4.2.9 Other Factors (e) Cost**

12 Appendix C presents the overall cost estimate for implementing this remedy. The total
13 present value of Alternative 2 is \$90,000.

14 **4.3 Alternative 3: Groundwater Recovery, Treatment, and**
15 **Discharge to the Sanitary Sewer and LUCs**

16 The following assumptions for Alternative 3 were made:

- 17 • A base-wide LUCMP will be developed for the CNC. The plan will allow for restrictions
18 on the use of groundwater at Combined SWMU 65 and other areas, and it will be
19 developed outside the scope of this CMS.
- 20 • The aquifer is assumed to have adequate capacity to yield approximately 2 gpm from a
21 single new recovery well that is installed near well E065GW003. Groundwater treatment
22 is assumed to be required for up to 1 year prior to discharge to the NCSS sewer.
23 Treatment is assumed to be precipitation and filtration for lead removal using a small
24 off-the-shelf package treatment system. It is assumed that after the first year, treatment
25 of the groundwater prior to discharge is no longer necessary.
- 26 • Active groundwater recovery would continue for up to 3 years, after which all COCs are
27 assumed to be below their respective MCS. An additional 1 year of monitoring is
28 assumed to be implemented to ensure that rebound of contaminant concentrations does
29 not occur after shutdown of the groundwater recovery system. Samples will be collected

1 from up to four existing monitoring wells, including the wells that have had past MCL
2 exceedances, on an annual basis. The samples will be analyzed for metal COCs (filtered
3 and unfiltered) and VOCs. Standard field parameters (DO, ORP, turbidity, temperature)
4 will be also monitored.

5 **4.3.1 Protection of Human Health and the Environment**

6 Alternative 3 is effective at protecting human health and the environment because it uses
7 LUCs to prevent ingestion of and direct contact with groundwater during the time period
8 when groundwater COC concentrations are greater than the MCS.

9 **4.3.2 Attain MCS**

10 Alternative 3 is expected to achieve the MCSs. The duration to achieve the MCSs is expected
11 to be less than that required by Alternative 1.

12 **4.3.3 Control the Source of Releases**

13 There are no ongoing sources of releases at Combined SWMU 65; therefore, this issue is not
14 applicable.

15 **4.3.4 Compliance with Applicable Standards for the Management of Generated 16 Wastes**

17 Alternative 3 does not generate any wastes that require special management. Purge water
18 and drill cuttings generated as part of this alternative can be handled using conventional
19 disposal methods. The recovered groundwater is assumed to be disposed to the NCSS
20 sewer without treatment.

21 **4.3.5 Other Factors (a) Long-term Reliability and Effectiveness**

22 Alternative 3 has long-term reliability because of the implementation of LUCs, the
23 permanent removal from the aquifer of contaminated groundwater, and the natural
24 attenuation of the VOCs.

25 **4.3.6 Other Factors (b) Reduction in the Toxicity, Mobility, or Volume of Wastes**

26 Alternative 3 reduces the toxicity, mobility, and volume of the contaminated groundwater
27 via groundwater recovery and natural attenuation.

1 **4.3.7 Other Factors (c) Short-term Effectiveness**

2 Because of the implementation of LUCs, this alternative will have short-term effectiveness in
3 preventing ingestion of, or contact with, the contaminated groundwater. No unmanageable
4 hazards would be created during its implementation.

5 **4.3.8 Other Factors (d) Implementability**

6 This alternative is moderately difficult to implement due to the need to ensure that the
7 recovery system continues to work effectively.

8 **4.3.9 Other Factors (e) Cost**

9 Appendix C presents the overall cost estimate for implementing this remedy. The total
10 present value of Alternative 3 is \$180,000.

11 **4.4 Comparative Evaluation of Corrective Measure**
12 **Alternatives**

13 Each corrective measure alternative's overall ability to meet the evaluation criteria is
14 described above. In Table 4-1, a comparative evaluation of the degree to which each
15 alternative meets a particular criteria is presented.

TABLE 4-1
 Comparative Evaluation of Corrective Measure Alternatives
 Corrective Measures Study Report, Combined SWMU 65, Zone E, Charleston Naval Complex

Criterion	Alternative 1 Monitored Natural Attenuation and LUCs	Alternative 2 In Situ Stabilization and LUCs	Alternative 3 Groundwater Recovery, Treatment, Disposal and LUCs
Overall Protection of Human Health and the Environment	Adequately protects human health and the environment	Adequately protects human health and the environment	Adequately protects human health and the environment
Attainment of MCS	Expected to attain MCSs within 10 to 15 years	Expected to attain MCSs within 10 years or less	Expected to attain MCSs within 10 years or less
Control of the Source of Releases	No sources present at this site	No sources present at this site	No sources present at this site
Compliance with Applicable Standards for the Management of Wastes	Can be implemented to comply with applicable standards	Can be implemented to comply with applicable standards	Can be implemented to comply with applicable standards
Long-term Reliability and Effectiveness	Expected to be reliable and effective in the long term	Expected to be reliable and effective in the long term	Expected to be reliable and effective in the long term
Reduction of Toxicity, Mobility, or Volume through Treatment	Reduces toxicity, mobility, and volume via natural attenuation	Reduces toxicity, mobility, and volume via in situ stabilization and natural attenuation	Reduces toxicity, mobility, and volume via groundwater extraction and natural attenuation
Short-term Effectiveness	Effective in short term via LUCs	Effective in short term via LUCs	Effective in short term via LUCs
Implementability	Easily implemented	Moderately easy to implement, provided aquifer has adequate permeability	Moderately easy to implement, provided aquifer has adequate permeability
Estimated Cost	\$63,000	\$90,000	\$180,000

5.0 Recommended Corrective Measure Alternative

Three corrective measure alternatives were evaluated for groundwater COCs using the criteria described in Section 2.0 of this CMS report: Alternative 1: Monitored Natural Attenuation and LUCs; Alternative 2: In Situ Stabilization and LUCs; and Alternative 3: Groundwater Recovery, Treatment, and Discharge to the Sanitary Sewer and LUCs.

Based on the alternatives evaluation and RAOs for the site as identified in Section 2.0 and the current uncertainties associated with each alternative, the preferred corrective measure alternative is Alternative 1: Monitored Natural Attenuation and LUCs. Alternative 1 would provide protection of human health and the environment by allowing natural attenuation mechanisms to reduce concentrations of COCs to below the MCSs. Alternative 1 is suitable because the areal extent of impacted groundwater is relatively limited, significant migration of contaminants away from impacted wells has not been observed, and natural attenuation mechanisms are expected to be adequate to reduce all COC concentrations to the MCS over time.

This alternative also provides for maintaining the current and planned future use of the site as industrial while site COCs exceed applicable levels for unrestricted land use. LUCs would prevent residential and other unrestricted land uses, including installation of water supply wells, that could expose sensitive populations.

Alternative 2 is potentially viable, but uncertainty exists regarding which stabilization reagent would be most effective for lead and antimony and whether the aquifer has adequate permeability to accept the stabilization injectate at a reasonable injection pressure. Alternative 2 is significantly more expensive than Alternative 1.

Alternative 3 may also be viable, but uncertainty exists regarding whether the aquifer has adequate permeability to allow for effective groundwater recovery to occur. Uncertainty also exists with regard to the required level of pretreatment needed prior to discharge to the sanitary sewer system. Alternative 3 is the most expensive of the available alternatives.

An LUCMP is being developed for the industrial areas of the CNC and Combined SWMU 65 will be added to the plan. The LUCMP will limit future site activities to those that would limit exposure to groundwater. The expected reliability of this alternative is good. Should

- 1 monitoring data indicate that this alternative is not as effective as expected, additional
- 2 measures could be safely implemented.

1 **6.0 References**

- 2 CH2M-Jones. *RFI Report Addendum and CMS Work Plan, Combined SWMU 67, Zone E,*
3 *Charleston Naval Complex. Revision 0. August 2002.*
- 4 CH2M-Jones. *RFI Report Addendum and CMS Work Plan, Combined SWMU 65, Zone E,*
5 *Charleston Naval Complex. Revision 0. April 2003.*
- 6 EnSafe Inc. *Zone E RFI Report, NAVBASE Charleston, Revision 0. November 1997.*
- 7 EnSafe Inc./Allen & Hoshall. *Zone E RFI Report Workplan. 1995.*
- 8 South Carolina Department of Health and Environmental Control (SCDHEC). RCRA Permit
9 SC0 170 022 560. Charleston Naval Complex, Charleston, South Carolina. August 17, 1988.
- 10 U.S. Environmental Protection Agency (EPA). *Use of Monitored Natural Attenuation at*
11 *Superfund, RCRA Corrective Action, and Underground Storage Tank Sites. Office of Solid*
12 *Waste and Emergency Response (OSWER) Final Directive 9200.4-17P. 1999.*
- 13 U.S. Environmental Protection Agency (EPA). *Draft Issue Paper on the Environmental*
14 *Chemistry of Metals. August 2003.*

EnSafe/Allen & Hoshall

Monitoring Well NBCE065001

Project: ZONE E - Naval Base Charleston

Coordinates: 2317543.39 E, 377256.57 N

Location: Charleston, SC

Surface Elevation: 7.1 feet msl

Started at 1000 on 12-7-95

TOC Elevation: 6.92 feet msl

Completed at 1150 on 12-7-95

Depth to Groundwater: 2.78 feet TOC Measured: 3/13/96

Drilling Method: 4.25" ID (7.5" OD) HSA with split spoon

Groundwater Elevation: 4.14 feet msl

Drilling Company: Atlantic Drilling (SC cert #1210)

Total Well Depth: 12.5 feet bgs

Geologist: B. Blythe

Well Screen: 2.5 to 11.5 feet bgs

DEPTH IN FEET	LITHOLOGIC SAMPLE	ANALYTICAL SAMPLE	SAMPLE NO.	% RECOVERY	PID (ppm)	GRAPHIC LOG	SOIL CLASS	GEOLOGIC DESCRIPTION	ELEV. (ft-msl)	WELL DIAGRAM
								Surface conditions: concrete walk		
5			1	60	0	SM GM OL	Sand: light brown, gravelly, muddy, dry to moist. Clay: dark gray-black, high organic content, fat, soft, moist to wet, low plasticity, H ₂ S odor --Marsh clay.	3.1 2.8 1.9		
10			2	85	0	OL PT	Clay: Marsh clay as above. Peat: dark brown with light brown root material and grass fibers, soft, moist, H ₂ S odor.	9 1.6 2.6		
15			3	100	0	PT	Peat: as above with interbedded clay laminae throughout.	3.9 5.9		
20										

EnSafe/Allen & Hoshall

Monitoring Well NBCE065002

Project: ZONE E - Naval Base Charleston

Coordinates: 2317574.05 E, 37716528 N

Location: Charleston, SC

Surface Elevation: 7.3 feet msl

Started at 1330 on 12-7-95

TOC Elevation: 7.16 feet msl

Completed at 1500 on 12-7-95

Depth to Groundwater: 3.79 feet TOC Measured: 3/13/96

Drilling Method: 4.25" ID (7.5" OD) HSA with split spoon

Groundwater Elevation: 3.37 feet msl

Drilling Company: Atlantic Drilling (SC cert #1210)

Total Well Depth: 12.5 feet bgs

Geologist: B. Blythe

Well Screen: 2.5 to 11.5 feet bgs

DEPTH IN FEET	LITHOLOGIC SAMPLE	ANALYTICAL SAMPLE	SAMPLE NO.	% RECOVERY	PTD (ppm)	GRAPHIC LOG	SOIL CLASS	GEOLOGIC DESCRIPTION	ELEV. (ft-msl)	WELL DIAGRAM
								Surface conditions: concrete walk		
5			1	60	0	SM GM OL	<p>Sand: light brown, gravelly, dry to moist.</p> <p>Clay: dark gray-black, high organic content, fat, soft, moist to wet, low plasticity--Marsh clay.</p>	3.3 3 2.1		
						OL	Clay: Marsh clay as above.	0.7		
10			2	100	0	PT	Peat: dark gray-green to black, with root material and grass fibers, soft, wet.	1.7 2.7		
						PT	Peat: as above.	3.7		
15			3	100	0			5.7		
20										

EnSafe/Allen & Hoshall

Monitoring Well NBCE065003

Project: ZONE E - Naval Base Charleston	Coordinates: 2317469.31 E, 37711229 N
Location: Charleston, SC	Surface Elevation: 8.3 feet msl
Started at 1015 on 10-26-95	TOC Elevation: 8.15 feet msl
Completed at 1200 on 10-26-95	Depth to Groundwater: 2.65 feet TOC Measured: 3/13/96
Drilling Method: 4.25" ID (7.5" OD) HSA with split spoon	Groundwater Elevation: 5.50 feet msl
Drilling Company: Atlantic Drilling (SC cert #1210)	Total Well Depth: 12.5 feet bgs
Geologist: T. Kafka	Well Screen: 2.5 to 11.5 feet bgs

DEPTH IN FEET	LITHOLOGIC SAMPLE	ANALYTICAL SAMPLE	SAMPLE NO.	% RECOVERY	PID (ppm)	GRAPHIC LOG	SOIL CLASS	GEOLOGIC DESCRIPTION	ELEV. (ft-msl)	WELL DIAGRAM
								Surface conditions: concrete lot.		<p>PVC Riser</p> <p>2" ID Sch. 40 PVC, 0.01 slot screen</p> <p>#1 sand filter</p> <p>bentonite seal</p> <p>grout</p> <p>end cap</p>
5			1	55	0	CL OL CL SC	Clay: black, silty, sandy, with wood fragments, wet, grading into dark gray to black, stiff, silty, low plasticity, wet clay.	3.3 2.5 2		
			2	100	0	SM SC QH OL QH OL	Sand: gray, very fine to fine, well-sorted, silty, with some clay pods, saturated. Clay: dark gray to black with light gray silty laminae, low plasticity, high organic content, wet.	3 1 12 14 22		
10			3	32			Shelby tube (9.7-11.7'): top and bottom--marsh clay as above.			
			4	87	0	QH OL PT	Clay: marsh clay as above. Peat: brown, with golden to orange wood fibers and grass, silty, high organic content, soft, wet, strong H ₂ S odor.	4.6 5.3 5.8		
15										
20										

EnSafe/Allen & Hoshall

Monitoring Well NBCE065004

Project: ZONE E - Naval Base Charleston	Coordinates: 2317441.43 E, 377076.90 N
Location: Charleston, SC	Surface Elevation: 8.3 feet msl
Started at 1055 on 10-18-95	TOC Elevation: 8.11 feet msl
Completed at 1140 on 10-23-95	Depth to Groundwater: 2.12 feet TOC Measured: 3/13/96
Drilling Method: 4.25" ID (7.5" OD) HSA with split spoon	Groundwater Elevation: 5.99 feet msl
Drilling Company: Atlantic Drilling (SC cert #1210)	Total Well Depth: 12.5 feet bgs
Geologist: T. Kafka	Well Screen: 2.5 to 11.5 feet bgs

DEPTH IN FEET	LITHOLOGIC SAMPLE	ANALYTICAL SAMPLE	SAMPLE NO.	% RECOVERY	PTD (ppm)	GRAPHIC LOG	SOIL CLASS	GEOLOGIC DESCRIPTION	ELEV. (ft-msl)	WELL DIAGRAM
								Surface conditions: concrete pad		
5			1	45	5.8	OL SM SC	Clay: black, silty, low plasticity, soft, wet. Sand: light to dark gray, very fine to fine, silty, moderately well sorted, trace clay, wet.	3.3 2.8 2.4		
10			2	100	11	OH LO	Clay: dark gray to black with light gray silty laminae, low plasticity, some wood and grass fibers, soft, wet.	1 1.4		
15			3	100	16.6	OH OL PT	Clay: as above with extensive yellow to orange brown wood/grass fibers. Peat: brown to orange brown, extensive wood and grass fibers, silty, wet.	4.1 4.9 5.6		
20										

EnSafe/Allen & Hoshall

Monitoring Well NBCE06504D

Project: ZONE E - Naval Base Charleston

Coordinates: 231742L31E, 377119.32 N

Location: Charleston, SC

Surface Elevation: 8.5 feet msl

Started at 1030 on 1-19-96

TOC Elevation: 8.41 feet msl

Completed at 1200 on 1-19-96

Depth to Groundwater: 6.97 feet TOC Measured: 3/13/96

Drilling Method: Rotasonic (6.5" OD casing, 3.8" ID coring bit)

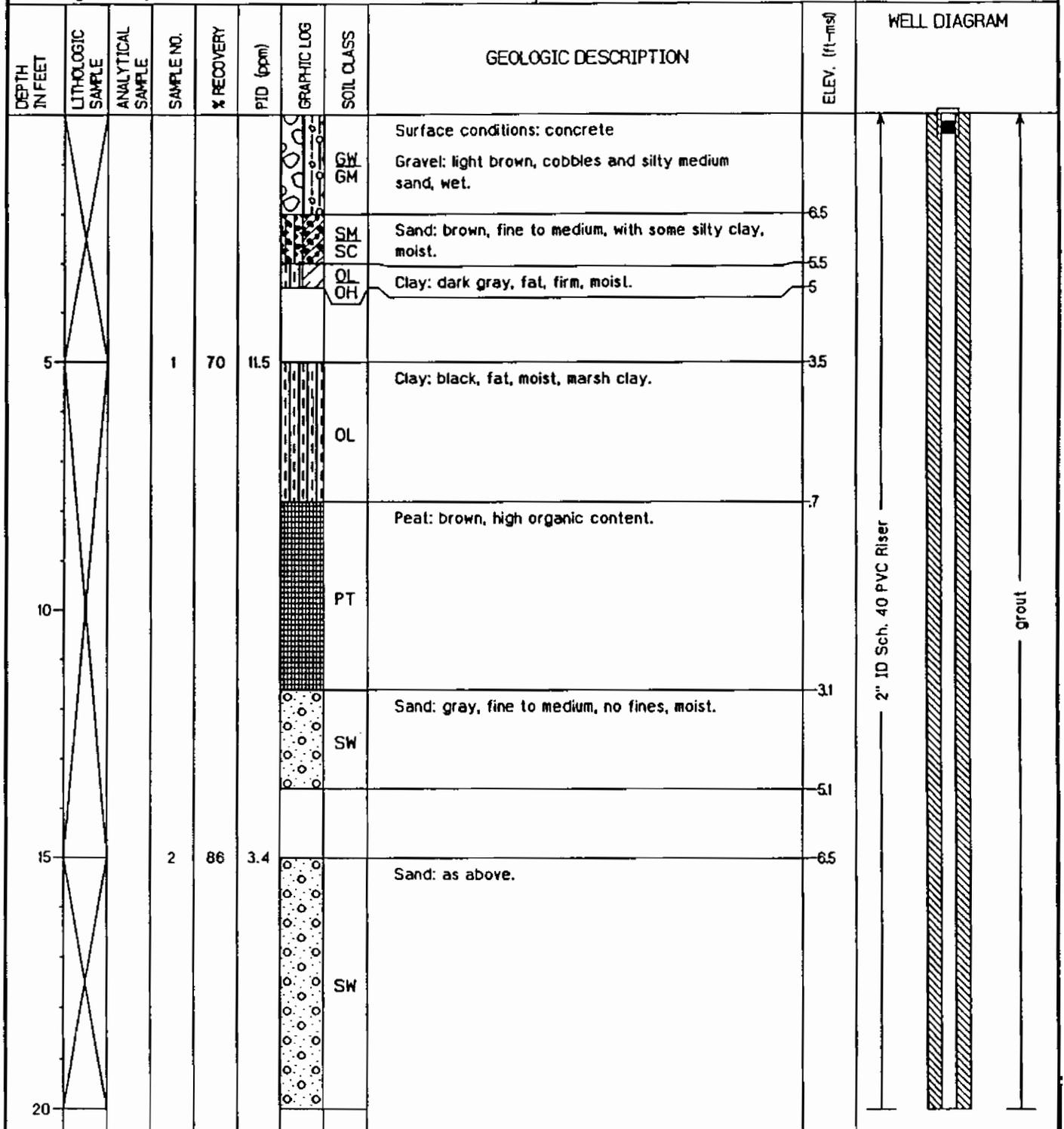
Groundwater Elevation: 1.44 feet msl

Drilling Company: Alliance Environmental (SC Cert #889)

Total Well Depth: 39.7 feet bgs

Geologist: B. Blythe

Well Screen: 29.8 to 39.2 feet bgs



EnSafe/Allen & Hoshall

Monitoring Well NBCE06504D

Project: ZONE E - Naval Base Charleston

Coordinates: 231742L31E, 377119.32 N

Location: Charleston, SC

Surface Elevation: 8.5 feet msl

Started at 1030 on 1-19-96

TOC Elevation: 8.41 feet msl

Completed at 1200 on 1-19-96

Depth to Groundwater: 6.97 feet TOC Measured: 3/13/96

Drilling Method: Rotasonic (6.5" OD casing, 3.8" ID coring bit)

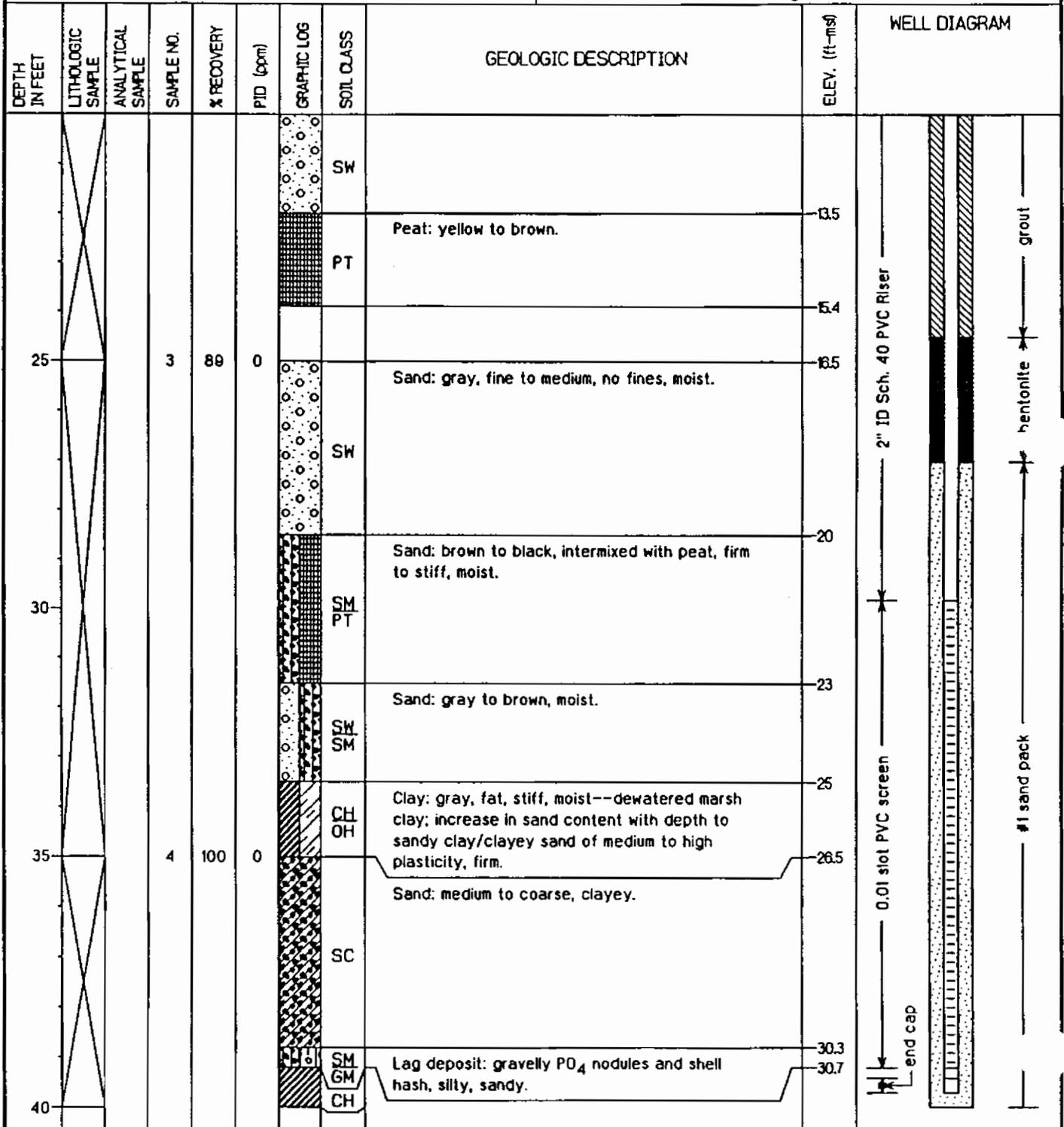
Groundwater Elevation: 1.44 feet msl

Drilling Company: Alliance Environmental (SC Cert #889)

Total Well Depth: 39.7 feet bgs

Geologist: B. Blythe

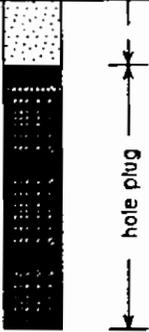
Well Screen: 29.8 to 39.2 feet bgs



EnSafe/Allen & Hoshall

Monitoring Well NBCE06504D

Project: ZONE E - Naval Base Charleston	Coordinates: 231742L31E, 377119.32 N
Location: Charleston, SC	Surface Elevation: 8.5 feet msl
Started at 1030 on 1-19-96	TOC Elevation: 8.41 feet msl
Completed at 1200 on 1-19-96	Depth to Groundwater: 6.97 feet TOC Measured: 3/13/96
Drilling Method: Rotasonic (6.5" OD casing, 3.8" ID coring bit)	Groundwater Elevation: 1.44 feet msl
Drilling Company: Alliance Environmental (SC Cert #889)	Total Well Depth: 39.7 feet bgs
Geologist: B. Bythe	Well Screen: 29.8 to 39.2 feet bgs

DEPTH IN FEET	LITHOLOGIC SAMPLE	ANALYTICAL SAMPLE	SAMPLE NO.	% RECOVERY	PTD (ppm)	GRAPHIC LOG	SOIL CLASS	GEOLOGIC DESCRIPTION	ELEV. (ft-msl)	WELL DIAGRAM
45			5	100	0		CH	Clay: gray, fat, firm to stiff, with fine sand and shell hash laminae interspersed throughout--dewatered marsh clay.		
45-47.5			6	100				Shelby tube 45-47.5': dewatered marsh clay as above.	39	
50										
55										
60										

EnSafe/Allen & Hoshall

Monitoring Well NBCE065005

Project: ZONE E - Naval Base Charleston

Coordinates: 2317412.39 E, 37716228 N

Location: Charleston, SC

Surface Elevation: 8.5 feet msl

Started at 1300 on 10-26-95

TOC Elevation: 8.22 feet msl

Completed at 1500 on 10-26-95

Depth to Groundwater: 5.48 feet TOC Measured: 3/13/96

Drilling Method: 4.25" ID (7.5" OD) HSA with split spoon

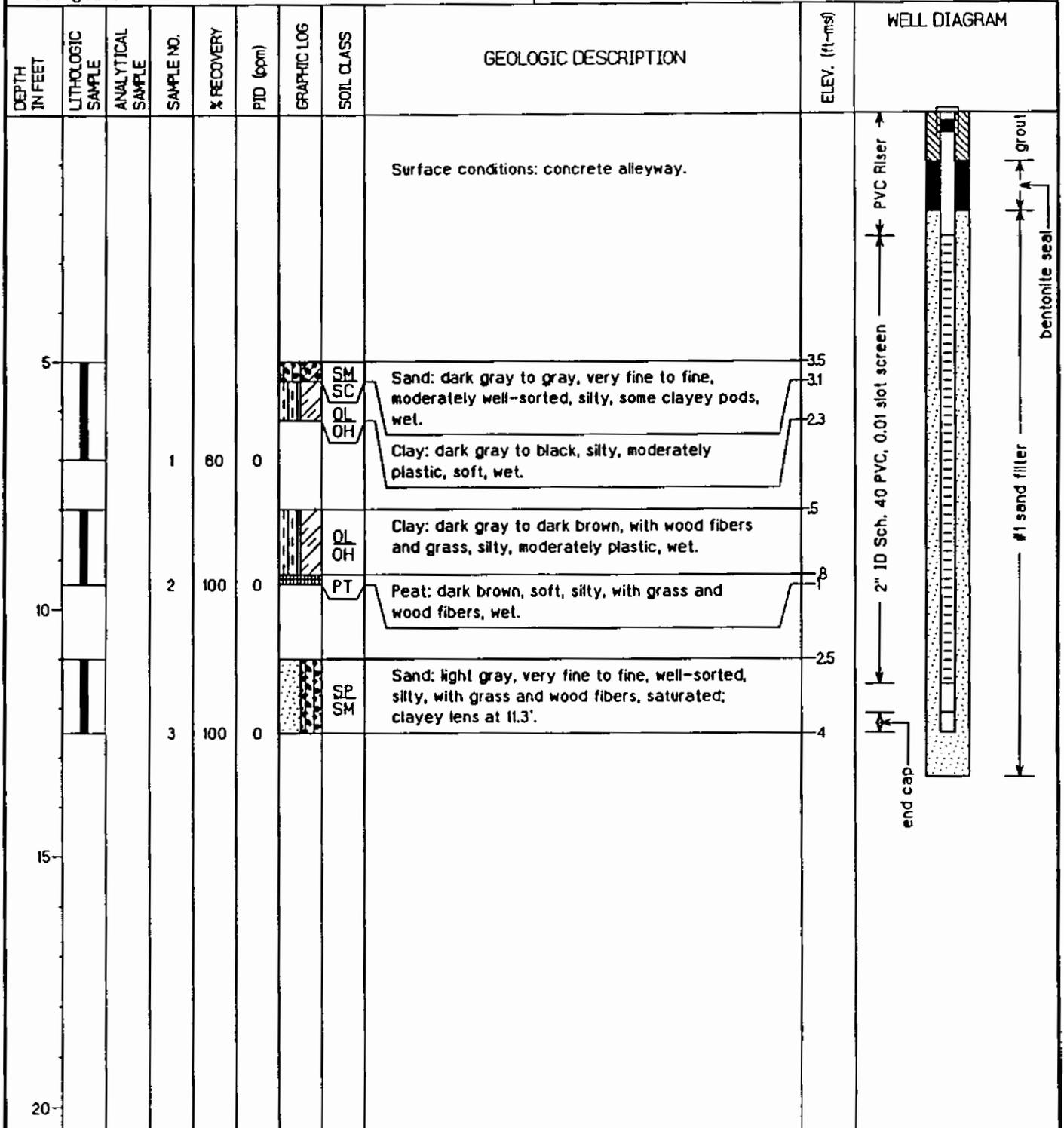
Groundwater Elevation: 2.74 feet msl

Drilling Company: Atlantic Drilling (SC cert #1210)

Total Well Depth: 12.5 feet bgs

Geologist: T. Kafka

Well Screen: 2.5 to 11.5 feet bgs



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Monitoring Well NBCE065006

Project: ZONE E - Naval Base Charleston

Coordinates: 2317402.43 E, 377243.38 N

Location: Charleston, SC

Surface Elevation: 8.3 feet msl

Started at 0905 on 11-7-95

TOC Elevation: 8.02 feet msl

Completed at 1300 on 11-7-95

Depth to Groundwater: 5.27 feet TOC Measured: 3/13/96

Drilling Method: 4.25" ID (7.5" OD) HSA with split spoon

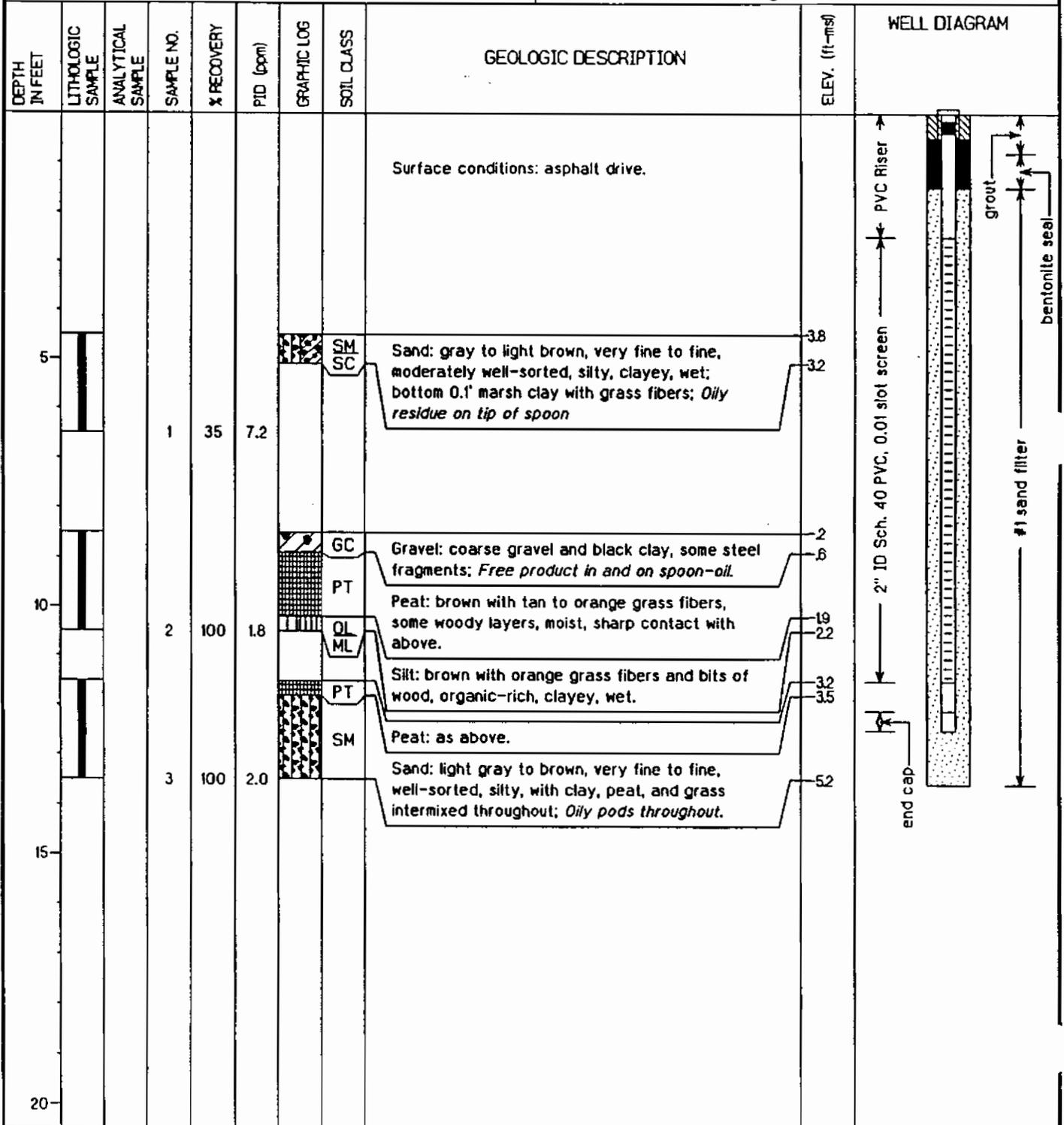
Groundwater Elevation: 2.75 feet msl

Drilling Company: Atlantic Drilling (SC cert #1210)

Total Well Depth: 25 feet bgs

Geologist: T. Kafka

Well Screen: 2.5 to 11.5 feet bgs



EnSafe/Allen & Hoshall

Monitoring Well NBCE065007

Project: ZONE E - Naval Base Charleston

Coordinates: 2317497.72 E, 377055.81 N

Location: Charleston, SC

Surface Elevation: 8.6 feet msl

Started at 0900 on 9-11-96

TOC Elevation: 8.31 feet msl

Completed at 1030 on 9-11-96

Depth to Groundwater: 2.83 feet TOC Measured: 10/16/96

Drilling Method: 4.25" ID (7.5" OD) HSA with split spoon

Groundwater Elevation: 5.48 feet msl

Drilling Company: Atlantic Drilling (S.C.# 1210)

Total Well Depth: 13.3 feet bgs

Geologist: J. Cooley

Well Screen: 3.3 to 12.3 feet bgs

DEPTH IN FEET	LITHOLOGIC SAMPLE	ANALYTICAL SAMPLE	SAMPLE NO.	% RECOVERY	PID (ppm)	GRAPHIC LOG	SOIL CLASS	GEOLOGIC DESCRIPTION	ELEV. (ft-msl)	WELL DIAGRAM
								Surface conditions: Asphalt.		
			1	100			SP	Sand: gray; fine to very fine, shell hash throughout.	4.6	
5								PID reading of 150 ppm in cuttings from 2.0 to 4.0 ft.	3.1	
			2	100			SP	Sand: gray; very fine.	8	
							ML	Silt: black; clayey.	4	
10								PID reading spike of 1710 ppm in cuttings from 10.0 to 13.0 ft.	14	
			3	100			SP	Sand: lt. gray; very fine to fine; w/shell fragments.	4.4	
							CL	Clay: dark gray-black; silty.	5.4	
15									6.4	
20										

EnSafe/Allen & Hoshall

Monitoring Well NBCE065008

Project: ZONE E - Naval Base Charleston	Coordinates: 2317407.86 E, 377029.95 N
Location: Charleston, SC	Surface Elevation: 8.3 feet msl
Started at 1104 on 9-11-96	TOC Elevation: 7.99 feet msl
Completed at 1225 on 9-11-96	Depth to Groundwater: 3.72 feet TOC Measured: 10/16/96
Drilling Method: 4.25" ID (7.5" OD) HSA with split spoon	Groundwater Elevation: 4.27 feet msl
Drilling Company: Atlantic Drilling (S.C.# 1210)	Total Well Depth: 14.5 feet bgs
Geologist: J. Cooley	Well Screen: 4.5 to 13.5 feet bgs

DEPTH IN FEET	LITHOLOGIC SAMPLE	ANALYTICAL SAMPLE	SAMPLE NO.	% RECOVERY	PID (ppm)	GRAPHIC LOG	SOIL CLASS	GEOLOGIC DESCRIPTION	ELEV. (ft-msl)	WELL DIAGRAM
								Surface conditions: Asphalt. Creosote odor in cuttings.		<p>WELL DIAGRAM</p> <p>Labels: PVC Riser, 2" ID Sch. 40 PVC, 0.01 slot screen, #1 sand filter, bentonite seal, end cap, grout.</p>
5			1	100		SP CL	Sand: gray; silty; interlayered with dark gray silty clay.	4.3		
								2.3		
						CL	Clay: dark gray.	3		
10			2	100		CL PT	Clay: as above with peat stringers, grass, and roots.	7		
								17		
									5.7	
15			3	100		SP	Sand: very fine.			
								7.7		
20										

Figure 6-1
 Groundwater Sampling Form

Groundwater Sampling		Sample ID: <u>NK65SW00101</u>
PROJECT NAME: <u>Naval Base Charleston</u>		JOB NO: <u>2905-05940</u> DATE: <u>4-17-90</u>
WELL NO.: <u>065-001</u>	LOCATION: <u>Zone E</u>	
WEATHER CONDITIONS: <u>Clear, slight breeze</u>	AMBIENT TEMP: <u>~80°</u>	
REVIEWED BY: _____	PERSONNEL: <u>M. Best J. Temple</u>	
PURGING DEVICE Type device? <u>Peristaltic pump</u> How was the device decontaminated? _____ How was the line decontaminated? <u>per CSAP</u> Which well was previously purged? _____		SAMPLING DEVICE Type device? <u>Peristaltic pump</u> How was the device decontaminated? _____ How was the line decontaminated? <u>per CSAP</u> Which well was previously sampled? _____
INITIAL WELL VOLUME Well diameter (in.) <u>2</u> Stickup (ft.) _____ Depth to bottom of well from TOC (ft.) <u>12.23</u> Depth to water surface from TOC (ft.) <u>2.77</u> Length of water (ft.) <u>9.46</u> Volume of water (ft.) _____ (gal.) <u>461</u> Amount of sediment at bottom of well (ft.) _____ 3 Volumes of water (gal.) <u>483</u>		PURGING Time started <u>1333</u> Finished <u>1358</u> Volume purged <u>4.85</u> Comments on Well Recovery <u>Moderate-Slow</u> Depth to water (ft.) _____ Completion <u>5.95 gal</u> Additional Comments _____ Sample Collected: Start <u>1440</u> Finish <u>1540</u>
IN-SITU TESTING		Time: <u>1340</u> <u>1346</u> <u>1352</u> <u>1358</u> _____
		1 2 3 4 5 6 7
Well Volume Purged (gal.)		<u>1</u> <u>2.5</u> <u>3.5</u> <u>4.85</u> _____
Turbidity		<u>0</u> <u>1</u> <u>0</u> <u>0</u> _____
Odor		<u>None</u> <u>slight petrol</u> <u>Mod. petrol</u> <u>Mod. petrol</u> _____
pH (units)		<u>6.85</u> <u>7.02</u> <u>7.00</u> <u>7.01</u> _____
Conductivity (umho)		<u>1.75</u> <u>1.70</u> <u>1.76</u> <u>1.80</u> _____
Water Temperature (°C)		<u>21.4</u> <u>20.5</u> <u>20.2</u> <u>19.8</u> _____
Depth to water (ft.)		<u>4.31</u> <u>4.92</u> <u>5.60</u> <u>5.95</u> _____
NOTES:	1 ft. length of 4" Turbidity choices: _____ = 0.087 ft ³ or 0.65 gal. clear, turbid, opaque	1 ft. length 2" = 0.022 ft ³ or 0.16 gal. Revision Date: 8/5/92

Figure 6-1
 Groundwater Sampling Form

Groundwater Sampling		Sample ID: <u>NBCE/065-003</u>
PROJECT NAME: <u>NAVAL Base Charleston</u>		JOB NO: <u>2905-08440</u> DATE: <u>4-18-96</u>
WELL NO.: <u>NBCE/065-003</u>		LOCATION: <u>Zone C</u>
WEATHER CONDITIONS: <u>Sunny, clear</u>		AMBIENT TEMP: <u>80°</u>
REVIEWED BY: <u>M. Best</u>		PERSONNEL: <u>A. Merrill, B. Blythe</u>
PURGING DEVICE Type device? <u>Peristaltic Pump</u> How was the device decontaminated? <u>Per CSAP</u> How was the line decontaminated? <u>Per CSAP</u> Which well was previously purged? <u>NBCE/065-040</u>	SAMPLING DEVICE Type device? <u>Peristaltic Pump</u> How was the device decontaminated? <u>Per CSAP</u> How was the line decontaminated? <u>Per CSAP</u> Which well was previously sampled? <u>NBCE/065-040</u>	
INITIAL WELL VOLUME Well diameter (in.) <u>2</u> Stickup (ft.) <u>FM</u> Depth to bottom of well from TOC (ft.) <u>12.31</u> Depth to water surface from TOC (ft.) <u>3.36</u> Length of water (ft.) <u>8.95</u> Volume of water (ft. ³) _____ (gal.) <u>1.43</u> Amount of sediment at bottom of well (ft.) <u>-</u> 3 Volumes of water (gal.) <u>4.29</u>	PURGING Time started <u>1334</u> Finished <u>1420</u> Volume purged <u>7.0</u> Comments on Well Recovery <u>Good</u> Depth to water (ft.) <u>4.19 - 5.63</u> Completion <u>Yes</u> Additional Comments <u>Org. stain (brn) ^{bit} strange odor?</u> Sample Collected: Start <u>1430</u> Finish <u>1510</u>	
IN-SITU TESTING	Time:	<u>1341</u> <u>1345</u> <u>1350</u> <u>1352</u> <u>1356</u> <u>1409</u> <u>1412</u>
Well Volume Purged (gal.)		<u>1</u> <u>2</u> <u>3</u> <u>4</u> <u>5</u> <u>6</u> <u>7</u>
Turbidity		<u>75</u> <u>1.8</u> <u>2.5</u> <u>3.0</u> <u>4.0</u> <u>5.0</u> <u>7.0</u>
Odor		<u>142</u> <u>166</u> <u>288</u> <u>240</u> <u>249</u> <u>191</u> <u>205</u>
pH (units)		<u>Pungent odor</u>
Conductivity (µmho)		<u>9.33</u> <u>9.36</u> <u>9.37</u> <u>9.30</u> <u>9.31</u> <u>9.31</u> <u>9.20</u>
Water Temperature (°C)		<u>1.10</u> <u>.93</u> <u>.856</u> <u>.854</u> <u>.897</u> <u>.885</u> <u>.882</u>
Depth to water (ft.)		<u>21.8</u> <u>23.1</u> <u>22.6</u> <u>22.0</u> <u>21.9</u> <u>22.0</u> <u>21.9</u>
Depth to water (ft.)		<u>4.19</u> <u>4.95</u> <u>5.02</u> <u>5.20</u> <u>5.35</u> <u>5.08</u> <u>5.62</u>
NOTES: 1 ft. length of 4" = 0.087 ft ³ or 0.65 gal. Turbidity choices: clear, turbid, opaque 1 ft. length 2" = 0.022 ft ³ or 0.16 gal. Revision Date: 8/5/92		

Figure 6-1
 Groundwater Sampling Form

Groundwater Sampling		Sample ID: <u>NBCE/0650604001</u>																																																																
PROJECT NAME: <u>Naval Base Charleston</u>		JOB NO: <u>205-08440</u> DATE: <u>April 18, 1994</u>																																																																
WELL NO.: <u>NBCE/065-040</u>		LOCATION: <u>Zone E</u>																																																																
WEATHER CONDITIONS: <u>Sunny, clear</u>		AMBIENT TEMP: <u>80°</u>																																																																
REVIEWED BY: <u>M Post</u>		PERSONNEL: <u>B. Alyine, A. Merrill</u>																																																																
PURGING DEVICE Type device? <u>Peristaltic Pump</u> How was the device decontaminated? <u>Per CSAP</u> How was the line decontaminated? <u>Per CSAP</u> Which well was previously purged? <u>NBCE/065-005</u>	SAMPLING DEVICE Type device? <u>Peristaltic Pump</u> How was the device decontaminated? <u>Per CSAP</u> How was the line decontaminated? <u>Per CSAP</u> Which well was previously sampled? <u>NBCE/065-005</u>																																																																	
INITIAL WELL VOLUME Well diameter (in.) <u>2</u> Stickup (ft.) <u>FM</u> Depth to bottom of well from TOC (ft.) <u>39.47</u> Depth to water surface from TOC (ft.) <u>7.40</u> Length of water (ft.) <u>32.07</u> Volume of water (ft.) _____ (gal.) <u>5.4</u> Amount of sediment at bottom of well (ft.) <u>-</u> 3 Volumes of water (gal.) <u>16.2</u>	PURGING 4/17 / 4/18 Time started <u>1504 / 0927</u> Finished <u>1545 / 1006</u> Volume purged <u>16 gal</u> Comments on Well Recovery <u>Good</u> Depth to water (ft.) <u>7.23 - 8.35</u> Completion <u>Yes</u> Additional Comments <u>Petro Odor. / Sheen</u> Sample Collected: Start <u>1010</u> Finish <u>1117</u>																																																																	
IN-SITU TESTING	Time:	<u>4/17 1526 1535 1545 4/18 0945 1006</u>																																																																
		<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th></th> <th>1</th> <th>2</th> <th>3</th> <th>4</th> <th>5</th> <th>6</th> <th>7</th> </tr> <tr> <td>Well Volume Purged (gal.)</td> <td><u>4.0</u></td> <td><u>6.0</u></td> <td><u>8.0</u></td> <td><u>12.0</u></td> <td><u>16.0</u></td> <td></td> <td></td> </tr> <tr> <td>Turbidity</td> <td><u>18</u></td> <td><u>21</u></td> <td><u>9</u></td> <td><u>1</u></td> <td><u>3</u></td> <td></td> <td></td> </tr> <tr> <td>Odor</td> <td><u>-</u></td> <td><u>Petro</u></td> <td><u>"</u></td> <td><u>"</u></td> <td><u>"</u></td> <td></td> <td></td> </tr> <tr> <td>pH (units)</td> <td><u>6.79</u></td> <td><u>6.68</u></td> <td><u>6.66</u></td> <td><u>6.15</u></td> <td><u>6.63</u></td> <td></td> <td></td> </tr> <tr> <td>Conductivity (µmho)</td> <td><u>235</u></td> <td><u>256</u></td> <td><u>265</u></td> <td><u>1.19</u></td> <td><u>2.91</u></td> <td></td> <td></td> </tr> <tr> <td>Water Temperature (°C)</td> <td><u>24.0</u></td> <td><u>23.4</u></td> <td><u>23.4</u></td> <td><u>22.0</u></td> <td><u>22.5</u></td> <td></td> <td></td> </tr> <tr> <td>Depth to water (ft.)</td> <td><u>7.88</u></td> <td><u>8.35</u></td> <td><u>8.00</u></td> <td><u>7.23</u></td> <td><u>6.52</u></td> <td></td> <td></td> </tr> </table>		1	2	3	4	5	6	7	Well Volume Purged (gal.)	<u>4.0</u>	<u>6.0</u>	<u>8.0</u>	<u>12.0</u>	<u>16.0</u>			Turbidity	<u>18</u>	<u>21</u>	<u>9</u>	<u>1</u>	<u>3</u>			Odor	<u>-</u>	<u>Petro</u>	<u>"</u>	<u>"</u>	<u>"</u>			pH (units)	<u>6.79</u>	<u>6.68</u>	<u>6.66</u>	<u>6.15</u>	<u>6.63</u>			Conductivity (µmho)	<u>235</u>	<u>256</u>	<u>265</u>	<u>1.19</u>	<u>2.91</u>			Water Temperature (°C)	<u>24.0</u>	<u>23.4</u>	<u>23.4</u>	<u>22.0</u>	<u>22.5</u>			Depth to water (ft.)	<u>7.88</u>	<u>8.35</u>	<u>8.00</u>	<u>7.23</u>	<u>6.52</u>		
	1	2	3	4	5	6	7																																																											
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NOTES: 1 ft. length of 4" = 0.087 ft ³ or 0.65 gal. 1 ft. length of 2" = 0.022 ft ³ or 0.16 gal. Turbidity choices: clear, turbid, opaque Revision Date: 8/5/92																																																																		

FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCE\ 0656W00102																																																																																								
PROJECT NAME: NAVAL BASE CHARLESTON (clean)		JOB NO: _____ DATE: 8/13/96																																																																																								
WELL NO: NBCE\ 065001		LOCATION: ZONE E																																																																																								
WEATHER CONDITIONS: Cloudy		AMBIENT TEMP: 86.75°F																																																																																								
REVIEWED BY: <i>J. H. ...</i>		PERSONNEL: P. Shaw, J. Heron																																																																																								
PURGING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously purged? NBCE\ 065006		SAMPLING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously sampled? NBCE\ 053001																																																																																								
INITIAL WELL VOLUME Well diameter (in.) 2 Stickup (ft.) 0 Depth to bottom of well from TOC (ft.) 12.47 Depth to water surface from TOC (ft.) 2.67 Length of water (ft.) 9.80 Volume of water (ft.) 7.66 ARL (gal.) 1.66 Amount of sediment at bottom of well (ft.) 0 3 volumes of water (gal.) 4.98		PURGING Time started 1011 Finished 1137 Volume purged 8.75 gal Comments on Well Recovery VERY SLOW Depth to water (ft.) 11.34 Completion Insufficient water to sample on Additional Comments 8/13/96. Will sample on 8/14/96 Sample Collected: Start 0922 (8/14/96) Finish 0954																																																																																								
IN-SITU TESTING																																																																																										
Time: 1119 1137 1015 1018 1024 1031 1035 1040 1048 1057																																																																																										
<table style="width:100%; border-collapse: collapse;"> <tr> <td></td> <td style="text-align: center;">9</td> <td style="text-align: center;">10</td> <td style="text-align: center;">1</td> <td style="text-align: center;">2</td> <td style="text-align: center;">3</td> <td style="text-align: center;">4</td> <td style="text-align: center;">5</td> <td style="text-align: center;">6</td> <td style="text-align: center;">7</td> <td style="text-align: center;">8</td> </tr> <tr> <td>Well Volume Purged (gal.)</td> <td style="text-align: center;">7.875</td> <td style="text-align: center;">8.75</td> <td style="text-align: center;">8.875</td> <td style="text-align: center;">1.75</td> <td style="text-align: center;">2.625</td> <td style="text-align: center;">3.5</td> <td style="text-align: center;">4.375</td> <td style="text-align: center;">5.25</td> <td style="text-align: center;">6.125</td> <td style="text-align: center;">7</td> </tr> <tr> <td>Turbidity</td> <td style="text-align: center;">2</td> <td style="text-align: center;">2</td> <td style="text-align: center;">191</td> <td style="text-align: center;">155</td> <td style="text-align: center;">1</td> <td style="text-align: center;">3</td> <td style="text-align: center;">1</td> <td style="text-align: center;">1</td> <td style="text-align: center;">1</td> <td style="text-align: center;">2</td> </tr> <tr> <td>Odor</td> <td style="text-align: center;">NO</td> </tr> <tr> <td>pH (units)</td> <td style="text-align: center;">6.51</td> <td style="text-align: center;">6.51</td> <td style="text-align: center;">6.46</td> <td style="text-align: center;">6.53</td> <td style="text-align: center;">6.57</td> <td style="text-align: center;">6.43</td> <td style="text-align: center;">6.90</td> <td style="text-align: center;">6.45</td> <td style="text-align: center;">6.62</td> <td style="text-align: center;">6.51</td> </tr> <tr> <td>Conductivity (umho)</td> <td style="text-align: center;">7.48</td> <td style="text-align: center;">7.02</td> <td style="text-align: center;">1.70</td> <td style="text-align: center;">1.87</td> <td style="text-align: center;">2.16</td> <td style="text-align: center;">2.71</td> <td style="text-align: center;">4.77</td> <td style="text-align: center;">6.38</td> <td style="text-align: center;">6.22</td> <td style="text-align: center;">7.01</td> </tr> <tr> <td>Water Temperature (deg. C)</td> <td style="text-align: center;">25.9</td> <td style="text-align: center;">25.7</td> <td style="text-align: center;">29.2</td> <td style="text-align: center;">28.9</td> <td style="text-align: center;">28.2</td> <td style="text-align: center;">27.5</td> <td style="text-align: center;">26.3</td> <td style="text-align: center;">25.5</td> <td style="text-align: center;">25.4</td> <td style="text-align: center;">25.2</td> </tr> <tr> <td>Depth to water (ft.)</td> <td style="text-align: center;">10.86</td> <td style="text-align: center;">11.34</td> <td style="text-align: center;">4.57</td> <td style="text-align: center;">6.25</td> <td style="text-align: center;">6.09</td> <td style="text-align: center;">7.06</td> <td style="text-align: center;">7.82</td> <td style="text-align: center;">8.64</td> <td style="text-align: center;">9.70</td> <td style="text-align: center;">10.42</td> </tr> </table>				9	10	1	2	3	4	5	6	7	8	Well Volume Purged (gal.)	7.875	8.75	8.875	1.75	2.625	3.5	4.375	5.25	6.125	7	Turbidity	2	2	191	155	1	3	1	1	1	2	Odor	NO	pH (units)	6.51	6.51	6.46	6.53	6.57	6.43	6.90	6.45	6.62	6.51	Conductivity (umho)	7.48	7.02	1.70	1.87	2.16	2.71	4.77	6.38	6.22	7.01	Water Temperature (deg. C)	25.9	25.7	29.2	28.9	28.2	27.5	26.3	25.5	25.4	25.2	Depth to water (ft.)	10.86	11.34	4.57	6.25	6.09	7.06	7.82	8.64	9.70	10.42									
	9	10	1	2	3	4	5	6	7	8																																																																																
Well Volume Purged (gal.)	7.875	8.75	8.875	1.75	2.625	3.5	4.375	5.25	6.125	7																																																																																
Turbidity	2	2	191	155	1	3	1	1	1	2																																																																																
Odor	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO																																																																																
pH (units)	6.51	6.51	6.46	6.53	6.57	6.43	6.90	6.45	6.62	6.51																																																																																
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FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCE\0656W00207																																																																																								
PROJECT NAME: NAVAL BASE CHARLESTON (clean)		JOB NO: _____ DATE: 8/13/96																																																																																								
WELL NO: NBCE\065002		LOCATION: ZONE E																																																																																								
WEATHER CONDITIONS: Cloudy		AMBIENT TEMP: 82°F																																																																																								
REVIEWED BY: <u>A. DePue</u>		PERSONNEL: P. Skaw, J. Herrow																																																																																								
PURGING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously purged? NBCE\528001		SAMPLING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously sampled? NBCE\528001																																																																																								
INITIAL WELL VOLUME Well diameter (in.) 2 Stickup (ft.) 0 Depth to bottom of well from TOC (ft.) 12.41 Depth to water surface from TOC (ft.) 3.51 Length of water (ft.) 8.90 Volume of water (ft.) _____ (gal.) 1.51 Amount of sediment at bottom of well (ft.) 0 3 volumes of water (gal.) 4.53		PURGING Time started 1200 Finished 1239 Volume purged 8.75 Comments on Well Recovery Fast Depth to water (ft.) 3.62 Completion _____ Additional Comments _____ Sample Collected: Start 1244 Finish 1302																																																																																								
IN-SITU TESTING Time: 1235-1239 1204 1208 1212 1217 1220 1224 1228 1231																																																																																										
<table style="width:100%; border-collapse: collapse;"> <tr> <td></td> <td style="text-align: center;">9</td> <td style="text-align: center;">10</td> <td style="text-align: center;">1</td> <td style="text-align: center;">2</td> <td style="text-align: center;">3</td> <td style="text-align: center;">4</td> <td style="text-align: center;">5</td> <td style="text-align: center;">6</td> <td style="text-align: center;">7</td> <td style="text-align: center;">8</td> </tr> <tr> <td>Well Volume Purged (gal.)</td> <td style="text-align: center;">2.875</td> <td style="text-align: center;">8.75</td> <td style="text-align: center;">8.75</td> <td style="text-align: center;">1.75</td> <td style="text-align: center;">2.625</td> <td style="text-align: center;">3.5</td> <td style="text-align: center;">4.375</td> <td style="text-align: center;">5.25</td> <td style="text-align: center;">6.125</td> <td style="text-align: center;">7</td> </tr> <tr> <td>Turbidity</td> <td style="text-align: center;">0</td> <td style="text-align: center;">0</td> <td style="text-align: center;">1</td> <td style="text-align: center;">0</td> <td style="text-align: center;">1</td> <td style="text-align: center;">0</td> </tr> <tr> <td>Odor</td> <td style="text-align: center;">NO</td> </tr> <tr> <td>pH (units)</td> <td style="text-align: center;">6.76</td> <td style="text-align: center;">6.72</td> <td style="text-align: center;">6.52</td> <td style="text-align: center;">6.55</td> <td style="text-align: center;">6.63</td> <td style="text-align: center;">6.65</td> <td style="text-align: center;">6.68</td> <td style="text-align: center;">6.68</td> <td style="text-align: center;">6.72</td> <td style="text-align: center;">6.72</td> </tr> <tr> <td>Conductivity (µmho)</td> <td style="text-align: center;">2.24</td> <td style="text-align: center;">2.21</td> <td style="text-align: center;">6.67</td> <td style="text-align: center;">5.26</td> <td style="text-align: center;">4.27</td> <td style="text-align: center;">3.48</td> <td style="text-align: center;">3.17</td> <td style="text-align: center;">2.67</td> <td style="text-align: center;">2.56</td> <td style="text-align: center;">2.44</td> </tr> <tr> <td>Water Temperature (deg. C)</td> <td style="text-align: center;">30.9</td> <td style="text-align: center;">31</td> <td style="text-align: center;">30.4</td> <td style="text-align: center;">30.5</td> <td style="text-align: center;">30.6</td> <td style="text-align: center;">30.7</td> <td style="text-align: center;">30.7</td> <td style="text-align: center;">30.8</td> <td style="text-align: center;">30.9</td> <td style="text-align: center;">30.9</td> </tr> <tr> <td>Depth to water (ft.)</td> <td style="text-align: center;">3.62</td> <td style="text-align: center;">3.62</td> <td style="text-align: center;">3.55</td> <td style="text-align: center;">3.55</td> <td style="text-align: center;">3.55</td> <td style="text-align: center;">3.61</td> <td style="text-align: center;">3.62</td> <td style="text-align: center;">3.62</td> <td style="text-align: center;">3.62</td> <td style="text-align: center;">3.62</td> </tr> </table>				9	10	1	2	3	4	5	6	7	8	Well Volume Purged (gal.)	2.875	8.75	8.75	1.75	2.625	3.5	4.375	5.25	6.125	7	Turbidity	0	0	1	0	0	0	0	0	1	0	Odor	NO	pH (units)	6.76	6.72	6.52	6.55	6.63	6.65	6.68	6.68	6.72	6.72	Conductivity (µmho)	2.24	2.21	6.67	5.26	4.27	3.48	3.17	2.67	2.56	2.44	Water Temperature (deg. C)	30.9	31	30.4	30.5	30.6	30.7	30.7	30.8	30.9	30.9	Depth to water (ft.)	3.62	3.62	3.55	3.55	3.55	3.61	3.62	3.62	3.62	3.62									
	9	10	1	2	3	4	5	6	7	8																																																																																
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Turbidity	0	0	1	0	0	0	0	0	1	0																																																																																
Odor	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO																																																																																
pH (units)	6.76	6.72	6.52	6.55	6.63	6.65	6.68	6.68	6.72	6.72																																																																																
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Water Temperature (deg. C)	30.9	31	30.4	30.5	30.6	30.7	30.7	30.8	30.9	30.9																																																																																
Depth to water (ft.)	3.62	3.62	3.55	3.55	3.55	3.61	3.62	3.62	3.62	3.62																																																																																
NOTES: 1 FT. LENGTH OF 4" Turbidity choices: _____ equals 0.087 ft or 0.65 gal. clear, turbid, opaque 1 ft. length 2" equals 0.022ft or 0.16 gal. Revision Date: 8/5/92																																																																																										

FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCE\ 0656W003 02	
PROJECT NAME: NAVAL BASE CHARLESTON (clean)		JOB NO: _____	DATE: 8-14-96
WELL NO: NBCE\ 065-003		LOCATION: ZONE E	
WEATHER CONDITIONS: Sunny		AMBIENT TEMP: 95°F	
REVIEWED BY: <i>[Signature]</i>		PERSONNEL: B. Kovich M. Litchfield	
PURGING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously purged? NBCE\ 526-01D		SAMPLING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously sampled? NBCE\ 526-01D	
INITIAL WELL VOLUME Well diameter (in.) 2 Stickup (ft.) None Depth to bottom of well from TOC (ft.) 12.32 Depth to water surface from TOC (ft.) 1.76 Length of water (ft.) 10.56 Volume of water (ft.) _____ (gal.) 1.8 Amount of sediment at bottom of well (ft.) None 3 volumes of water (gal.) 5.4		PURGING Time started 10:20 Finished 11:18 Volume purged 10 gal Comments on Well Recovery Excellent Depth to water (ft.) 2.99 Completion _____ Additional Comments _____ Sample Collected: Start 1123 Finish 1230 1039 1045	
IN-SITU TESTING		Time: 1114 1118 1024 1029 1034 1045 1053 1053 1100 1107 9 10 1 2 3 4 5 6 7 8 Well Volume Purged (gal.) 9 10 1 2 3 4 5 6 7 8 Turbidity 12 8 6 10 15 14 13 13 12 Odor None None None None None None None None None pH (units) 9.38 9.38 9.31 9.40 9.42 9.41 9.40 9.39 9.38 9.36 Conductivity (umho) 515 460 446 498 529 513 489 496 495 485 Water Temperature (deg. C) 30.3 30.5 29.5 30.0 30.1 30.1 30.2 30.1 30.2 30.4 Depth to water (ft.) 2.72 2.99 2.43 2.59 2.70 2.61 2.65 2.65 2.67 ?	
NOTES: 1 FT. LENGTH OF 4" Turbidity choices:		equals 0.087 ft or 0.65 gal. clear, turbid, opaque 1 ft. length 2" equals 0.022ft or 0.16 gal. Revision Date: 8/5/92	

FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCE\ 065GW00402
PROJECT NAME: NAVAL BASE CHARLESTON (clean)		JOB NO: _____ DATE: 80°F
WELL NO: NBCE\ 065-004		LOCATION: ZONE E F-15-96
WEATHER CONDITIONS: _____		AMBIENT TEMP: 80°F
REVIEWED BY: <i>[Signature]</i>		PERSONNEL: B. Herrick M. Hitchfield
PURGING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously purged? NBCE\ 065-003		SAMPLING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously sampled? NBCE\ 065-003
INITIAL WELL VOLUME Well diameter (in.) 2 Stickup (ft.) None Depth to bottom of well from TOC (ft.) 12.47 Depth to water surface from TOC (ft.) 2.13 Length of water (ft.) 10.34 Volume of water (ft.) _____ (gal.) 1.75 Amount of sediment at bottom of well (ft.) None 3 volumes of water (gal.) 5.25		PURGING Time started 0650 Finished 0718 Volume purged 5.275 gal Comments on Well Recovery excellent Depth to water (ft.) 3.81' Completion _____ Additional Comments _____ Sample Collected: Start 0723 Finish 0805
IN-SITU TESTING		
	Time:	0655 0700 0705 0710 0714 0718
Well Volume Purged (gal.)		1 2 3 4 5 6 7 .875 1.75 2.625 3.5 4.375 5.275
Turbidity		2 0 1 0 0 0
Odor		None None None None None None
pH (units)		6.62 6.81 6.89 6.92 6.94 6.96
Conductivity (umho)		.535 .537 .545 .540 .538 .536
Water Temperature (deg. C)		29.6 29.9 30.1 30.1 30.1 30.1
Depth to water (ft.)		2.84 3.23 3.47 3.61 3.71 3.81
NOTES:	1 FT. LENGTH OF 4" Turbidity choices:	equals 0.087 ft or 0.65 gal. clear, turbid, opaque 1 ft. length 2" equals 0.022ft or 0.16 gal. Revision Date: 8/5/92

FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCE\ 0656W04002
PROJECT NAME: NAVAL BASE CHARLESTON (clean)		JOB NO: _____ DATE: 8-15-96
WELL NO: NBCE\ 065-040		LOCATION: ZONE E
WEATHER CONDITIONS: Cloudy		AMBIENT TEMP: 50°F
REVIEWED BY: <i>[Signature]</i>		PERSONNEL: B. Herrick M. Litchfield
PURGING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously purged? NBCE\ 065-004		SAMPLING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously sampled? NBCE\ 065-004
INITIAL WELL VOLUME Well diameter (in.) 2 Stickup (ft.) None Depth to bottom of well from TOC (ft.) 39.62 Depth to water surface from TOC (ft.) 6.20 Length of water (ft.) 33.42 Volume of water (ft.) _____ (gal.) 5.7 Amount of sediment at bottom of well (ft.) None 3 volumes of water (gal.) 17		PURGING Time started 0826 Finished 0948 Volume purged 18 gal Comments on Well Recovery Excellent Depth to water (ft.) 7.10' Completion _____ Additional Comments _____ Sample Collected: Start 0953 Finish 1020
IN-SITU TESTING		Time: 0842 0856 0909 0922 0935 0948
		1 2 3 4 5 6 7 3 6 9 12 15 18 0 7 2 1 1 0 None None None None None None 6.53 6.56 6.60 6.61 6.62 6.62 662 2.31 2.37 2.38 2.38 2.38 22.9 23.0 23.1 23.1 23.1 23.1 7.14 7.14 7.13 7.12 7.11 7.10
Well Volume Purged (gal.) Turbidity Odor pH (units) Conductivity (umho) Water Temperature (deg. C) Depth to water (ft.)		
NOTES: 1 FT. LENGTH OF 4" Turbidity choices:		equals 0.087 ft or 0.65 gal. clear, turbid, opaque 1 ft. length 2" equals 0.022ft or 0.16 gal. Revision Date: 8/5/92

FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCE\0656W00602																																																																
PROJECT NAME: NAVAL BASE CHARLESTON (clean)		JOB NO: _____ DATE: 8/13/96																																																																
WELL NO: NBCE\065006		LOCATION: ZONE E																																																																
WEATHER CONDITIONS: Cloudy		AMBIENT TEMP: 75°F																																																																
REVIEWED BY: <i>M. Ching</i>		PERSONNEL: P. Shaw, J. Harrow																																																																
PURGING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously purged? NBCE\053001		SAMPLING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously sampled? NBCE\053001																																																																
INITIAL WELL VOLUME Well diameter (in.) 2 Stickup (ft.) -0- Depth to bottom of well from TOC (ft.) 12.05 Depth to water surface from TOC (ft.) 5.52 Length of water (ft.) 6.53 Volume of water (ft.) _____ (gal.) 1.11 Amount of sediment at bottom of well (ft.) -0- 3 volumes of water (gal.) 3.33		PURGING Time started 0813 Finished 0938 Volume purged 3.75 Comments on Well Recovery Very Slow Depth to water (ft.) 12.03 Completion Insufficient water to Additional Comments Sample on 8/13/96 Return on 8/14/96 for sample Sample Collected: Start 1037 (8/14/96) Finish 1136																																																																
IN-SITU TESTING		Time: 0817 0927 0842 0902 0917 0938																																																																
		<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <td></td> <td>1</td> <td>2</td> <td>3</td> <td>4</td> <td>5</td> <td>6</td> <td>7</td> </tr> <tr> <td>Well Volume Purged (gal.)</td> <td>.625</td> <td>1.25</td> <td>1.875</td> <td>2.5</td> <td>3.125</td> <td>3.75</td> <td></td> </tr> <tr> <td>Turbidity</td> <td>10</td> <td>7</td> <td>4</td> <td>52</td> <td>6</td> <td>2</td> <td></td> </tr> <tr> <td>Odor</td> <td>NO</td> <td>NO</td> <td>NO</td> <td>NO</td> <td>NO</td> <td>NO</td> <td></td> </tr> <tr> <td>pH (units)</td> <td>6.30</td> <td>6.63</td> <td>6.71</td> <td>6.71</td> <td>6.75</td> <td>6.77</td> <td></td> </tr> <tr> <td>Conductivity (umho)</td> <td>.549</td> <td>.677</td> <td>.678</td> <td>.657</td> <td>.650</td> <td>.649</td> <td></td> </tr> <tr> <td>Water Temperature (deg. C)</td> <td>26.6</td> <td>24.7</td> <td>24.3</td> <td>24.1</td> <td>24.4</td> <td>24.5</td> <td></td> </tr> <tr> <td>Depth to water (ft.)</td> <td>8.78</td> <td>10.33</td> <td>11.02</td> <td>11.56</td> <td>12.03</td> <td>12.03</td> <td></td> </tr> </table>		1	2	3	4	5	6	7	Well Volume Purged (gal.)	.625	1.25	1.875	2.5	3.125	3.75		Turbidity	10	7	4	52	6	2		Odor	NO	NO	NO	NO	NO	NO		pH (units)	6.30	6.63	6.71	6.71	6.75	6.77		Conductivity (umho)	.549	.677	.678	.657	.650	.649		Water Temperature (deg. C)	26.6	24.7	24.3	24.1	24.4	24.5		Depth to water (ft.)	8.78	10.33	11.02	11.56	12.03	12.03	
	1	2	3	4	5	6	7																																																											
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FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCE\ 065640031 03																																																																
PROJECT NAME: NAVAL BASE CHARLESTON (clean)		JOB NO: _____ DATE: 12-11-96																																																																
WELL NO: NBCE\ 065.001		LOCATION: ZONE E																																																																
WEATHER CONDITIONS: Sunny		AMBIENT TEMP: 50°F																																																																
REVIEWED BY: <i>A. Bryant</i>		PERSONNEL: B. Hornick, M. Fitchfield																																																																
PURGING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously purged? NBCE\ 065-002	SAMPLING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously sampled? NBCE\ 065-002																																																																	
INITIAL WELL VOLUME Well diameter (in.) 2 Stickup (ft.) None Depth to bottom of well from TOC (ft.) 12.47 Depth to water surface from TOC (ft.) 2.65 Length of water (ft.) 9.82 Volume of water (ft.) _____ (gal.) 1.66 Amount of sediment at bottom of well (ft.) None 3 volumes of water (gal.) 5	PURGING Time started 0908 Finished 1016 Volume purged 6.125 gal Comments on Well Recovery Pass. Depth to water (ft.) 7.74 Completion - Additional Comments - Sample Collected: Start 1021 Finish 1045																																																																	
IN-SITU TESTING	Time:	0918 0927 0937 0946 0956 1006 1016																																																																
Well Volume Purged (gal.) Turbidity Odor pH (units) Conductivity (umho) Water Temperature (deg. C) Depth to water (ft.)	<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th></th> <th>1</th> <th>2</th> <th>3</th> <th>4</th> <th>5</th> <th>6</th> <th>7</th> </tr> </thead> <tbody> <tr> <td>Well Volume Purged (gal.)</td> <td>0.875</td> <td>1.75</td> <td>2.625</td> <td>3.5</td> <td>4.375</td> <td>5.25</td> <td>6.125</td> </tr> <tr> <td>Turbidity</td> <td>5</td> <td>4</td> <td>1</td> <td>2</td> <td>2</td> <td>3</td> <td>3</td> </tr> <tr> <td>Odor</td> <td>None</td> <td>None</td> <td>None</td> <td>None</td> <td>None</td> <td>None</td> <td>None</td> </tr> <tr> <td>pH (units)</td> <td>6.71</td> <td>6.67</td> <td>6.70</td> <td>6.41</td> <td>6.60</td> <td>6.56</td> <td>6.51</td> </tr> <tr> <td>Conductivity (umho)</td> <td>1.62</td> <td>1.72</td> <td>1.63</td> <td>3.35</td> <td>2.10</td> <td>2.09</td> <td>2.24</td> </tr> <tr> <td>Water Temperature (deg. C)</td> <td>19.0</td> <td>20.3</td> <td>20.2</td> <td>21.8</td> <td>21.3</td> <td>21.5</td> <td>21.8</td> </tr> <tr> <td>Depth to water (ft.)</td> <td>3.91</td> <td>4.56</td> <td>5.23</td> <td>5.78</td> <td>6.4</td> <td>7.08</td> <td>7.74</td> </tr> </tbody> </table>			1	2	3	4	5	6	7	Well Volume Purged (gal.)	0.875	1.75	2.625	3.5	4.375	5.25	6.125	Turbidity	5	4	1	2	2	3	3	Odor	None	pH (units)	6.71	6.67	6.70	6.41	6.60	6.56	6.51	Conductivity (umho)	1.62	1.72	1.63	3.35	2.10	2.09	2.24	Water Temperature (deg. C)	19.0	20.3	20.2	21.8	21.3	21.5	21.8	Depth to water (ft.)	3.91	4.56	5.23	5.78	6.4	7.08	7.74						
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FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCEI 065 6W00203															
PROJECT NAME: NAVAL BASE CHARLESTON (clean)		JOB NO: _____	DATE: 12-1-96														
WELL NO: NBCEI 065-002		LOCATION: ZONE E															
WEATHER CONDITIONS: Sunny		AMBIENT TEMP: 50°F															
REVIEWED BY: <i>A. Newquist</i>		PERSONNEL: B. Herron, M. Fitzfield															
PURGING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously purged? NBCEI 065-005		SAMPLING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously sampled? NBCEI 065-005															
INITIAL WELL VOLUME Well diameter (in.) 2 Stickup (ft.) None Depth to bottom of well from TOC (ft.) 12.41 Depth to water surface from TOC (ft.) 3.43 Length of water (ft.) 8.98 Volume of water (ft.) _____ (gal.) 1.52 Amount of sediment at bottom of well (ft.) None 3 volumes of water (gal.) 4.57		PURGING Time started 0750 Finished 0832 Volume purged 4.8 gal Comments on Well Recovery good Depth to water (ft.) 3.49 Completion _____ Additional Comments _____ Sample Collected: Start 0837 Finish 0852															
IN-SITU TESTING		Time: 0758 0805 0812 0819 0826 0832															
Well Volume Purged (gal.)		<table style="width:100%; text-align: center;"> <tr> <td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td> </tr> <tr> <td>8</td><td>1.6</td><td>2.4</td><td>3.2</td><td>4</td><td>4.8</td><td></td> </tr> </table>		1	2	3	4	5	6	7	8	1.6	2.4	3.2	4	4.8	
1	2	3	4	5	6	7											
8	1.6	2.4	3.2	4	4.8												
Turbidity		<table style="width:100%; text-align: center;"> <tr> <td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td>0</td><td></td> </tr> </table>		1	1	1	1	1	0								
1	1	1	1	1	0												
Odor		<table style="width:100%; text-align: center;"> <tr> <td>None</td><td>None</td><td>None</td><td>None</td><td>None</td><td></td><td></td> </tr> </table>		None	None	None	None	None									
None	None	None	None	None													
pH (units)		<table style="width:100%; text-align: center;"> <tr> <td>6.38</td><td>6.43</td><td>6.47</td><td>6.48</td><td>6.52</td><td>6.54</td><td></td> </tr> </table>		6.38	6.43	6.47	6.48	6.52	6.54								
6.38	6.43	6.47	6.48	6.52	6.54												
Conductivity (µmho)		<table style="width:100%; text-align: center;"> <tr> <td>3.62</td><td>3.19</td><td>2.95</td><td>2.76</td><td>2.57</td><td>2.60</td><td></td> </tr> </table>		3.62	3.19	2.95	2.76	2.57	2.60								
3.62	3.19	2.95	2.76	2.57	2.60												
Water Temperature (deg. C)		<table style="width:100%; text-align: center;"> <tr> <td>18.6</td><td>18.5</td><td>18.3</td><td>18.3</td><td>18.4</td><td>18.3</td><td></td> </tr> </table>		18.6	18.5	18.3	18.3	18.4	18.3								
18.6	18.5	18.3	18.3	18.4	18.3												
Depth to water (ft.)		<table style="width:100%; text-align: center;"> <tr> <td>3.47</td><td>3.47</td><td>3.48</td><td>3.49</td><td>3.49</td><td>3.49</td><td></td> </tr> </table>		3.47	3.47	3.48	3.49	3.49	3.49								
3.47	3.47	3.48	3.49	3.49	3.49												
NOTES: 1 FT. LENGTH OF 4" Turbidity choices:		equals 0.087 ft or 0.65 gal. clear, turbid, opaque															
		1 ft. length 2" equals 0.022ft or 0.16 gal. Revision Date: 8/5/92															

FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCE\ 0656W 00303
PROJECT NAME: NAVAL BASE CHARLESTON (clean)		JOB NO: _____ DATE: 12-10-96
WELL NO: NBCE\ 065-003		LOCATION: ZONE E
WEATHER CONDITIONS: Sunny		AMBIENT TEMP: 50°
REVIEWED BY: A. Hanapure		PERSONNEL: B. Herrick M. Fitchell
PURGING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously purged? NBCE\ 065-040		SAMPLING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously sampled? NBCE\ 065-040
INITIAL WELL VOLUME Well diameter (in.) 2 Stickup (ft.) None Depth to bottom of well from TOC (ft.) 12.32 Depth to water surface from TOC (ft.) 1.76 Length of water (ft.) 10.56 Volume of water (ft. ³) - (gal.) 1.8 Amount of sediment at bottom of well (ft.) None 3 volumes of water (gal.) 5.4		PURGING Time started 0806 Finished 0858 Volume purged 6 gal Comments on Well Recovery Excellent Depth to water (ft.) 2.77 Completion - Additional Comments - Sample Collected: Start 0903 Finish 0950
IN-SITU TESTING		Time: 0814 0822 0832 0840 0849 0858
		1 2 3 4 5 6 7
Well Volume Purged (gal.)		1 2 3 4 5 6
Turbidity		2 4 4 5 5 6
Odor		None None None None None None
pH (units)		9.15 9.34 9.36 9.40 9.42 9.44
Conductivity (µmho)		302 336 336 382 386 405
Water Temperature (deg. C)		17.0 17.0 16.9 17.2 17.0 17.0
Depth to water (ft.)		2.43 2.53 2.61 2.67 2.72 2.77
NOTES: 1 FT. LENGTH OF 4" equals 0.087 ft or 0.65 gal. Turbidity choices: clear, turbid, opaque		
1 ft. length 2" equals 0.022ft or 0.16 gal. Revision Date: 8/5/92		

FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCE\0656W00407																																																																	
PROJECT NAME: NAVAL BASE CHARLESTON (clean)		JOB NO: _____	DATE: 12-9-96																																																																
WELL NO: NBCE\065-004		LOCATION: ZONE E																																																																	
WEATHER CONDITIONS: Sunny		AMBIENT TEMP: 50° F																																																																	
REVIEWED BY: <i>A. Bunge</i>		PERSONNEL: B. Herrick M. Tuttle																																																																	
PURGING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously purged? NBCE\023-010		SAMPLING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously sampled? NBCE\023-010																																																																	
INITIAL WELL VOLUME Well diameter (in.) 2 Stickup (ft.) None Depth to bottom of well from TOC (ft.) 12.47 Depth to water surface from TOC (ft.) 1.84 Length of water (ft.) 10.63 Volume of water (ft.) - (gal.) 1.8 Amount of sediment at bottom of well (ft.) None 3 volumes of water (gal.) 5.42		PURGING Time started 0925 Finished 0957 Volume purged 6 gal Comments on Well Recovery excellent Depth to water (ft.) 3.05' Completion - Additional Comments - Sample Collected: Start 1002 Finish 1025																																																																	
IN-SITU TESTING		Time: 0921 0926 0941 0947 0952 0957																																																																	
		<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <td></td> <td>1</td> <td>2</td> <td>3</td> <td>4</td> <td>5</td> <td>6</td> <td>7</td> </tr> <tr> <td>Well Volume Purged (gal.)</td> <td>1</td> <td>2</td> <td>3</td> <td>4</td> <td>5</td> <td>6</td> <td></td> </tr> <tr> <td>Turbidity</td> <td>1</td> <td>1</td> <td>6</td> <td>1</td> <td>2</td> <td>1</td> <td></td> </tr> <tr> <td>Odor</td> <td colspan="7" style="text-align: center;"><i>sulfur duff</i></td> </tr> <tr> <td>pH (units)</td> <td>6.78</td> <td>7.17</td> <td>7.30</td> <td>7.23</td> <td>7.57</td> <td>7.39</td> <td></td> </tr> <tr> <td>Conductivity (µmho)</td> <td>273</td> <td>269</td> <td>284</td> <td>272</td> <td>272</td> <td>271</td> <td></td> </tr> <tr> <td>Water Temperature (deg. C)</td> <td>16.8</td> <td>16.7</td> <td>17.3</td> <td>17.3</td> <td>17.1</td> <td>17.2</td> <td></td> </tr> <tr> <td>Depth to water (ft.)</td> <td>2.43</td> <td>2.54</td> <td>2.68</td> <td>2.82</td> <td>2.96</td> <td>3.08</td> <td></td> </tr> </table>			1	2	3	4	5	6	7	Well Volume Purged (gal.)	1	2	3	4	5	6		Turbidity	1	1	6	1	2	1		Odor	<i>sulfur duff</i>							pH (units)	6.78	7.17	7.30	7.23	7.57	7.39		Conductivity (µmho)	273	269	284	272	272	271		Water Temperature (deg. C)	16.8	16.7	17.3	17.3	17.1	17.2		Depth to water (ft.)	2.43	2.54	2.68	2.82	2.96	3.08	
	1	2	3	4	5	6	7																																																												
Well Volume Purged (gal.)	1	2	3	4	5	6																																																													
Turbidity	1	1	6	1	2	1																																																													
Odor	<i>sulfur duff</i>																																																																		
pH (units)	6.78	7.17	7.30	7.23	7.57	7.39																																																													
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Water Temperature (deg. C)	16.8	16.7	17.3	17.3	17.1	17.2																																																													
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NOTES: 1 FT. LENGTH OF 4" Turbidity choices:		equals 0.087 ft or 0.65 gal. clear, turbid, opaque																																																																	
		1 ft. length 2" equals 0.022ft or 0.16 gal. Revision Date: 8/5/92																																																																	

FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCE\ <u>065 6W 040 03</u>																																																																	
PROJECT NAME: <u>NAVAL BASE CHARLESTON (clean)</u>		JOB NO: _____	DATE: <u>12-9-96</u>																																																																
WELL NO: <u>NBCE\ 065-040</u>		LOCATION: <u>ZONE E</u>																																																																	
WEATHER CONDITIONS: <u>clear</u>		AMBIENT TEMP: <u>59°</u>																																																																	
REVIEWED BY: <u>A. Dineyich</u>		PERSONNEL: <u>B. Kersch M. Litchfield</u>																																																																	
PURGING DEVICE Type device? <u>Peristaltic Pump</u> How was the device decontaminated? <u>Per CSAP</u> How was the line decontaminated? <u>Per CSAP</u> Which well was previously purged? <u>NBCE\ 065-004</u>		SAMPLING DEVICE Type device? <u>Peristaltic Pump</u> How was the device decontaminated? <u>Per CSAP</u> How was the line decontaminated? <u>Per CSAP</u> Which well was previously sampled? <u>NBCE\ 065-004</u>																																																																	
INITIAL WELL VOLUME Well diameter (in.) <u>2</u> Stickup (ft.) <u>None</u> Depth to bottom of well from TOC (ft.) <u>39.62</u> Depth to water surface from TOC (ft.) <u>6.12</u> Length of water (ft.) <u>33.5</u> Volume of water (ft.) _____ (gal.) <u>5.7</u> Amount of sediment at bottom of well (ft.) <u>None</u> 3 volumes of water (gal.) <u>17.0</u>		PURGING Time started <u>0921</u> Finished <u>1057</u> Volume purged <u>18 gal</u> Comments on Well Recovery <u>Excellent</u> Depth to water (ft.) <u>7.52</u> Completion _____ Additional Comments _____ Sample Collected: Start <u>1102</u> Finish <u>1117</u>																																																																	
IN-SITU TESTING		Time: <u>0937 0953 1010 1025 1041 1057</u>																																																																	
		<table style="width:100%; text-align: center;"> <tr> <td></td> <td><u>1</u></td> <td><u>2</u></td> <td><u>3</u></td> <td><u>4</u></td> <td><u>5</u></td> <td><u>6</u></td> <td><u>7</u></td> </tr> <tr> <td>Well Volume Purged (gal.)</td> <td><u>3</u></td> <td><u>6</u></td> <td><u>9</u></td> <td><u>12</u></td> <td><u>15</u></td> <td><u>18</u></td> <td>_____</td> </tr> <tr> <td>Turbidity</td> <td><u>3</u></td> <td><u>10</u></td> <td><u>4</u></td> <td><u>4</u></td> <td><u>1</u></td> <td><u>0</u></td> <td>_____</td> </tr> <tr> <td>Odor</td> <td><u>None</u></td> <td><u>None</u></td> <td><u>slight</u></td> <td><u>slight</u></td> <td><u>slight</u></td> <td><u>slight</u></td> <td>_____</td> </tr> <tr> <td>pH (units)</td> <td><u>6.54</u></td> <td><u>6.71</u></td> <td><u>6.71</u></td> <td><u>6.72</u></td> <td><u>6.72</u></td> <td><u>6.73</u></td> <td>_____</td> </tr> <tr> <td>Conductivity (umho)</td> <td><u>510</u></td> <td><u>1.71</u></td> <td><u>1.86</u></td> <td><u>1.90</u></td> <td><u>1.93</u></td> <td><u>1.96</u></td> <td>_____</td> </tr> <tr> <td>Water Temperature (deg. C)</td> <td><u>21.6</u></td> <td><u>21.4</u></td> <td><u>21.7</u></td> <td><u>21.1</u></td> <td><u>21.7</u></td> <td><u>21.7</u></td> <td>_____</td> </tr> <tr> <td>Depth to water (ft.)</td> <td><u>7.19</u></td> <td><u>7.28</u></td> <td><u>7.35</u></td> <td><u>7.4</u></td> <td><u>7.45</u></td> <td><u>7.52</u></td> <td>_____</td> </tr> </table>			<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	Well Volume Purged (gal.)	<u>3</u>	<u>6</u>	<u>9</u>	<u>12</u>	<u>15</u>	<u>18</u>	_____	Turbidity	<u>3</u>	<u>10</u>	<u>4</u>	<u>4</u>	<u>1</u>	<u>0</u>	_____	Odor	<u>None</u>	<u>None</u>	<u>slight</u>	<u>slight</u>	<u>slight</u>	<u>slight</u>	_____	pH (units)	<u>6.54</u>	<u>6.71</u>	<u>6.71</u>	<u>6.72</u>	<u>6.72</u>	<u>6.73</u>	_____	Conductivity (umho)	<u>510</u>	<u>1.71</u>	<u>1.86</u>	<u>1.90</u>	<u>1.93</u>	<u>1.96</u>	_____	Water Temperature (deg. C)	<u>21.6</u>	<u>21.4</u>	<u>21.7</u>	<u>21.1</u>	<u>21.7</u>	<u>21.7</u>	_____	Depth to water (ft.)	<u>7.19</u>	<u>7.28</u>	<u>7.35</u>	<u>7.4</u>	<u>7.45</u>	<u>7.52</u>	_____
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>																																																												
Well Volume Purged (gal.)	<u>3</u>	<u>6</u>	<u>9</u>	<u>12</u>	<u>15</u>	<u>18</u>	_____																																																												
Turbidity	<u>3</u>	<u>10</u>	<u>4</u>	<u>4</u>	<u>1</u>	<u>0</u>	_____																																																												
Odor	<u>None</u>	<u>None</u>	<u>slight</u>	<u>slight</u>	<u>slight</u>	<u>slight</u>	_____																																																												
pH (units)	<u>6.54</u>	<u>6.71</u>	<u>6.71</u>	<u>6.72</u>	<u>6.72</u>	<u>6.73</u>	_____																																																												
Conductivity (umho)	<u>510</u>	<u>1.71</u>	<u>1.86</u>	<u>1.90</u>	<u>1.93</u>	<u>1.96</u>	_____																																																												
Water Temperature (deg. C)	<u>21.6</u>	<u>21.4</u>	<u>21.7</u>	<u>21.1</u>	<u>21.7</u>	<u>21.7</u>	_____																																																												
Depth to water (ft.)	<u>7.19</u>	<u>7.28</u>	<u>7.35</u>	<u>7.4</u>	<u>7.45</u>	<u>7.52</u>	_____																																																												
NOTES: 1 FT. LENGTH OF 4" Turbidity choices:		equals 0.087 ft or 0.65 gal. clear, turbid, opaque																																																																	
		1 ft. length 2" equals 0.022ft or 0.16 gal. Revision Date: 8/5/92																																																																	

FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCE\ 0656W00503															
PROJECT NAME: NAVAL BASE CHARLESTON (clean)		JOB NO: _____	DATE: 12-10-96														
WELL NO: NBCE\ 065-005		LOCATION: ZONE E															
WEATHER CONDITIONS: Sunny		AMBIENT TEMP: 55°															
REVIEWED BY: <i>[Signature]</i>		PERSONNEL: B. Horvath M. Fitchfield															
PURGING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously purged? NBCE\ 065-003		SAMPLING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously sampled? NBCE\ 065-003															
INITIAL WELL VOLUME Well diameter (in.) 2 Stickup (ft.) None Depth to bottom of well from TOC (ft.) 12.3 Depth to water surface from TOC (ft.) 4.72 Length of water (ft.) 7.58 Volume of water (ft.) _____ (gal.) 1.28 Amount of sediment at bottom of well (ft.) None 3 volumes of water (gal.) 3.86		PURGING <i>Went 12-10-96</i> Time started 1007 1007 Finished 1108 Volume purged 4.5 gal Comments on Well Recovery Poor Depth to water (ft.) 7.6 Completion - Additional Comments - Sample Collected: Start 1113 Finish 1135															
IN-SITU TESTING		Time: 1017 1025 1037 1049 1059 1148															
Well Volume Purged (gal.)		<table style="width:100%; text-align: center;"> <tr> <td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td> </tr> <tr> <td>.75</td><td>1.5</td><td>2.25</td><td>3</td><td>3.75</td><td>4.5</td><td></td> </tr> </table>		1	2	3	4	5	6	7	.75	1.5	2.25	3	3.75	4.5	
1	2	3	4	5	6	7											
.75	1.5	2.25	3	3.75	4.5												
Turbidity		<table style="width:100%; text-align: center;"> <tr> <td>31</td><td>46</td><td>21</td><td>11</td><td>.7</td><td>5</td><td></td> </tr> </table>		31	46	21	11	.7	5								
31	46	21	11	.7	5												
Odor		<table style="width:100%; text-align: center;"> <tr> <td>None</td><td>None</td><td>None</td><td>None</td><td>None</td><td>None</td><td></td> </tr> </table>		None	None	None	None	None	None								
None	None	None	None	None	None												
pH (units)		<table style="width:100%; text-align: center;"> <tr> <td>6.65</td><td>6.66</td><td>6.69</td><td>6.67</td><td>6.67</td><td>6.66</td><td></td> </tr> </table>		6.65	6.66	6.69	6.67	6.67	6.66								
6.65	6.66	6.69	6.67	6.67	6.66												
Conductivity (umho)		<table style="width:100%; text-align: center;"> <tr> <td>.719</td><td>.686</td><td>.741</td><td>.719</td><td>.712</td><td>.714</td><td></td> </tr> </table>		.719	.686	.741	.719	.712	.714								
.719	.686	.741	.719	.712	.714												
Water Temperature (deg. C)		<table style="width:100%; text-align: center;"> <tr> <td>17.4</td><td>18.1</td><td>17.9</td><td>18.8</td><td>19.3</td><td>19.3</td><td></td> </tr> </table>		17.4	18.1	17.9	18.8	19.3	19.3								
17.4	18.1	17.9	18.8	19.3	19.3												
Depth to water (ft.)		<table style="width:100%; text-align: center;"> <tr> <td>7.13</td><td>7.61</td><td>7.49</td><td>7.53</td><td>7.6</td><td>7.6</td><td></td> </tr> </table>		7.13	7.61	7.49	7.53	7.6	7.6								
7.13	7.61	7.49	7.53	7.6	7.6												
NOTES: 1 FT. LENGTH OF 4" Turbidity choices:		equals 0.087 ft or 0.65 gal. clear, turbid, opaque 1 ft. length 2" equals 0.022ft or 0.16 gal. Revision Date: 8/5/92															

FIGURE 6-1

Groundwater Sampling Form

Groundwater Sampling		Sample ID: NBCE\ 0656W0404	
PROJECT NAME: NAVAL BASE CHARLESTON (clean)		JOB NO: _____	DATE: 2-25-97
WELL NO: NBCE\ 065-004		LOCATION: ZONE E	
WEATHER CONDITIONS: Cloudy Rainy		AMBIENT TEMP: 55°F	
REVIEWED BY: J. Humphreys		PERSONNEL: Shannon M. Stephens	
PURGING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously purged? NBCE\ 065-005		SAMPLING DEVICE Type device? Peristaltic Pump How was the device decontaminated? Per CSAP How was the line decontaminated? Per CSAP Which well was previously sampled? NBCE\ 065-015	
INITIAL WELL VOLUME Well diameter (in.) 2 Stickup (ft.) None Depth to bottom of well from TOC (ft.) 12.47 Depth to water surface from TOC (ft.) 1.72 Length of water (ft.) 10.75 Volume of water (ft.) _____ (gal.) 1.8 Amount of sediment at bottom of well (ft.) None 3 volumes of water (gal.) 5.4		PURGING Time started 1102 Finished 1131 Volume purged 6 gal Comments on Well Recovery Excellent Depth to water (ft.) 3.14 3.14' Completion _____ Additional Comments _____ Sample Collected: Start 1135 Finish 1158	
IN-SITU TESTING		Time: 1107 1112 1116 1121 1126 1131	
Well Volume Purged (gal.)		1 2 3 4 5 6 7	
Turbidity		1 2 3 4 5 6 7	
Odor		None None None None None	
pH (units)		6.91 7.35 7.47 7.52 7.56 7.60	
Conductivity (µmho)		0.177 0.182 0.184 0.187 0.188 0.189	
Water Temperature (deg. C)		15.9 16.2 16.4 16.4 16.4 16.5	
Depth to water (ft.)		2.48 2.59 2.71 2.85 2.99 3.14	
NOTES: 1 FT. LENGTH OF 4" Turbidity choices:		equals 0.087 ft or 0.65 gal. clear, turbid, opaque	
		1 ft. length 2" equals 0.022R or 0.16 gal. Revision Date: 8/5/92	

ISSUE PAPER ON THE ENVIRONMENTAL CHEMISTRY OF METALS

DRAFT

Donald Langmuir,¹ Paul Chrostowski,²
Rufus Chaney,³ and Bernard Vigneault⁴

Submitted to:

U.S. Environmental Protection Agency
Risk Assessment Forum
1200 Pennsylvania Avenue, NW
Washington, DC 20460
Contract #68-C-98-148

Submitted by:

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110 Hartwell Avenue
Lexington, MA 02421

August 2003

¹Hydrochem Systems Corp./Colorado School of Mines, Golden, CO

²CPF Associates, Inc., Takoma Park, MD

³U.S. Department of Agriculture, Beltsville, MD

⁴CANMET Mining & Mineral Sciences Laboratories/
Natural Resources Canada, Ottawa, ON

NOTICE

This paper has been developed in support of an ongoing effort within the U.S. Environmental Protection Agency (EPA) to develop an integrated framework for metals risk assessment. In September 2002, the cross-Agency technical panel, organized under the auspices of the Agency's Science Policy Council, discussed plans for the development of the framework and associated guidance with the Agency's Science Advisory Board (SAB). During the advisory, the SAB affirmed the importance of incorporating external input into the Agency's effort. *As part of the effort to engage stakeholders and the scientific community and to build on existing experience*, the Agency commissioned external experts to lead the development of papers on issues and state-of-the-art approaches in metals risk assessment for several key topics. Topics identified include: environmental chemistry; exposure; ecological effects; human health effects; and bioavailability and bioaccumulation. (Some individual EPA experts contributed specific discussions on topic(s) for which he or she has either specific expertise or knowledge of current Agency practice). Although Agency technical staff, as well as representatives from other Federal agencies, reviewed and commented on previous drafts, the comments were addressed at the discretion of each respective author or group of authors. Therefore, the views expressed are those of the authors and should not be construed as implying EPA consent or endorsement.

This draft paper is being made available for public comment consistent with EPA's commitment to provide opportunities for external input. Science-based comments received on this paper will be made available to authors for final disposition. The material contained in this paper may be used in total, or in part, as source material for the Agency's framework for metals risk assessment and EPA's evaluation of this material will therefore include consideration of the Assessment Factors recently published by EPA for use in evaluating the quality of scientific and technical information. The draft framework, as an Agency document, will undergo scientific peer review by the SAB.

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ENVIRONMENTAL CHEMISTRY

1. INTRODUCTION

Metals and metalloids in the environment are of concern to almost all EPA programs. The Safe Drinking Water Act mandates maximum contaminant levels and maximum contaminant level goals for a variety of metals; the Clean Water Act mandates the development of ambient water quality criteria for the protection of human health and aquatic life against the potential toxic effects of metals; CERCLA requires that hazardous metals released into the environment be remediated to levels which do not pose an unacceptable risk to human health or the environment; and RCRA regulates the management of waste containing metals and metal compounds. To varying degrees, each of these programs relies on scientific information regarding the metals. For example, toxicity, bioavailability, bioaccumulation, and environmental fate and transport are all significant characteristics of metals that should be considered by EPA risk managers.

Over time, EPA has developed a paradigm for the assessment of the behavior and effects of organic compounds in the environment. Key elements of this framework are the fundamental principle of lipophilicity as a driving force for many environmental and exposure events, the significance of Henry's law for intermedia transfers, the degradability and potential for chemical transformation of a hazardous material, and the fact that most organics in the environment typically exist in one form.¹ With few exceptions (mainly for strongly covalent inorganic compounds or organo-metallics), metals do not exhibit these simplifying behaviors. In particular, although metals can undergo a variety of intermedia transfers and chemical reactions, they are indefinitely persistent and conservative in the environment. Possibly most important, the speciation, or chemical form, of a metal has a profound impact on its environmental behavior and effects.

The term "speciation" as used by many environmental chemists is poorly defined. Forstner (1995) refers to speciation as those aspects of metal chemistry including precipitation-dissolution, adsorption-desorption, and complex formation in relation to pH; redox conditions; and the content of soluble chelating agents. Bodek et al. (1988) identify a group of properties or processes that are important for the environmental behavior of metals, including volatilization, photolysis, sorption, atmospheric deposition, acid/base equilibria, polymerization, complexation, electron-transfer reaction, solubility and precipitation equilibria, microbial transformation, and diffusivity. For regulatory purposes, a functional definition might be more useful. Speciation may be defined functionally as those properties of an element that determine its environmental mobility, persistence, toxicity, bioavailability, bioaccumulation potential, or characterization as a regulated material.

¹ There are a few exceptions to this rule. Organic acids and bases can exist in ionized or neutral forms, and some organics exist as structural isomers (e.g., the hexachlorocyclohexanes).

The oxidation state of a metal is often a significant feature of its speciation due to its impact on other processes. The well-known example of the high mobility of Cr(VI) compared to Cr(III) demonstrates the significance of oxidation state. Toxicity depends both on the oxidation state and form of a metal (as cation or anion) and its tendency to form complexes with ligands. For example, the toxicity of As(III) to aquatic life is significantly different from the toxicity of As(V). Cr(VI) is considered a known human inhalation carcinogen, whereas Cr(III) is generally considered to have low human toxicity. Cupric ion is more toxic to fish than is the cupric carbonate complex. Dimethyl mercury is generally thought to be more toxic and to have a greater bioaccumulation potential than mercuric chloride.

Mobility is affected by a variety of factors. The ability of a metal to sorb to a substrate is usually the determining factor in its mobility. Physical adsorption—which is important for molecular organic compounds—is largely inapplicable to the sorption of the toxic trace metals, which are usually adsorbed as ionic species. Ion exchange, too, rarely applies, in part because of the relatively low concentrations of toxic metals compared to those of major ions. In fact toxic metal adsorption is often relatively independent of the concentrations of the major ions. Metal sorption is usually strongly pH-dependent and a function of metal complex formation and ionic strength. The most accurate and mechanistic approach to modeling and predicting metal adsorption is surface complexation modeling, which ideally can take into account all of these variables (cf. Stumm and Morgan, 1996; Langmuir, 1997a). Factors that are important to metal sorption in soils, aquifers, and sediments include:

Soil mineral composition	pH	Chemical identity
Specific surface areas of metal sorbing solids	Eh	Complexation chemistry
Surface site density or cation exchange capacity of metal sorbing solids	Dissolved oxygen	Solubility
Aeration status	Solute composition and concentrations (activities)	Precipitation chemistry
Microbial type, activity, and population	Dissolved organic carbon	Redox behavior
Organic matter content and character	Ionic strength	Vapor pressure
Temperature	Temperature	

The degree of mobility of organic contaminants is often expressed by means of a single partition coefficient that describes the extent of equilibrium between sorbed and dissolved forms of a compound (U.S. EPA, 1995). Mobility is then calculated from the partition coefficient. Such an approach is only applicable to metal adsorption when the conditions listed above are practically constant, which is rarely the case. In fact when metal adsorption is described using partition coefficients, the value of such coefficients typically needs to be varied by two or more orders of magnitude to reproduce metal adsorption behavior.

Human/animal bioavailability is the rate and extent of absorption of a xenobiotic chemical that enters the systemic circulation in the unaltered form from the exposure site (Hrudey et al., 1996). Bioavailability refers to a specific route of exposure—oral, inhalation, or dermal in the case of a human; oral, gill, or dermal in the case of a fish. Oral bioavailability varies with oxidation state, chemical form, and mineralogy. Inhalation bioavailability is strongly dependent on solubility and particle size. Uptake of metals by biota or bioaccumulation is important for determining concentrations and species of metals to which organisms can be exposed. EPA is typically interested in the biouptake of metals by aquatic life (including aquatic vegetation), terrestrial vegetation, terrestrial and avian wildlife, and farm animals. The concentration of a chemical in an organism is usually calculated by application of a bioconcentration factor or a transfer coefficient (U.S. EPA, 1998) that relates the concentration of a chemical in an organism to the concentration in its food. Sorption, solubility, oxidation state, chemical form, complexation, and competing chemical species are all important to the biouptake of metals.

In a few cases, metabolism may impact the speciation and subsequent fate and effects of a chemical at a given location in a food chain. For example, fish are capable of metabolizing carcinogenic inorganic arsenic to non-carcinogenic forms (Nriagu, 1994). Various microorganisms are capable of creating organic forms of mercury (e.g., methyl-, ethyl-) from inorganic mercury. The organic mercury forms are more toxic and better absorbed by animals than the inorganic forms (U.S. EPA, 1997).

Some regulatory programs rely heavily on chemical characterization. In SARA/CERCLA, the characterization of a material as a hazardous substance and the reportable quantity depend on metal speciation. For example, reportable quantities for nickel range from 1 pound for nickel carbonyl to 1,000 pounds for nickel hydroxide to 500 pounds for nickel chloride. The RCRA characteristic of toxicity is based on performance in a leaching test that is used to predict the mobility of a metal under specified laboratory conditions.

Thus, at least in theory, EPA needs to have methods, either analytical or mathematical, for evaluating and/or predicting dissolved vs. sorbed metals, oxidation states, solubility, complexation, and chemical form for a group of elements with widely diverse physicochemical and chemical properties.

EPA has published few standardized analytical protocols for metal species. Dissolved metals are often separated from sorbed metals by physical methods such as filtration or centrifugation. Environmental soil or sediment samples are typically analyzed for metal content in terms of total metals or total recoverable metals, often by atomic absorption or inductively coupled plasma spectroscopy following digestion in strong acid.

Methods exist for determining speciation of metals extracted from porous media, e.g., chromium speciation by the colorimetric diphenylcarbazide method (Method 3500 Cr-D in *Standard Methods for the Examination of Water and Wastewater* (APHA, 1992), and Method 7196A from *Test Methods for Evaluating Solid Waste*, SW-846 (U.S. EPA, 1996a) and by ion chromatography. A hot alkaline extraction technique for use as a sample preparation step with

colorimetric analysis of the extract has been developed to extract soluble and insoluble forms of Cr(VI) from soils, based on oxidation-reduction and solubility interactions of Cr (James et al., 1994 and 1995; James, 1994). Incomplete recovery of added Cr(VI) spikes and the oxidation of soluble Cr(III) spikes to Cr(VI) in certain soils have been suggested as deficiencies in older versions of this method (Vitale et al., 1994). The current modified version of this soil extraction method (Method 3060A) in the EPA method manual SW-846 has overcome the problem associated with the prior version of potentially converting Cr(III) to Cr(VI). New data indicate that the proper interpretation of the spike recovery information requires measurement of other soil chemistry parameters to learn whether the sample is reduced or contains materials which can reduce chromate. The newer hot alkaline extraction method (Method 3060A) for total Cr(VI) in soils and sediments selectively solubilizes Cr(VI) and can be used to aid in the interpretation of Cr(VI) spike recovery data (Vitale et al., 1997). Currently there is a joint effort among EPA, NJ DEP, and NIST to develop a standard reference material for Cr(VI) in soil/sludge.

EPA has identified three types of regulatory risk assessments where information regarding speciation of metals is useful and desirable: national hazard/risk ranking and characterization, site-specific assessments, and National Regulatory Assessments. National hazard or risk ranking assessments are typically used by EPA for broad priority setting. An example of this type of assessment is the Hazard Ranking System (HRS) used to determine the eligibility of a contaminated site for inclusion on the National Priorities List. Site-specific assessments are performed to determine if a site requires remediation and, if so, what the type and extent of remediation should be. A Superfund risk assessment is an example of this type of assessment. The third type, the National Regulatory Assessment, is typically used for standard setting. Development of ambient water quality criteria is an example of this type of assessment. These three examples will be used to illustrate the concepts of metal chemistry developed in this paper.

2. METALS OF CONCERN

Because of their abundance at contaminated sites and potential toxicity to plants or animals, the elements of concern are aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, molybdenum, nickel, selenium, silver, strontium, thallium, vanadium, and zinc. Phillips and Williams (1965) consider all of these elements to be metals, with the exception of arsenic and selenium, which are nonmetals. Webster's New World Dictionary (1968) defines a metal as an element that acts as a cation in chemical reactions, forms a base with the hydroxyl radical, and can replace the hydrogen of an acid to form a salt. Unlike the other elements listed, antimony, arsenic, molybdenum, selenium, and vanadium generally occur as oxyanions in waters and soils, and not as cations. These elements are sometimes described as metalloids. Regardless, in following discussion for simplicity all of the elements listed above are termed metals.

3. NATURAL OCCURRENCE OF METALS IN THE ENVIRONMENT

For reasons that may be unrelated to human activity, many surface and ground waters contain natural concentrations of metals that exceed the EPA drinking water standards (cf.

Runnells et al., 1992). Soils can also contain naturally elevated levels of metals (cf. McBride, 1984; Salminen and Tarvainen, 1997). When a regulatory decision is made to restore affected waters or soils to a presumed earlier state, it is obviously unrealistic to assign clean-up goals that are below preexistent metal levels. It is critically important therefore, to attempt to distinguish between metal amounts that were naturally present and amounts added as a result of human activities.

3.1 Baseline and Background Metal Concentrations

It is useful to introduce two concepts at this point. The first is that of geochemical baseline (cf. Salminen and Tarvainen, 1997; Salminen and Gregorauskiene, 2000), which may also be described as ambient concentration. This is the regional metal concentration in a medium, a concentration that has not been further increased by a local source of contamination. Baseline values may have been elevated by regional contamination. For example, arsenic concentrations in soils exceed 9 parts per million (ppm) in a 100-kilometer-wide, 1,000-kilometer-long belt that extends southwest from New York state across Pennsylvania, Ohio, and Kentucky (Gustavsson et al., 2001). There is evidence that these high arsenic values are chiefly derived from the burning of coal (Smith, 2003). An assessment of arsenic contamination of soils by a local source in this area would need to account for the high regional baseline values.

The second concept is that of background, which is the concentration of a metal in a medium as it existed before being affected by human activity. Background concentrations are a function of regional geology and local soil and sediment conditions. The metal background in soils also depends on the depth of the sampling (i.e., location within the soil profile) and whether the analysis is of the total soil or of a specific size fraction (cf. Salminen and Tarvainen, 1997). Metal concentrations are generally higher in the fine-grained fraction of soils than in the coarse fraction (sand fractions and medium/coarse silt fraction). It is important to note that baseline and background metal concentrations are not single values, but a distribution of values that can range over orders of magnitude over distances of a few centimeters in porous media and meters in surface waters (cf. Gustavsson et al., 2001).

3.2 Mean and Median Metal Concentrations

Though metal concentrations in the environment can range widely, it is still useful to consider their mean and median values in waters and soils and the Earth's crust (Table 1). Values for iron and sulfur are included in Table 1 for purposes of comparison and later reference. It is often assumed that species present in water at less than 1 milligram per liter (mg/L) but more than 1 microgram per liter ($\mu\text{g/L}$) are minor species, while those present at below 1 $\mu\text{g/L}$ are termed trace species (Langmuir, 1997a). Based on these definitions, most of the metals of concern are minor species and some are trace species, particularly in surface waters which are in general more dilute than soil or ground waters.

Median ground water concentrations of metals and major species (>1 mg/L) given in Tables 2a and 2b, do not differ much from the median metal values for surface and ground waters in Table 1, or the averages for major species in Table 3. Average and median values can

be deceiving given the wide variability of metal concentrations in waters, soils, and rocks. Shown in Figures 1 and 2 are plots of the cumulative percentages of some major, minor, and trace constituents in surface and ground waters. The data for trace metals, which are most complete for ground waters (see Table 2b), show that their concentrations range over 2 to 6–7 orders of magnitude in the case of As, Cd, Cu, and Zn.

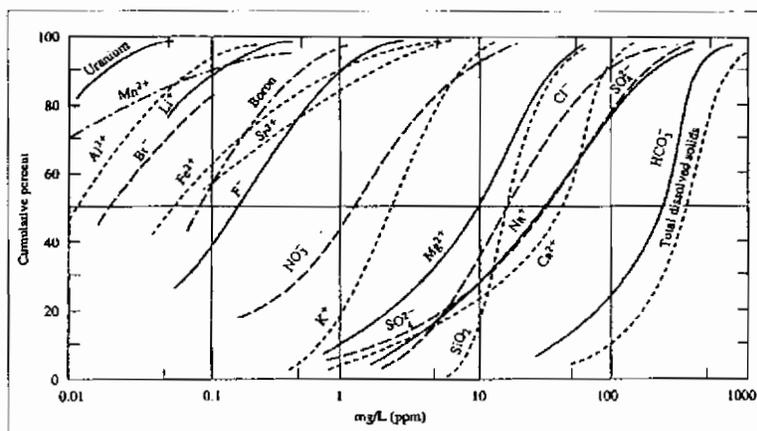


Figure 1. Cumulative percentages showing the frequency distribution of various constituents in potable (chiefly surface) waters. From Davis and DeWiest, 1966.

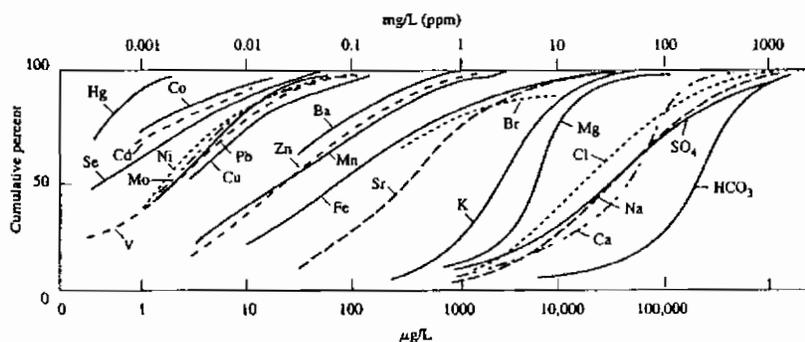


Figure 2. Cumulative percentages of some major and trace elements in ground waters. Number of analyses: 13,000 to 18,000 for major elements, 750 to 8,000 for trace elements. From Rose et al., 1979.

Although the data are limited for metals, their concentrations in soils are generally higher than in surface or ground waters, presumably because of concentration in soils by evapotranspiration and because of the relatively high solid to water ratio of soils. In recent years, methods of chemical analysis such as ICP-ES and ICP-MS have been adapted for the

determination of metals in soils and soil moisture. These methods have vastly lowered metal detection limits and improved the accuracy of analysis of trace metals at low concentrations. Shown in Table 4 is a chemical analysis of the metals of concern and some major elements in a Swedish Cambisol (Tyler and Olsson, 2001a). The soil has 8% organic matter, 10% clay, and a pH of 5.2. Metal concentrations were determined either by ICP-ES or ICP-MS.

Table 1. Median or Mean Concentrations of Some Metals and Related Elements in Natural Waters, Soils, and the Earth's Crust

Metal	Symbol	Surface and Ground Waters (medians)	World Rivers, Mean Dissolved (left) and Mean Suspended (right)		Ground Waters (mean detects)	Ground Waters (mean)	Soils (mean)	Earth's Crust (mean)
		(Turekian, 1977)	(Martin and Whitfield, 1983)		(U.S. EPA, 2002)	(Newcomb and Rimstidt, 2002)	(Shacklette and Boerngen, 1984)	(Fortescue, 1992)
		(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(mg/kg)	(mg/kg)
Aluminum	Al	10	50	94,000			72,000	83,600
Antimony	Sb	2	1	2.5	5		0.66	0.2
Arsenic	As	2	1.7	5	8	13.9	7.2	1.8
Barium	Ba	20	60	600	140	77	580	390
Beryllium	Be	5			2		0.92	2.0
Cadmium	Cd	0.03	0.02	1	1		0.35	0.16
Chromium	Cr	1	1	100	7	4.4	54	122
Cobalt	Co	0.1	0.2	20		4.3	9.1	29
Copper	Cu	3	1.5	100		70.6	25	68
Iron	Fe	100	40	48,000			26,000	62,200
Lead	Pb	3	0.1	100		2.6	19	13
Manganese	Mn	15	8.2	1050			550	1,060
Mercury	Hg	0.07			2		0.09	0.086
Molybdenum	Mo	1.5	0.5	3			0.97	1.2
Nickel	Ni	1.5	0.5	90		11.5	19	99
Selenium	Se	0.4			5	2.5	0.39	0.050
Silver	Ag	0.3	0.3	0.07		0.5	0.05	0.08
Strontium	Sr	400	60	150			240	384
Sulfur	S	20.6 ^a						340
Thallium	Tl				6		0.2 ^b	0.72
Vanadium	V	2	1	170		12.5	80	136
Zinc	Zn	20	30	250		265	60	76

^aU.S. EPA (2002a), occurring as sulfate.

^bBowen, 1979.

Table 2a. Median Concentrations of Metals and Other Species in Ground Waters of the United States

Species	Median (µg/L)	Species	Median (mg/L)
Ba	<30	Na	30
Cd	<1	K	3
Co	<1	Mg	6
Cu	2.5	Ca	45
Fe	80	Cl	15
Hg	<0.3	SO ₄	30
Mo	1.5	HCO ₃	200
Mn	20	TDS (sum)	329
Ni	0.15	Specific conductance	700 µS
Pb	2		
Se	0.25		
Sr	350		
V	2		
Zn	20		

This table is based on 13,000 to 18,000 analyses for major species, and 750 to 8,000 analyses for trace species. Data are from Rose, 2003. The same data are the basis of Figure 2 from Rose et al., 1979.

Table 2b. Sample Population Distribution Parameter Estimates for Trace Elements Dissolved in Ground Water

Element	No. of Records	% Below Detection	Correl. Coef.	Min.	Max.	Mean	Median
Antimony	1893	94	92	0.2	44	-	-
Arsenic	7199	53	95	0.03	42,600	13.9	1.4
Barium	9957	6	99	1.0	5,000	77	35
Beryllium	5550	94	90	0.03	10	-	-
Cadmium	7088	90	96	0.02	19,200	-	-
Chromium	9097	76	90	0.5	3,800	4.4	1.0
Copper	9582	70	90	0.1	74,000	70.6	1.1
Lead	9061	76	97	0.1	2,020	2.6	0.3
Mercury	2031	91	92	0.02	7.3	-	-
Nickel	8460	70	97	1.0	10,300	11.5	2.0
Selenium	4674	81	95	1.0	186	2.5	0.2
Silver	9528	87	95	0.04	139	0.5	0.2
Thallium	670	90	88	0.02	60	-	-
Vanadium	4498	80	96	0.4	19,000	12.5	1.1
Zinc	9464	40	94	0.09	633,000	265	5.7

This table is based on 104,280 dissolved-fraction ground water concentration records for samples obtained in 1996–1998 from the STORET database (U.S. EPA, 2000). Concentrations are in µg/L.

From Newcomb and Rimstidt, 2002. Robust data analysis techniques (Helsel, 1990; Helsel and Hirsch, 1992) were used to determine central value estimates and variables in sample populations with <90% censored (below detection) data. See discussion in Newcomb and Rimstidt, 2002.

Table 3. Fe, Al, and Major Constituents (>1 mg/L) or Parameters in Some Surface and Ground Waters

Constituent or Parameter	Average River, World ^a	Average River, N. America ^a	Average Ground Water, World ^b
Na ⁺	6.3	9	30
K ⁺	2.3	1.4	3
Mg ²⁺	4.1	5	7
Ca ²⁺	15	21	50
Fe	0.67	0.16	
Al	0.07		
Cl ⁻	7.8	8	20
NO ₃ ⁻	1	1	
HCO ₃ ⁻	58.4	68	200
SO ₄ ²⁻	11.2	20	30
SiO ₂ (aq)	13.1	9	16
pH			7.4
TDS	120	142	350

^aLivingstone, 1963.

^bTurekian, 1977.

Table 4. Metals in an Acid Cambisol (10% Clay) Formed on a Mixed Shale-Gneiss Moraine in Southern Sweden: Metal Concentrations in Dried Soil and in Soil Solution (pH = 5.2)

	Dried Soil ($\mu\text{g}/\text{kg}$)	Soil Solution ($\mu\text{g}/\text{L}$)
Ag	0.88	0.1
Al	75,500	297
As	65.9	3.2
Ba	646	132
Be	3	0.025
Cd	0.72	0.36
Co	7.72	0.4
Cr	66	1.3
Cu	142	59
Hg	0.16	0.13
Mn	231	66
Mo	93.1	5.7
Ni	11.4	11
Pb	43.9	2.4
Sb	0.4	0.86

	Dried Soil ($\mu\text{g}/\text{kg}$)	Soil Solution	
		$\mu\text{g}/\text{L}$	mg/L
Se	1.74	1.7	
Sr	73.6	77	
Tl	3.9	0.15	
V	815	7.2	
Zn	63	90	
Ca	1,620	27,300	27
Fe	50,800	280	0.28
K	25,000	6,800	6.8
Mg	2,750	2,170	2.2
Na	170	4,550	4.6
P	527	119	0.12
S	4,938	23,900	23.9
C (org)	80,000		45

From Tyler and Olsson, 2001b.

Table 5. U.S. Environmental Protection Agency (2002b) Drinking Water Standards for Select Inorganic Species in Community Water Supplies

Contaminant	MCL($\mu\text{g/L}$)	Note	Contaminant	SMCL ($\mu\text{g/L}$)	Note
Antimony	6	a	Aluminum	50 to 200	a
Arsenic	10	a	Iron	300	a
Barium	2,000	a	Manganese	50	a
Beryllium	4	a	Silver	100	a
Cadmium	5	a	Copper	1,000	a
Copper	1,300	b	Uranium	30	a
Chromium	100	a	Zinc	5,000	a
Lead	15	b			
Mercury	2	a			
Nickel	100	a			
Selenium	50	a			
Thallium	2	a			

Maximum contaminant levels (MCLs) are enforceable standards for substances that may constitute a health hazard at higher concentrations. Secondary maximum contaminant levels (SMCLs) are not enforceable, but are set for aesthetic reasons, to avoid tastes, odors, and staining of plumbing fixtures.

^aCurrent standard.

^bTreatment triggered at 1.3 mg/L Cu and 0.015 mg/L Pb.

It is instructive to compare U.S. EPA drinking water standards for inorganic species in water supplies (Table 5) to the average concentrations of the same species in surface and ground waters (Table 1). The comparison shows that: (1) the median concentration of Be exceeds the drinking water standard; (2) median concentrations of As and Pb are 20% of the standard; and (3) Sb is 33% of the standard. This suggests that a large percentage of background waters will have natural concentrations of these metals that exceed drinking water standards.

3.3 General Sources of Metals Data and Maps

The U.S. Environmental Protection Agency, the U.S. Geological Survey of the Department of Interior, and the Department of Energy have all compiled extensive databases of chemical analyses of various environmental media that are readily available on CD-ROM or for downloading from the World Wide Web. EPA's STORET (STORage and RETrieval) data system, which can be accessed at <http://www.epa.gov/storet/>, contains 200 million water samples.

observations from about 700,000 sampling sites for both surface and ground waters. Reported data include stream flow information and measured concentrations for most of the metals of concern. There is no requirement that the data in STORET be evaluated using quality assurance procedures, however. For the data from STORET, or from the other sources listed below, it is important that prospective users be aware that such data may or may not have been screened for accuracy.

The U.S. Geological Survey Water Web site (<http://waterdata.usgs.gov/nwis>) provides access to chemical and physical records for 1.5 million sampling sites in all 50 states, the District of Columbia, and Puerto Rico as part of the National Water Quality Assessment Program (NAWQA). A stated goal of NAWQA is “to describe the status and trends in the quality of a large representative part of the Nation’s surface and ground-water resources and to identify the natural and human factors that affect their quality.” Available through the Web site are chemical analyses and physical data for streams, stream sediments, lakes, springs, and wells that include their metals concentrations. A map of arsenic in 31,350 samples of ground water in the contiguous United States based on Welch et al. (2000) is featured on the Web site. As part of the NAWQA program, Rice (1999) reported on the concentrations of As, Cd, Cr, Cu, Pb, Hg, Ni, Se, and Zn in 541 streambed samples obtained from across the conterminous United States. In the analysis she takes into account background and baseline metal concentrations.

The USGS also maintains the National Geochemical Data Base (NGDB), which contains more than 2 million data records for samples of stream sediment, soil, rocks, water, and vegetation. This database is also accessible via the Web. The NGDB includes approximately 260,000 sediment and soil samples collected by the U.S. DOE in the 1970s and 1980s as part of the National Uranium Resource Evaluation (NURE) program. Most of the soil, sediment, and rock samples from which the NGDB was generated are held in archival storage and are available for further study. Data in the NGDB are available on CD-ROM, and can be used to generate metal concentration maps, so as to help determine metal baseline and background concentrations and contamination levels. The Geological Survey also maintains the PLUTO.RASS database, which lists geochemical data for about 500,000 samples—chiefly rocks, but also stream sediments, soils, heavy-mineral concentrates, waters, and vegetation.

A number of national surveys of metals concentrations in soils have been published. The most famous and still useful was that of Boerngen and Shacklette (1981) and Shacklette and Boerngen (1984), which involved collecting soil and other regolith samples from 1,323 sites in the conterminous United States. Samples were obtained at a depth of 20 centimeters from untilled, naturally vegetated soils away from roads in the period 1961–1975. The results of Shacklette and Boerngen have been reviewed and statistically assessed by Gustavsson et al. (2001), who present colored national maps for Al, As, Ba, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sr, V, and Zn among other metals. Metals in soils results from the U.S. study of Shacklette and Boerngen (1984) are included in an assessment of metals and other elements in soils worldwide in a report by Darnley et al. (1995).

Detailed soil survey maps are available from the offices of the USDA/ARS Natural Resources Conservation Service (formerly the U.S. Soil Conservation Service). These generally

include areal maps that show soil types and classifications by county, along with the pH and organic matter contents of typical soil types. The soil surveys also describe soil associations and soil-forming processes for the soils within specific areas.

3.4 National and Regional Metals Problem Areas

In the section titled “General Sources of Metals Data and Maps,” a number of published and Web-accessible sources of metals data for streams, ground waters, and soils were cited. Of particular value to anyone identifying and prioritizing metal problems regionally or nationally are maps on which metals data for soils, sediments, and waters have been plotted and the metals concentrations contoured. Such maps have been published for soils, although they are based on limited data (see Gustavsson et al., 2001), but are less available for surface and ground waters. Welch et al. (2000) have published a map of arsenic in U.S. ground waters, and discuss geologic and climatic (e.g., evapotranspiration) controls on elevated arsenic values. David B. Smith of the U.S. Geological Survey maintains a national database of metals data for stream sediments and has colored regional maps of such data for Al, As, Ba, Be, Co, Cr, Cu, Mn, Hg, Ni, Pb, Se, Sr, V, and Zn for a large part of the U.S. (See <http://water.usgs.gov/osw/techniques/workshop/smith.html>.)

Dissolved metals in lower order streams, which are often fed by ground water, can be expected to correlate with local geology. However, metal concentrations in major rivers tend to be more affected by climate than local geology (cf. Langmuir, 1997a).

A comparison of maps for the metals with a geologic map of the United States often shows a correlation between local or regional geologic formations and metal levels in soils and ground waters. The correlations are most obvious in areas away from major urban and industrial centers, which have contributed important metal amounts to the environment through their waste disposal and land use practices. Colored national and state geological maps are available in digital form on the Web at <http://pubs.usgs.gov/dds/dds11/> and <http://nationalatlas.gov/geologym.html>.

Broad-scale soil survey data for the contiguous United States are available in the State Soil Geographic (STATSGO) database (cf. Schwarz and Alexander, 1995). Shirazi et al. (2001) developed mathematical models relating the soil characteristics of soil map units from the STATSGO to predict water quality parameters. They found that with statistical information on soil particle size distribution, they could estimate soil, lake, and stream water quality parameters including acid neutralizing capacity, pH, dissolved organic carbon, nitrate, and turbidity. Because such water quality parameters importantly influence the concentrations and mobility of the metals of concern, such soil information can be used to predict metal behavior.

3.5 Local Sources of Metals Data

In studies of localized environmental contamination by metals (e.g., as associated with a Superfund Site cleanup), it is especially important to define background and baseline metals concentrations, which will in some cases exceed health standards for aquatic life and drinking

water. If data and maps describing metal concentrations at a site prior to its contamination are not available, the preferred approach is to take water, soil, sediment, rock, or plant samples from a nearby area with similar characteristics, but that is unaffected by contamination as a measure of background (cf. Banks et al., 1995; Lahermo et al., 1995; Miller and McHugh, 1999). In populated and urbanized or extensively mined areas, however, it may be difficult to locate a sample that has not been contaminated. All that may be available are baseline values. A second approach to determine background for waters is to assume that background water quality is the same as that measured in similar streams or well waters in similar topographic, climatic, and geological settings. Lacking this information for ground waters, White et al. (1963) have summarized typical ground water compositions from different rock types that may be useful.

Perhaps the most defensible way to distinguish background or baseline concentrations and more elevated metal values in the waters of a given area is to use statistical analysis. Cumulative probability plots can be drawn onto which all of the concentration data for a metal is plotted (Levinson et al., 1987; Fleischhauer and Korte, 1990). Such plots may allow the classification of samples into a background or baseline group and one or more contaminated groups, with an estimate of the median and standard deviation for each group. Such a plot for Cd in ground waters of Front Range of Colorado is shown in Figure 3 (Langmuir and Klusman, 1997).

4. METAL SPECIATION: METAL COMPLEXES

Chemical analytical laboratories generally determine and report total metal concentrations. However, in recent years it has become increasingly apparent that metal toxicity is a function of the concentrations of specific metal species, not of the total metal (cf. Stumm and Morgan, 1996; Langmuir, 1997a). In fact, the chief toxicant is usually the free metal cation. In natural waters its concentration, or those of other toxic metal species, can sometimes be measured directly, although often with difficulty. Alternatively, given the appropriate solution analysis and thermodynamic database, the concentrations of individual species can be computed using a geochemical equilibrium modeling program such as MINTEQA2 (U.S. EPA, 1991) or PHREEQC (Parkhurst and Appelo, 1999). Unfortunately, MINTEQA2 is a DOS-based program and cannot be used on computers with Windows operating systems more recent than Windows 98. However, a Windows version of MINTEQA2 version 4.0 (1999), a program called Visual MINTEQ (VMINTEQ, version 2.14: Gustafson, 2003), is available and may be downloaded free of charge from the Web.

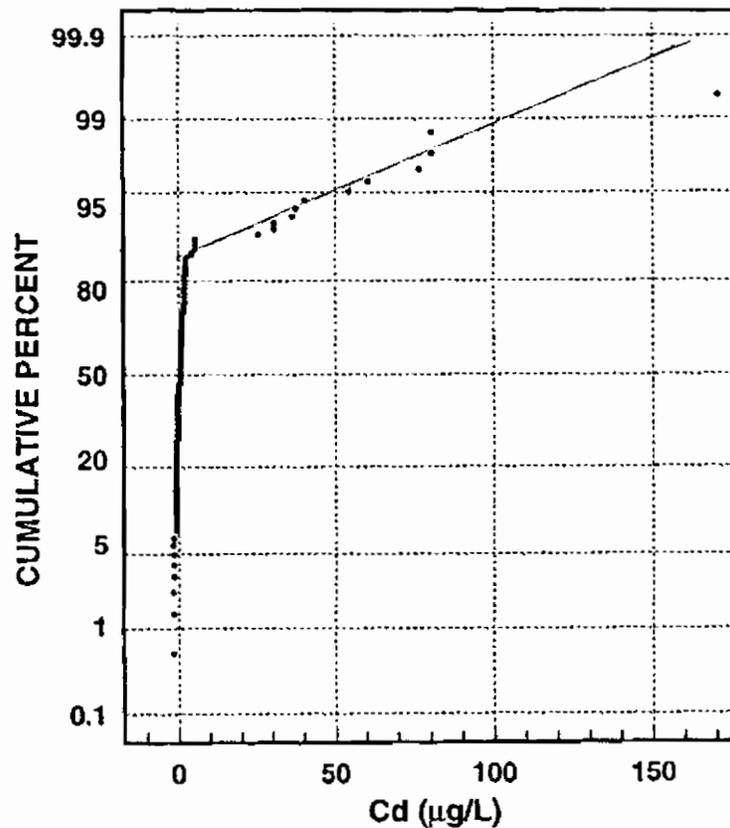


Figure 3. Cumulative percent plot of cadmium concentrations in Colorado Front Range ground waters. Concentrations below 10 µg/L are presumably background values. The linear trend of higher values can be derived from contamination. From Langmuir and Klusman, 1997.

4.1 Metal Complexes: Concepts and Importance

Dissolved species in water can be described as free ions or aquo-complexes, or simply complexes. A complex is a dissolved species that exists because of the association of a cation with an anion or neutral molecule (Langmuir, 1997a). A ligand is an anion or neutral molecule that can combine with a cation to form a complex. The total analytical concentration of a given metal in water is the sum of the concentrations of its free ion and complexes and any metal associated with suspended solids, whether organic or mineral. For example, the total molal concentration of lead, ΣPb , in a natural water might equal:

$$\Sigma\text{Pb} = m\text{Pb}^{2+} + m\text{PbOH}^+ + m\text{PbCO}_3^{\circ} + m\text{PbHCO}_3^+ + m\text{PbSO}_4^{\circ} + m\text{Pb}(\text{suspended solids}) \quad (1)$$

In most natural waters the concentration of free lead ion, $m\text{Pb}^{2+}$, is less than the sum of the concentrations of its complexes, which in this case are lead complexes with hydroxyl, carbonate, bicarbonate, and sulfate ions. Other metals that are found in natural waters most often as complexes and not as free ions include Al^{3+} , Ag^+ , Cu^{2+} , Fe^{3+} , and Hg^{2+} . The metalloids As and Se and the metals Cr, Mo, Sb, and V occur most often in aerobic waters and soils not as cations

but covalently bonded to oxygen in oxyanions that under oxidizing conditions include arsenate, selenate, chromate, molybdate, and vanadate, which themselves are complexes. Important chemical species (including metal complexes common in soils and waters at intermediate pH values) are listed in Table 6.

Complexes that incorporate metals play a major role in controlling the availability and fate of metals in the environment. Increasing the fraction of a metal that is complexed increases the solubility of minerals of that metal (Langmuir, 1997a). For example, the solubility of lead sulfate is related to the molal concentrations of free lead and sulfate ions, through the expression:

$$K_{sp} = [(\gamma_{Pb} \cdot m_{Pb^{2+}})(\gamma_{SO_4} \cdot m_{SO_4^{2-}})] \quad (2)$$

where the terms γ_{Pb} and γ_{SO_4} are the activity coefficients of the ions.² The product of the ion activity coefficient and molal concentration of each species equals the activity of the ion. Equation 2 shows that the activity of free lead ion controls the solubility of lead sulfate. For a given total lead concentration (Equation 1), the more of the lead that is complexed, the lower will be the concentration of free lead ion. This means that as the extent of lead complexing increases, the total lead concentration must also increase in order to reach saturation with lead sulfate. In other words, metal complexing increases total metal solubility.

Metal complexing also has a direct influence on metal adsorption to organic matter or mineral surfaces. For example, metal carbonate, sulfate, and fluoride complexes are usually poorly adsorbed, whereas metal hydroxide complexes are strongly adsorbed (Langmuir, 1997a). In summary, metal complexing generally increases the solubility and mobility of metals in surface and ground waters.

4.2 Hard and Soft Acids and Bases: The Stability of Complexes and Metal Toxicity

Complexes are formed between metals (acids) and ligands (bases) both in solution and at the surfaces of minerals and of organisms. Toxic reaction of organisms to metals can be directly related to the nature of the metal complexes formed in solution and at the surface of the organism.

² By definition, the product of the activity coefficient and the molal (or molar) concentration for an ion, i , is equal to the activity (a_i) of that ion. That is: $a_i = \gamma_i \cdot m_i$. Activity coefficients of ions are generally less than one in fresh waters, and decrease with increasing salinity or ionic strength (cf. Stumm and Morgan, 1996; Langmuir, 1997a). The activity of an ion can be considered its effective concentration in water.

Table 6. Dominant Chemical Species of Metals in Soils and Natural Waters, Not Considering Most (Especially Weak) Metal Complexing

Metal	Soils	Waters	Most Toxic Species
Ag	Ag^+	Ag^+ , AgCl	Ag^+
As	AsO_4^{3-}	AsO_4^{3-} , AsO_3^{3-}	AsO_3^{3-}
Ba	Ba^{2+}	Ba^{2+}	Ba^{2+}
Be	Be^{2+} , $\text{Be}_x\text{O}_y^{2x-2y}$	Be^{2+}	Be^{2+}
Cd	Cd^{2+}	Cd^{2+}	Cd^{2+}
Co	Co^{2+}	Co^{2+}	Co^{2+}
Cr	Cr^{3+}	CrO_4^{2-} , Cr^{3+}	CrO_4^{2-}
Cu ^a	Cu^{2+} , Cu-OM^b	Cu^{2+} , -fulvate	Cu^{2+}
Hg	Hg^{2+} , CH_3Hg	Hg(OH)_2^0 , HgCl_2^0	CH_3Hg
Mn	Mn^{4+} , Mn^{2+}	Mn^{2+}	Mn^{2+}
Mo	MoO_4^{2-}	MoO_4^{2-}	MoO_4^{2-}
Ni	Ni^{2+}	Ni^{2+}	Ni^{2+}
Pb	Pb^{2+}	Pb(OH)^+	Pb^{2+}
Sb	$\text{Sb}_{\text{III}}\text{O}_x?$	Sb(OH)_6^-	?
Se	SeO_4^{2-} , HSeO_3	SeO_4^{2-}	SeO_4^{2-}
V	$\text{V}_{\text{IV}}\text{O}_x?$	HVO_4^{2-}	?
Zn	Zn^{2+}	Zn^{2+}	Zn^{2+}

Modified after Logan and Traina, 1993.

^aTypically, much or most of Cu in soils is complexed with organic matter.

^bCu-OM denotes copper complexed with organic matter.

A useful definition that helps to explain the strength of metal complexing and metal toxicity is that of hard and soft acids and bases (Pearson, 1973). In this definition, cations are Lewis acids and ligands Lewis bases, with the metal cation and ligand in a complex acting as electron acceptor and donor, respectively. Soft implies that the species' electron cloud is deformable or polarizable with the electrons mobile and easily moved. Such species prefer to participate in covalent bonding. Hard species are comparatively rigid and nondeformable, have low polarizability, hold their electrons firmly, and prefer to participate in ionic bonds in complex formation (Langmuir, 1997a). Hard acids form strong, chiefly ionic bonds with hard bases, whereas soft acids and soft bases form strong, chiefly covalent bonds when they form complexes. In contrast, the bonds formed between hard-soft or soft-hard acids and bases are weak, such that their complexes tend to be rare. Table 7 summarizes hard and soft acid and base relationships for the metals of concern. Its footnotes summarize the applicability of hard and soft concepts to the formation of metal complexes.

Table 7. Hard and Soft Acids (Cations) and Bases (Ligands)

Hard acids	Al^{3+} , Ba^{2+} , Be^{2+} , Co^{3+} , Cr^{3+} , Fe^{3+} , Mn^{2+} , Sr^{2+} , U^{4+} , UO_2^{2+} , VO^{2+}
Borderline acids (between hard and soft)	Co^{2+} , Cu^{2+} , Fe^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}
Soft acids	Ag^+ , Cd^{2+} , Cu^+ , Hg^{2+} , Hg^+ , CH_3Hg^+ , Tl^{3+} , Tl^+
Hard bases	F^- , H_2O , oxyanions: OH^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , $\text{C}_2\text{O}_4^{2-}$, CrO_4^{2-} , MoO_4^{2-} , $\text{H}_n\text{PO}_4^{n-3}$, $\text{H}_n\text{AsO}_4^{n-3}$, SeO_4^{2-} , H_2VO_4^- , NH_3 , RNH_2 , N_2H_4 , ROH , RO^- , R_2O , CH_3COO^- , etc.
Borderline bases (between hard and soft)	Cl^- , Br^- , NO_2^- , SO_3^{2-} , $\text{H}_n\text{AsO}_3^{n-3}$, $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_5\text{H}_5\text{N}$, N_3^- , N_2
Soft bases	I^- , HS^- , S^{2-} , CN^- , SCN^- , Se^{2-} , $\text{S}_2\text{O}_3^{2-}$, $-\text{SH}$, $-\text{SCH}_3$, $-\text{NH}_2$, R^- , C_2H_4 , C_6H_6 , RNC , CO , R_3P , $(\text{RO})_3\text{P}$, R_3As , R_3S , RSH , RS^-

Modified after Huheey et al., 1993, and Langmuir, 1997a. "R" refers to an organic molecule.

Hard acids and hard bases. Complexes formed between divalent hard acid cations and monovalent or divalent hard bases are ionic and relatively weak, and are often termed "ion pairs." Complexes formed between Be^{2+} or trivalent hard acids, and hard bases tend to be ionic and relatively strong.

Soft acids and soft bases. Strong, relatively covalent bonds are formed in complexes between soft and borderline soft acid cations and soft bases. Ligand binding sites on the external or internal surfaces of organisms are often of soft base character, and so bond strongly with soft and borderline soft acid cations.

The Lewis acids in natural waters include H^+ and metabolically essential metal cations such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} , and the toxic metal species Hg^{2+} , CH_3Hg^+ , Pb^{2+} , and Cd^{2+} , which are soft acids. These species, along with the soft acid thallium (Tl) and the essential protein and enzyme metals Fe^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} , which are borderline soft, form strong bonds with soft base sulfur species. The ligands at the surfaces of biota are chiefly sulfur, nitrogen and oxygen electron donor groups, and also include the solute bases HCO_3^- , HPO_4^{2-} , and OH^- (Stumm and Morgan, 1996).

Although the hard acid metals Ca, Mg, and Na bond weakly with soft base sites on the surfaces of biota, their concentrations in most waters are typically 10^3 times greater than those of the toxic metals, so that they often effectively compete with toxic metals such as Zn^{2+} and Cd^{2+} for surface bonding sites. However, when metal adsorption is by organic matter, metals such as Cu^{2+} in particular may be strongly adsorbed, practically independent of concentrations of the major metals (cf. Lu and Allen, 2002).

The proton is the most effective competitor of all with adsorbed metals. The proton can displace essential and toxic metals from surface sites at pH values as high as 6. The role of pH as a fundamental control on metal concentrations and metal transport is discussed extensively below.

Toxicity to plants is termed phytotoxicity. Shown in Table 8 from Sposito (1989) are observed toxicity sequences for some plants. For each class of plants, the metal order from left to right in Table 8 reflects the increasing metal concentration in moles per cubic meter required to produce a substantial toxic effect, with the smallest concentration associated with the most toxic metal. Soft-acid cations, Hg(II), Ag(I), and Cd(II), are generally the most toxic of the metals. Close behind are the borderline hard-soft-acid metal cations. The only toxic hard metal cations are Cr(III) and Mn(II). Although not listed in Table 8, in poorly buffered soils affected by acid rain, hard acid Al(III) presents a serious toxicity problem to plants (Bohn et al., 1985).

Mechanisms by which toxic metals poison plants and animals relate to their tendency to form strong complexes with the generally soft functional groups on biomolecules (cf. Sposito, 1989; Morel and Herring, 1993). Sposito (1989) proposes several processes by which soft-metal cations cause phytotoxicity. First, a soft metal such as Cd can displace an essential metal such as Ca bound to a bioligand. Also, complexation of a bioligand by a soft-metal cation can block that ligand from reacting normally or modify it structurally and thus interfere with its intended activity. Enzymes have active or catalytic sites with which they bind to biological substrates and that facilitate enzyme function. These sites are especially vulnerable to damage by soft-metal cations. The amino acids cysteine and methionine present at the active sites in some enzymes contain $-SH$ and SCH_3 groups (Manahan, 1994). These sulfur-containing groups are soft ligands and form strong covalent bonds with soft-metal cations such as Hg, Ag, Cd, Cu, and Pb. Such bond formation can result in the breakdown of normal enzyme function and a toxic reaction by the affected organism.

Table 8. Representative Sequences of Toxicity Threshold Concentrations Within Plants

Organisms	Sequence of Decreasing Toxicity
Algae	Hg > <i>Cu</i> > Cd > <i>Fe</i> >Cr> <i>Zn</i> >Co>Mn
Flowering plants	Hg > <i>Pb</i> > <i>Cu</i> > Cd >Cr> <i>Ni</i> > <i>Zn</i>
Fungi	Ag > Hg > <i>Cu</i> > Cd >Cr> <i>Ni</i> > <i>Pb</i> >Co> <i>Zn</i> > <i>Fe</i>
Phytoplankton (freshwater)	Hg > <i>Cu</i> > Cd > <i>Zn</i> > <i>Pb</i>

Modified after Sposito, 1989.

Metals in bold are soft acids. Italicized metals are borderline hard-soft acids. Cr(III) and Mn(II) are hard acids. Hg = Hg(II), Fe = Fe(II), Cr = Cr(III), Co = Co(II), Mn = Mn(II), Pb = Pb(II).

4.3 Predominant Inorganic Species in Fresh Waters

It is instructive to compute the distribution of dissolved metal species including their complexes in a typical natural water. Such computations are readily accomplished using a geochemical computer code such as MINTQA2 (U.S. EPA, 1991). Stumm and Morgan (1996) discuss such a calculation for an oxygenated fresh water with a pH of 8.0 that has the following total concentrations: Na = 5.7 mg/L, Mg = 73 mg/L, Ca = 40 mg/L, Cl = 8.9 mg/L, SO₄ = 29 mg/L, and HCO₃⁻ = 122 mg/L. Aqueous speciation for the metals of concern is given in Table 9. Also shown is the percentage of the metal present as the free ion, which in most cases is the percentage of the total metal present in toxic form. Note that at pH 8, Al, Be, Cu, Fe(III), Hg, Ni, Pb, Tl, and Zn are chiefly present as complexes.

The anionic species of As, Cr, Mo, Se, and V generally form weak complexes with monovalent or divalent cations, but may be precipitated as minerals by high concentrations of dissolved Fe(III) and Al(III), which are generally present only in acid systems.

4.4 Effect of pH on Metal Complexing

Sulfate, phosphate, fluoride, and strong organic complexes of metal cations (e.g., citrate and EDTA) tend to be important in acid waters (cf. Langmuir, 1997a), whereas carbonate and hydroxide complexes become increasingly important at pH values above 6–8. This is evident from Figure 4, which shows the concentrations of species of Pb and Zn as a function of pH, as computed with a geochemical model for the same concentrations used to derive Table 9. Total lead and zinc concentrations assumed for these figures are 10⁻⁹ M (0.2 µg/L) for lead and 10⁻⁸ M (0.65 µg/L) for zinc. As the salinity and thus chloride content of water increases, the borderline soft chloride ion forms important complexes with the soft and borderline soft metal cations Ag⁺, Cd²⁺, Hg²⁺, Ni²⁺ and Zn²⁺.

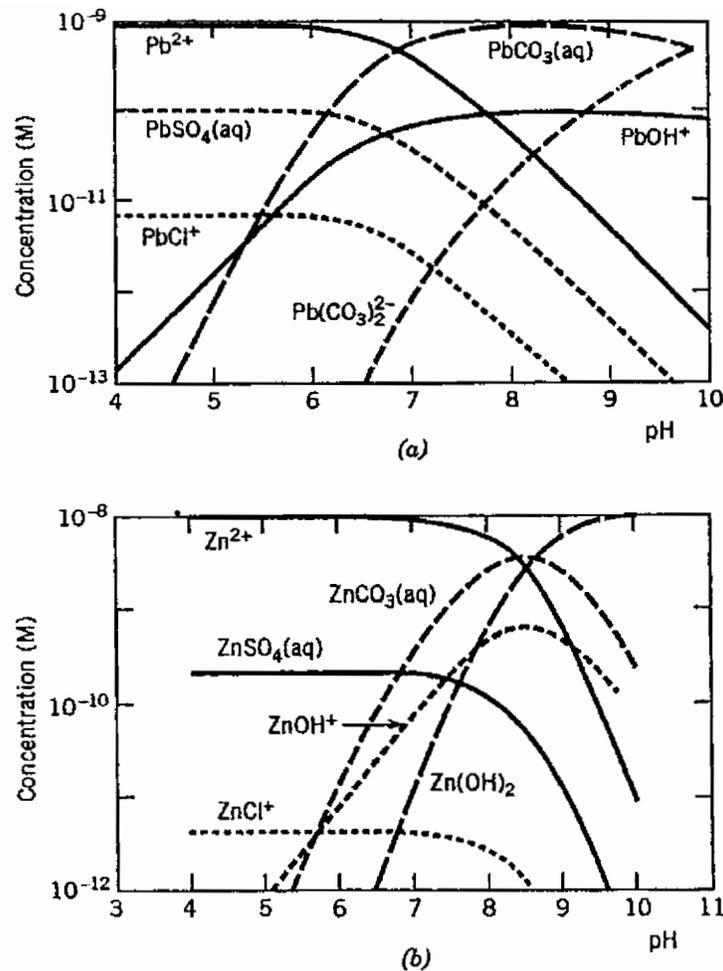


Figure 4. Speciation of Pb(II) (10^{-9} M) and Zn(II) (10^{-8} M) under freshwater conditions. Total carbonate equals 2×10^{-3} M. Figure is computed. From Stumm and Morgan, 1996.

Several milligrams of dissolved organic carbon (DOC) per liter of soil solution is common in humid climate soils. The DOC is composed of humic substances, which include humic and fulvic acids. These acids form metal complexes under the same pH conditions that favor metal carbonate and hydroxide complexes (Stumm and Morgan, 1996). Metal bonding is with carboxylic and phenolic hydroxyl groups of the acid anions. Shown in Figure 5 is the effect of increasing pH and total copper on the extent of copper-fulvic complexing. Free Cu^{2+} ion concentrations can be seen to decrease with increasing DOC and increasing pH in the presence of Suwannee River fulvic acid. Increasing DOC should thus reduce the toxicity of a given concentration of dissolved Cu^{2+} or other toxic metal that forms fulvic acid complexes.

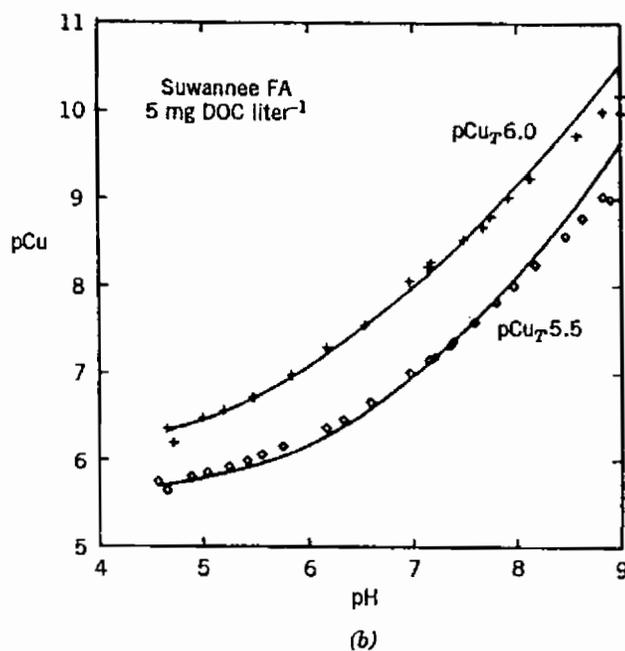
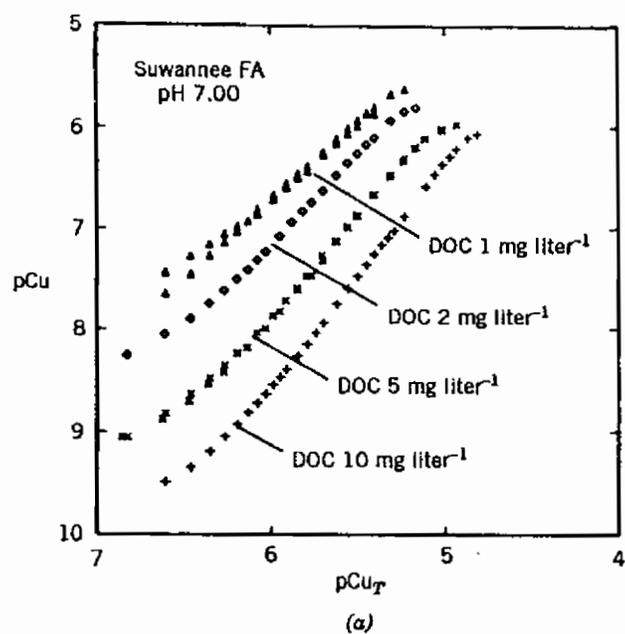


Figure 5. Titrations of fulvic acid (FA) and copper. (a) shows dissolved Cu^{2+} ion concentration as pCu ($-\log \text{Cu} [\text{mol/L}]$), plotted as a function of total copper ($[\text{Cu}]_T$) for different fulvic concentrations at pH 7. (b) shows pCu as a function of pH for two total copper concentrations. From Cabaniss and Shuman, 1988.

Table 9. Major Inorganic Species in an Hypothetical Natural Water (see text)

Condition	Metal/ Element	Major Species	Percent as Free Metal Cation
Hydrolyzed, anionic	As(V)	HAsO_4^{2-}	
	Cr(VI)	CrO_4^{2-}	
	Mo(VI)	MoO_4^{2-}	
	Se(VI)	SeO_4^{2-}	
	V(V)	$\text{HVO}_4^{2-}, \text{H}_2\text{VO}_4^-$	
Predominantly free aquo-ions	Na^+	Na^+	100
	K^+	K^+	100
	Mg^{2+}	Mg^{2+}	94
	Ca^{2+}	Ca^{2+}	94
	Sr^{2+}	Sr^{2+}	94
	Ba^{2+}	Ba^{2+}	95
Complexed with OH^- , CO_3^{2-} , HCO_3^- , Cl^-	Ag(I)	$\text{Ag}^+, \text{AgCl}^0$	60
	Al(III)	$\text{Al}(\text{OH})_3(\text{s}), \text{Al}(\text{OH})_2^+, \text{Al}(\text{OH})_4^-$	1×10^{-7}
	Be(II)	$\text{BeOH}^+, \text{Be}(\text{OH})_2^0$	0.15
	Cd(II)	$\text{Cd}^{2+}, \text{CdCO}_3^0$	50
	Co(II)	$\text{Co}^{2+}, \text{CoCO}_3^0$	50
	Cu(II)	$\text{CuCO}_3^0, \text{Cu}(\text{OH})_2^0$	2
	Fe(III)	$\text{Fe}(\text{OH})_3(\text{s}), \text{Fe}(\text{OH})_2^+, \text{Fe}(\text{OH})_4^-$	2×10^{-9}
	Hg(II)	$\text{Hg}(\text{OH})_2^0$	1×10^{-8}
	Mn(IV)	$\text{MnO}_2(\text{s})$	
	Ni(II)	$\text{Ni}^{2+}, \text{NiCO}_3^0$	40
	Pb(II)	PbCO_3^0	5
	Tl(I), Tl(III) ^a	$\text{Tl}^+, \text{Tl}(\text{OH})_3, \text{Tl}(\text{OH})_4^-$	2×10^{-19}
Zn(II)	$\text{Zn}^{2+}, \text{ZnCO}_3^0$	40	

The right-hand column is the percent of the total metal concentration present as the free metal cation. Based on Stumm and Morgan (1996).

^aRedox state of Tl(I) under natural conditions is uncertain; ratio is for Tl(III).

5. ADSORPTION CONTROLS ON METAL CONCENTRATIONS AND MOBILITIES

5.1 Introduction

Except for Al and sometimes Mn, concentrations of toxic metals in the environment are generally too low for those metals to exceed the solubility products of their pure metal solids and thus to precipitate. Instead, *toxic metal concentrations are generally limited by sorption onto the surfaces of minerals, and onto organic matter including microbial cell wall surfaces*. As metal concentrations further increase, and fill available sorption sites, most metals tend then to be incorporated in the structures of major mineral precipitates as “coprecipitates” in which they substitute for major metal cations, forming so-called solid solutions (Langmuir, 1997a). At higher metal concentrations, the metals may be precipitated in pure metal phases, limiting further increases in metal concentration. For a hypothetical metal, M, the general trend of such reactions with increasing metal concentrations in soil moisture or surface or ground water might be:

- Adsorption control of M
($M < 100 \mu\text{g/L}$)
- Coprecipitation of M in a major metal hydroxide, carbonate, sulfate or silicate mineral (etc.)
($M > 100 \mu\text{g/L}$ and $< 10 \text{ mg/L}$)
- Precipitation of M in a “pure” metal phase
($M = 10 \text{ mg/L}$)

Practically, it is difficult to distinguish adsorption and coprecipitation reactions. These concepts are illustrated in Figure 6, which shows adsorption of lead from a landfill leachate by kaolinite clay as a function of pH. In the figure the adsorbed lead in mg/g of clay is plotted against the total lead in the leachate. The plot indicates that lead adsorption increases with increasing pH. Geochemical modeling of the leachate solution at pH 5 and 6 shows that at about 240 and 40 mg/L lead, respectively, (as indicated by the vertical dotted lines) further increases in dissolved lead are limited by precipitation of solid lead hydroxy-carbonate ($\text{Pb}_3[\text{OH}]_2[\text{CO}_3]_2$).

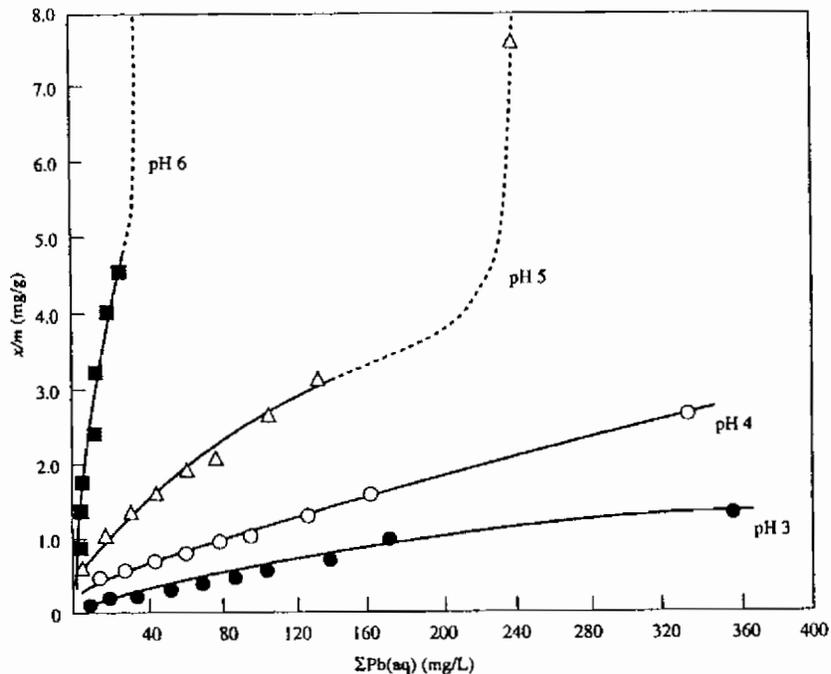


Figure 6. Adsorption of Pb from DuPage landfill leachate by kaolinite at 25°C, as a function of pH. Dashed vertical lines show the Pb concentration at saturation with Pb-hydroxycarbonate solid. From Griffin and Shimp, 1976.

5.2 Metal Adsorption and Desorption

Distribution Coefficients, Isotherm Equations and Ion Exchange:
They Don't Generally Apply to Adsorption of the Metals of Concern

The distribution coefficient (K_d) for lead adsorption by kaolinite is defined as $K_d = (x/m)/\Sigma\text{Pb(aq)}$, where x/m is the weight of lead adsorbed, x , divided by the weight of sorbent, m , at a specific concentration of total dissolved lead, $\Sigma\text{Pb(aq)}$. Based on this definition, every tangent to a curve in Figure 6 has a different value of K_d . The solid curves in Figure 6 are termed sorption isotherms, and can be model-fit with Langmuir or Freundlich isotherm equations (cf. Stumm and Morgan, 1996; Langmuir, 1997a). Clearly, a single distribution coefficient or isotherm equation cannot predict lead adsorption for all of the conditions described in Figure 6. This is because the extent of lead adsorption depends on the total lead concentration and the pH. Further analysis shows that adsorption also varies with the amount of lead complexed by carbonate, sulfate, chloride, and organic ligands, and by the nature and amounts of one or more sorbent phases present. Given all of these variables, K_d values for metal adsorption can vary by two to three orders of magnitude for a single soil or sediment. In other words, adsorption of

metals is far more complicated than adsorption of organics, which can often be adequately modeled using a distribution coefficient or isotherm approach.

Ion exchange models are also generally inappropriate to explain and model adsorption of toxic metals. Simple ion exchange models best apply when concentrations of competing ions are at comparable values, which is not the case for most toxic metals most of the time. Except in highly metal-contaminated waters and sediments, concentrations of toxic metal cations are typically 10^2 to 10^3 times lower than concentrations of the major cations Na^+ and Ca^{2+} which are competing for sorption sites on clays, for example. Concentrations of the anionic toxic metals are also in most cases less than 1% of the concentrations of major anions such as sulfate. (See Tables 1 and 2.) At trace concentrations, toxic metals are preferentially adsorbed relative to major metal ions, but not according to the principles of simple ion exchange (Langmuir, 1997a).

5.3 Adsorption Behavior of the Metals of Concern

In porous media the most important sorbent solids for metals are clay minerals, organic matter, and oxyhydroxides of Fe and Mn. Their important surface properties are given in Table 10. For a given weight of sorbent, metal sorption capacity is proportional to surface area and surface site density. The greatest surface site densities (positively or negatively charged sites) and cation exchange capacities (negatively charged sites only) are those of organic material and the oxyhydroxides. These phases are the strongest and most important sorbents of toxic metals. The clays, except for kaolinite, have a surface charge that is largely independent of pH, whereas the surface charge of organic matter and the oxyhydroxides is strongly pH dependent. Thus, the negative surface charge of the oxyhydroxides increases with increasing pH, which means their sorptive capacity for metals increases with increasing pH. Conversely, the positive surface charge of the oxyhydroxides increases as the pH drops, making these phases more effective sorbents for anions under low pH conditions.

These effects are shown in Figure 7, which is a plot of percent sorbed versus pH for metal adsorption by ferrihydrite, or hydrous ferric oxide (HFO). The curves are called *sorption edges* for each metal. The diagram shows that the oxyanions are strongly adsorbed by HFO under acid conditions, but are desorbed (become mobile) with increasing pH. Based on Figure 7, combined with adsorption data assembled by Dzombak and Morel (1990), the order of desorption from HFO with increasing pH is, selenate, antimonate, molybdate, chromate, vanadate, arsenate, and phosphate. Selenate desorbs between pH 3 and 8, whereas arsenate is strongly held at lower pH values and desorbed between pH 9 and 11. Also based on Figure 7 and Dzombak and Morel (1990), with increasing pH, HFO preferentially adsorbs metals in the order $\text{Hg}^{2+} > \text{Be}^{2+} > \text{Ba}^{2+} > \text{Cr}^{3+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} \approx \text{Zn}^{2+} > \text{Ni}^{2+}$.

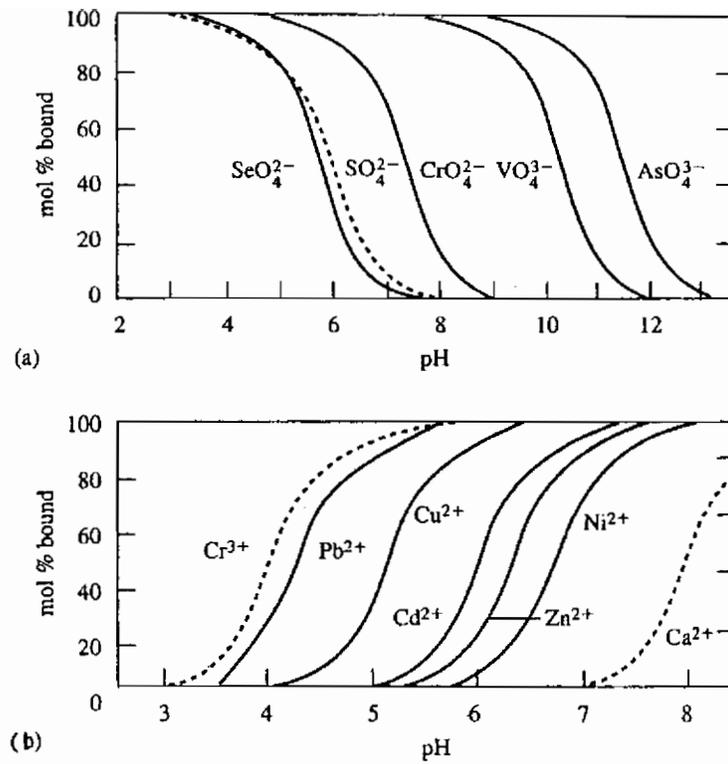


Figure 7. Adsorption of various metal cations and oxyanions, each at 5×10^{-7} M, by ferrihydrite ($\Sigma\text{Fe[III]} = 10^{-3}$ M) as a function of pH at an ionic strength of 0.1 mol/kg. There are 2×10^{-4} M of reactive sites on the oxyhydroxide. The dashed curves are calculated. After Stumm, 1992.

Table 10. Surface Areas, Surface Site Densities, and Cation Exchange Capacities (CECs) of Some Important Sorbent Phases and the pH Dependence of Metal Sorption

Sorbent Mineral/Phase	Surface Area (m ² /g)	Site Density (sites/nm ²)	Site Density (mmol sites/g)	CEC (meq/100g)	pH Dependence
Kaolinite	10 to 38	1.3 to 3.4	0.022 to 0.21	3 to 15	Strong
Illite and chlorite	65 to 100	0.4 to 5.6	0.043 to 0.93	10 to 40	Slight
Smectite-montmorillonite	600 to 800	0.4 to 1.6	0.4 to 2.1	80 to 150	Absent or negligible
Organics in soils, humic materials ^a	260 to 1300	2.31	1.0 to 5.0	110 to 500	Strong
Mn oxyhydroxides	143 to 290	2 to 18	0.48 to 8.7	100 to 740	Strong
Fe(III) oxyhydroxides (ferrihydrite)	250 to 600	20	8.3 to 20	100 to 740	Strong

Modified after Langmuir (1997a).

^aPaulson and Balistrieri (1999) suggest 1 mmol of sites per gram of organic carbon.

Metal adsorption onto soils and sediments is probably more dependent on changes in pH than on any other solution variable. For a divalent metal cation, M²⁺, the general sorption reaction can be written:



where SOH and SOM⁺ are surface sites with an adsorbed proton and a metal ion. For adsorption of a divalent metal anion, L²⁻, we can similarly write:



Sorption edges for metal adsorption, by amorphous Al(OH)₃ and by soil humus material, are given in Figure 8. The plots show a strong pH dependence of metal adsorption on both substrates. Metal selectivity with increasing pH is similar to what was observed for adsorption by HFO.

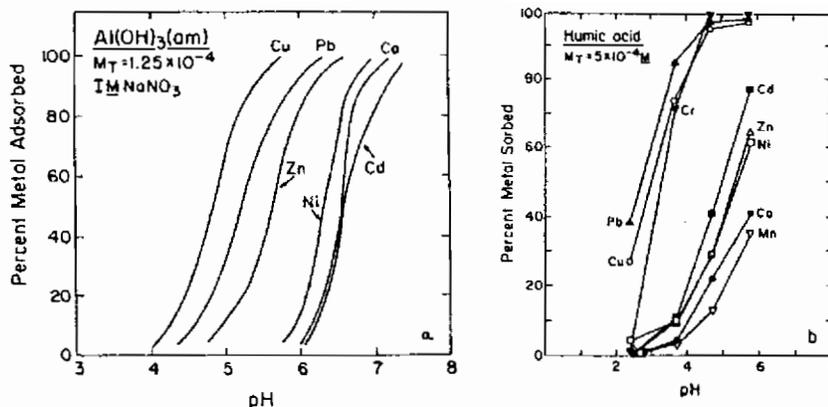


Figure 8. Percent metal adsorbed: (a) by Al(OH)₃(am) at total metal concentrations of 1.25 x 10⁻⁴ M in 1 M NaNO₃ solutions, and (b) by humic acid at total metal concentrations of 5 x 10⁻⁴ M. From Sposito, 1984.

5.4 Surface Complexation Adsorption Models

The most useful and mechanistic sorption models for predicting and modeling toxic metal adsorption in surface and ground waters are probably the *electrostatic or surface complexation (SC) adsorption models* (cf. Westall and Hohl, 1980; Davis and Kent, 1990; Langmuir, 1997a). These include the constant capacitance (CC), diffuse layer (DL), and triple layer (TL) models, all of which are available in the EPA geochemical program MINTEQA2 (U.S. EPA, 1991). The DL model is also included in the U.S. Geological Survey program PHREEQC (Parkhurst and Apello, 1999).

The SC models employ electrical double layer (EDL) theory, according to which it is assumed that the concentration of a sorbed ion (X_s^z), which is not measurable, is related to the ion's concentration in the bulk solution (X^z) by an exponential Boltzmann expression:

$$(X_s^z) = (X^z)[e^{-\psi F/RT}]^z \quad (5)$$

in which z is the charge of the ion, $e^{-\psi F/RT}$ is the Boltzmann factor (unitless), ψ is the potential in volts at the plane of adsorption, and F , R , and T are the Faraday constant (96,480 C/mol), the ideal gas constant (8.314 J/mol), and the absolute temperature, respectively.

The SC models consider and compute activity coefficients of ions and ion activities, as well as the concentrations of free and complexed metals in solution. The models treat metal adsorption onto surface sorption sites as a complexation reaction. Required model inputs include the specific surface area of sorbent phases (m²/g), the site density (moles of sites/moles of sorbent), and intrinsic surface complexation constants for adsorption of each metal by each sorbent phase. These constants are analogous to the equilibrium constants that describe the

formation of metal complexes in solution. Because the SC models are relatively atomistic and mechanistic in the way they treat adsorption, they are far better at predicting metal adsorption behavior for conditions beyond those used to determine model parameters than are models based on adsorption isotherms or ion exchange.

The diffuse layer (DL) model is the simplest of the SC models (U.S. EPA, 1991; Langmuir, 1997a). Both MINTEQA2 and PHREEQC contain a database of sorption parameters (intrinsic constants) for the adsorption of metals by HFO from Dzombak and Morel (1990). Sorption parameters for all of the toxic metal cations and anions of concern, except for Al and Tl, are included in the database. Diffuse layer model parameters for adsorption of H^+ , Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} by δ - MnO_2 have recently been published by Pretorius and Linder (2001), but are not yet included in MINTEQA2 or PHREEQC.

5.5 Applications of the Diffuse Layer Model to Natural Systems

It has been observed that in many soils and sediments low in organic matter, HFO is the most important metal sorbent, and the only sorbent that needs to be considered in predictions of toxic metal sorption behavior (cf. Benjamin and Leckie, 1981). The diffuse layer model (also called the generalized two-layer model, or GTLM) in MINTEQA2 has been extensively applied in aquatic environmental studies of metal transport and attenuation. Loux et al. (1990) used the DL model and MINTEQA2 to predict the adsorption and precipitation behavior of eight metals in an oxidized, sandy aquifer as a function of pH. Assuming that HFO was the only sorbent, DL model adsorption adequately described changes in the concentrations of Ni, Pb, and Zn. Cadmium behavior was better understood, assuming its precipitation in $CdCO_3$ (otavite). Changes in Cu, Ba, Be, and Tl were not simply explained. Copper may have been adsorbed by organic matter, which was not considered in the modeling.

More recently, adsorption of metals by organic matter and aluminum oxyhydroxides, as well as HFO, has been included in DL modeling with MINTEQA2 (Paulson and Balistieri, 1999). These authors studied neutralization of acidic ground waters by ambient surface and ground waters using a mixing model approach. Particulate organic matter (POC) and HFO were the chief metal sorbents. In pristine systems, Cu is usually the chief metal associated with POC; however, in their study, Zn and Cd were mostly adsorbed by POC and Cu was mostly adsorbed by HFO.

In another study of metals in acid mine waters, Smith et al. (1998) measured and modeled the adsorption of Cd, Cu, Ni, Pb, and Zn by streambed sediments as a function of pH using MINTEQA2 and the DL (GLTM) model. Figure 9 shows their measured adsorption results, obtained in batch experiments, assuming 2.9 g/L of HFO as the only sorbent. The plot shows fair to excellent agreement between measured and predicted metal adsorption values. These authors also measured and predicted metal concentrations in three mine drainage waters, assuming that metal adsorption was by suspended HFO. The results, listed in Table 11, show good general agreement between measured and predicted metal concentrations.

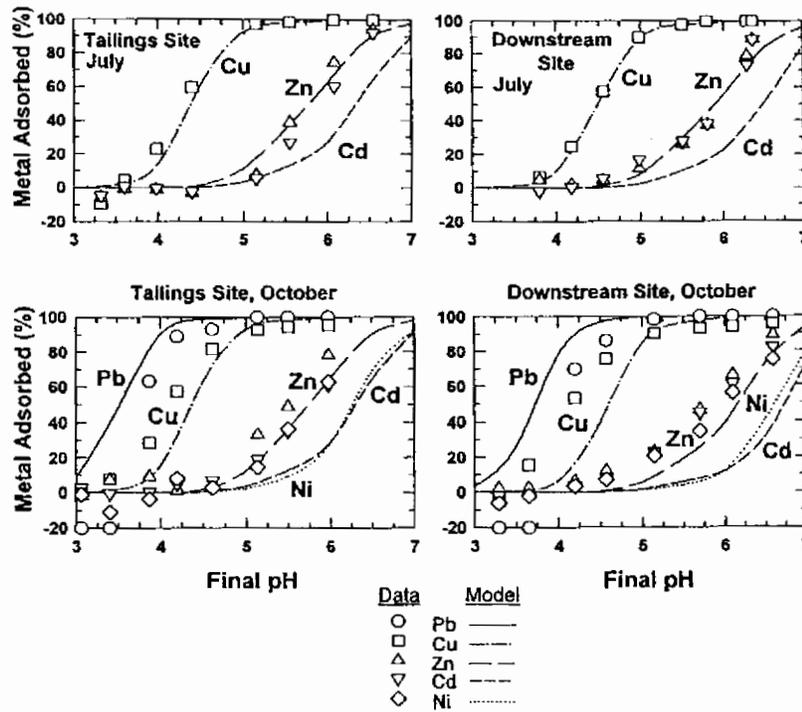


Figure 9. Comparison of experimental data (symbols) for Pb, Cu, Zn, Ni, and Cd sorption onto streambed sediment from St. Kevin Gulch, Colorado, with computer-model simulations (curves) for sorption onto hydrous ferric oxide, at a streambed concentration of 2.9 g/L. From Smith et al., 1998.

Table 11. Comparison of Model Predictions and Measured Values of Percent Metals Associated With the Suspended Particulate Fraction of Mine-Drainage Waters From Selected Sites

	Argo-3 (pH 5.6, HFO = 0.007 g/L)		Rawley-3 (pH 6.2, HFO = 0.11 g/L)		Leadville Drain (pH 7.2, HFO = 0.001 g/L)	
	Predicted (%)	Measured (%)	Predicted (%)	Measured (%)	Predicted (%)	Measured (%)
As	--	--	98	<78 ^a	--	--
Pb	82	<71 ^a	80	<93 ^a	86	<71 ^a
Cu	18	27	60	63	--	--
Zn	<1	0 to 8	<1	0 to 9	2	3
Ni	<1	<1	<1	1	--	--
Cd	<1	<1	<1	6	<1	<1

Model predictions made with the DL model and MINTEQA2. From Smith et al., 1998.

^aDissolved concentration was below the detection limit. Value computed using the limit of detection for the dissolved concentration.

Cederberg et al. (1985) and Yeh and Tripathi (1991) considered surface complexation modeling of metal adsorption and metal transport in ground water. Parkhurst (2002) has developed a computer model called PHAST,³ which is a 3D reactive transport model that combines PHREEQC, which has the DL metal adsorption model, with HST3D, a ground-water flow and transport model.

Several recent studies have measured and modeled trace metal adsorption and metal transport in streams using a surface complexation approach to adsorption. U.S. Geological Survey researchers of the Toxic Substances Hydrology Program have published a number of papers using the OTEQ and OTIS models. OTEQ is a one-dimensional model for studying the fate and transport of metals in streams and rivers. The model couples the OTIS transient storage model with MINTEQ, which includes DL model adsorption of metals by HFO (cf. Ball et al., 1999; Runkel et al., 1999). In their study, Runkel et al. (1999) considered in-stream metal transport, metal oxide precipitation-dissolution, and pH-dependent sorption of copper and zinc.

³ See http://wwwbrr.cr.usgs.gov/projects/GWC_coupled.

5.6 WHAM and Related Models for Predicting Metal Activities in Soil Moisture

MINTEQA2 (U.S. EPA, 1991) and VMINTEQ (Gustafson, 2003) both contain subroutines that allow estimates of the importance of metal-organic complexing if the concentration of dissolved organic carbon (DOC) is known. Perhaps more useful in studies of metals in soil moisture are programs such as WHAM (Tipping, 1994, 1998), and NICA (Goody et al., 1995). Application of the chemical speciation model WHAM has been discussed by Tye et al. (2003), who successfully predicted Zn^{2+} and Cd^{2+} activities in soil pore water assuming the metals were adsorbed by soil humus according to a pH-dependent Freundlich isotherm model. Competitive adsorption between Ca^{2+} and Zn^{2+} and Cd^{2+} could be ignored because it did not improve model fits.

6. SOLUBILITY CONTROLS ON METAL CONCENTRATIONS AND MOBILITIES

6.1 The Importance of pH

The solubility of most metals that occur as cations is strongly pH dependent. Their greatest solubilities are usually measured in acid systems, with solubilities that decrease as the pH rises. For a few metals (e.g., Be[II], Zn[II], Al[III], and Fe[III]), metal solubility increases again at alkaline pH values, a property which is termed amphoteric behavior (Figures 13 and 17). In following discussions of solubility, we will focus on the pH range between 4 and 9, which includes that of most natural waters and soils.

Tyler and Olsson (2001a, 2001b) mixed calcium carbonate with an acid Swedish Cambisol to vary the soil pH from 5.2 to 7.8. They then studied the effect of the pH change in the oxidized soil on concentrations of 60 elements in soil moisture. With increasing pH, concentrations of As, Mo, S, Sb, and to a lesser degree Co, Cr, Hg, and Sr increased, whereas Al, Ba, Fe, Mn, and Tl concentrations decreased. The pH effect on Be and Cu concentrations was poorly defined. Metal concentration changes with increasing pH may have been caused by increasing desorption of anionic elements (As, Mo, S, Sb, and Cr), increasing adsorption of cationic species (Ba, Mn, and Tl?), and the precipitation of oxyhydroxide solids (Al, Fe, Mn). The ill-defined behavior of Cu with rising pH may reflect its participation in competing reactions: (1) complexation by increasing amounts of dissolved humic substances with increasing pH, which tend to solubilize Cu^{2+} ; and (2) increased Cu^{2+} adsorption by solid organic matter and metal oxyhydroxides.

6.2 Oxidation Potential and pH

Shown in Table 12⁴ are the possible oxidation states and speciation of the toxic metals in natural systems. Also indicated are their hard or soft acid or base character, which depends on the oxidation state, their forms in oxidized and reduced systems, and whether they can

⁴ Information for Table 12 was obtained from the following sources: Baes and Mesmer, 1976; Bodek et al., 1988; Brookins, 1988; Langmuir, 1978, 1997a; Pourbaix, 1966; and Rai et al., 1984.

precipitate in sulfide minerals. This distinction is important because the metal sulfides are extremely insoluble, and if precipitated tend to reduce metal concentrations to below the microgram per liter range.

The table shows that all metals forming sulfide phases (sulfide is a soft ligand) are either soft or borderline soft.

In following discussion, the figures describe oxidation state in terms of Eh and/or pe or pE. At 25° C and 1 bar pressure, the two are related through the expression:

$$\text{pe or pE} = \text{Eh(volts)}/(0.0592) \quad (6)$$

Figure 10 describes the locus of measured pH and Eh values in natural waters, and the types of waters in which the measurements have been made.⁵ Oxygenated surface and near surface environments have Eh values that plot near the area titled “Environments in contact with the atmosphere.” Ground waters, because they are out of direct contact with the atmosphere, tend to be more reducing. Waterlogged soils and sediments are among the most reduced aqueous systems. Differences in the oxidation potential or Eh of these environments are usually related to the abundance of organic matter and their isolation from air. Oxygen is relatively insoluble in water, with a solubility of 8.25 mg/L at 25° C. It takes only 2–3 mg/L of DOC in water to deplete this oxygen content (Langmuir, 1997a). Leenheer et al. (1974) reported a median DOC of 0.7 mg/L for U.S. ground waters. In temperate and tropic regions, soils have a mean organic matter content of about 2–4% (Bohn et al., 1985). Langmuir (1997a) has observed that 4 mg/L of DOC in ground water is sufficient to make the water anaerobic.

An Eh-pH diagram for carbon is shown in Figure 11. The stability field of organic matter, generally, if it could be plotted, would overlay the stability fields of methane and native C (graphite) in the low Eh part of the diagram. When organic matter is in excess, and oxygen not replenished fast enough, microbial activity can generate reducing conditions. The sequence of reductions that result is shown in Figure 12. In waters and sediments where oxygen or other oxidants are in excess, the sequence of oxidations shown in Figure 12 may proceed.

Oxidation of the organic matter in an isolated aquatic environment can deplete the oxygen and provide conditions suitable for sulfate reduction. Precipitation of metal sulfides is preceded by reduction of more abundant soil Fe(III) oxyhydroxides to dissolved Fe(II) (Figure 12). This is then followed by precipitation of Fe(II) sulfides in association with the less abundant sulfides of Cd, Zn, Co, Ni, Pb, Ag, Cu, Hg, and Mo.

⁵ Problems with measuring Eh and the difference between measured and theoretical Eh values are discussed at length elsewhere (cf. Langmuir, 1997a).

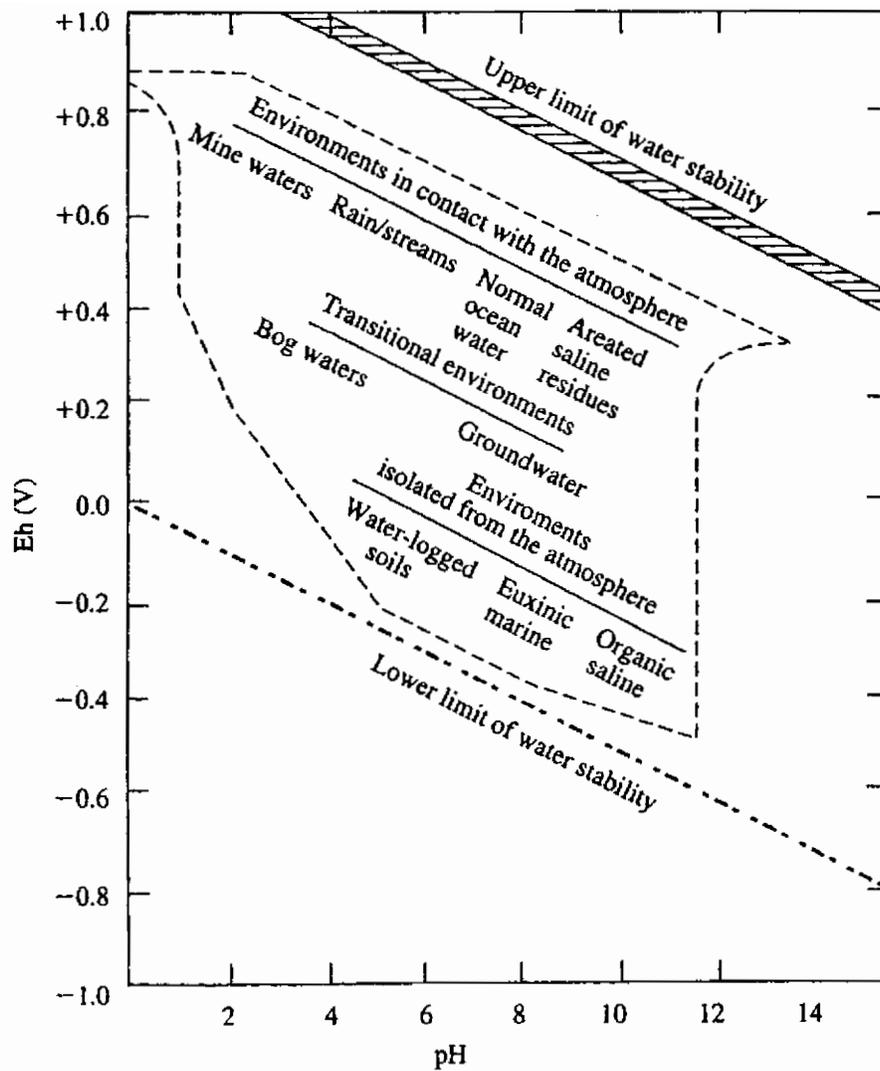


Figure 10. Approximate positions of some natural environments in terms of Eh and pH. The dashed line represents the limits of measurements in natural environments, as reported by Baas-Becking et al. (1960).

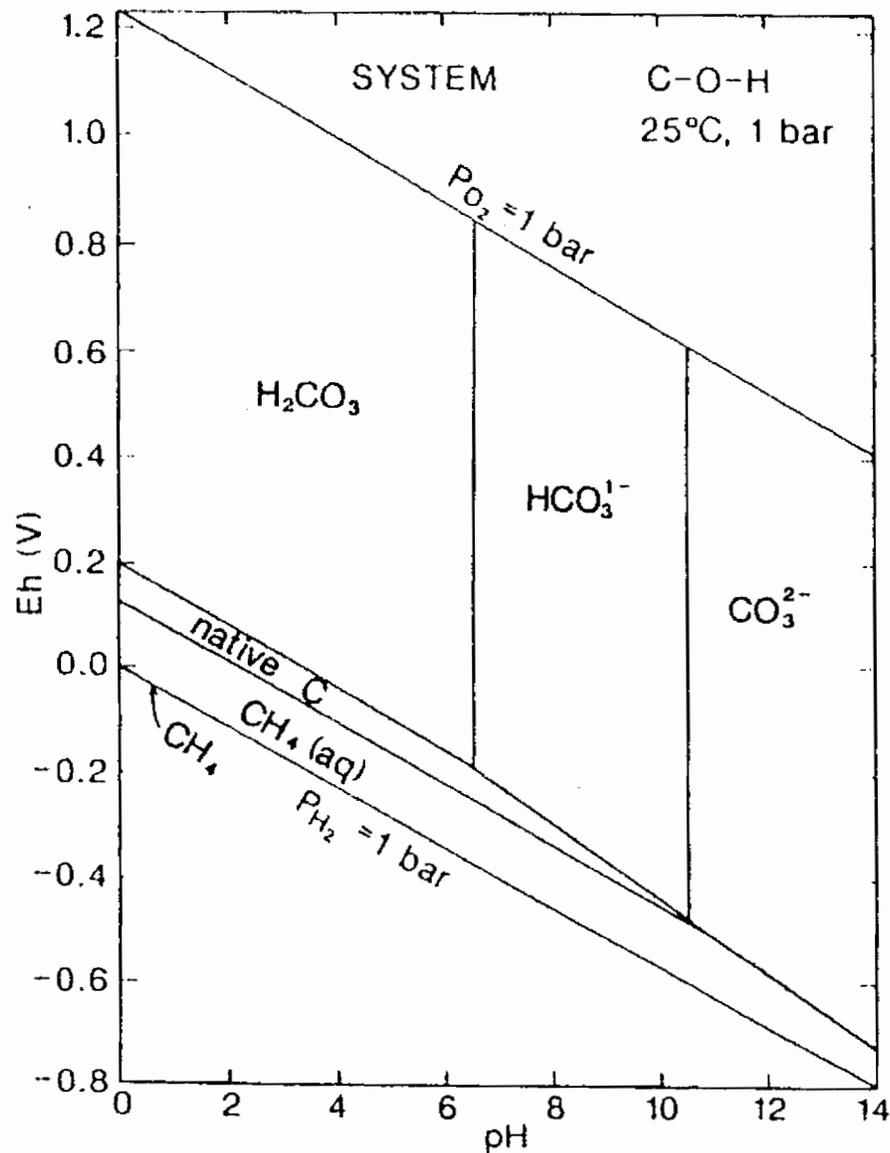


Figure 11. Eh-pH diagram for the system C-O₂-H₂ at a total carbonate concentration of 10⁻³ M. Native C is graphite. If shown, the upper boundary of the stability field for carbohydrates would be at slightly higher Eh values than the methane/carbonate boundary. After Brookins, 1988.

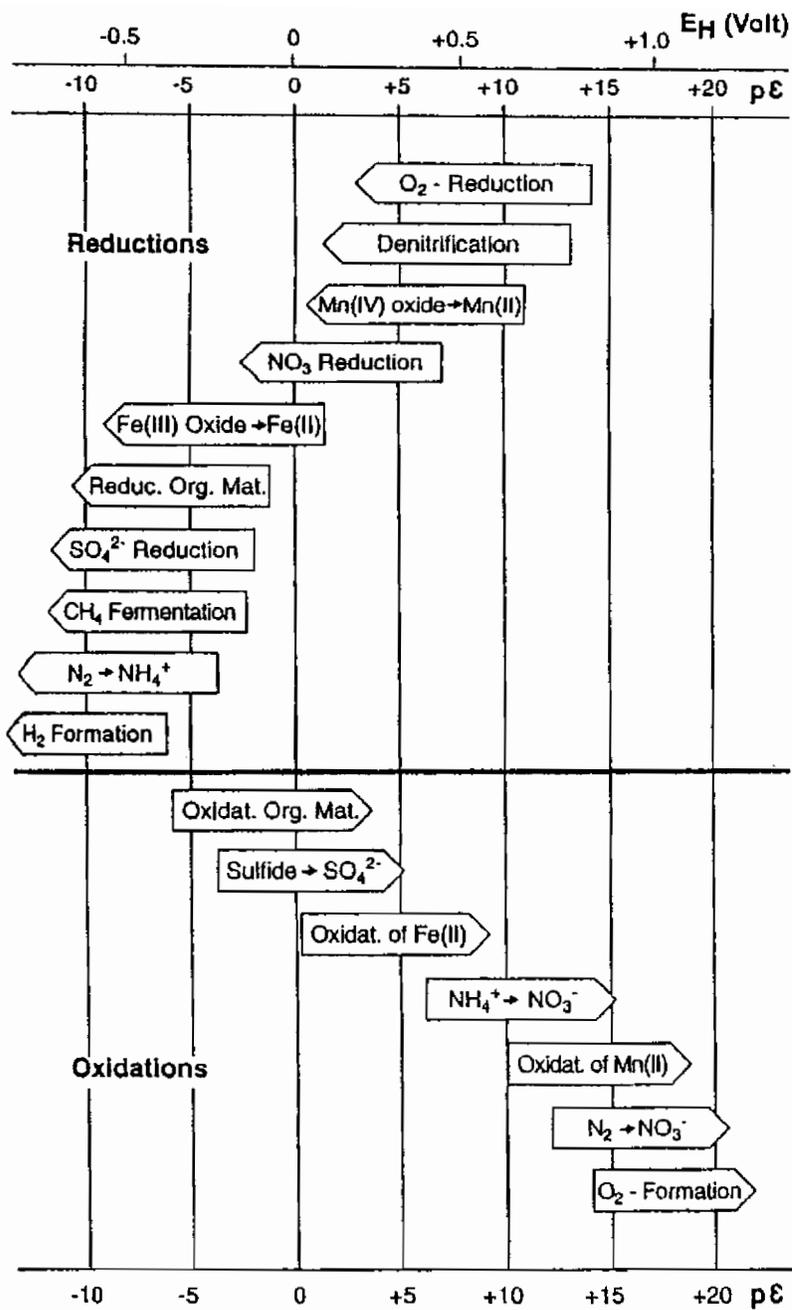


Figure 12. Sequence of microbially mediated oxidation-reduction reactions. This sequence is often observed in natural systems and represents the thermodynamic order of the reactions. Modified from Stumm and Morgan, 1996.

Table 12. Oxidation States of Toxic Metals as They Occur in Natural Waters and Mineral Systems, Their Redox Sensitivity, and Their Tendency To Form Sulfides at Low Eh

Metal	Symbol	Hard or Soft	Oxidation States	Oxidized Forms	Reduced Forms ^a	Can Form Sulfides at Low Eh
Aluminum	Al	H	3+	Al ³⁺	Al ³⁺	no
Beryllium	Be	H	2+	Be ²⁺	Be ²⁺	no
Barium	Ba	H	2+	Ba ²⁺	Ba ²⁺	no
Strontium	Sr	H	2+	Sr ²⁺	Sr ²⁺	no
Cadmium	Cd	S	2+	Cd ²⁺	Cd ²⁺	yes
Zinc	Zn	B	2+	Zn ²⁺	Zn ²⁺	yes
Cobalt	Co	B	(3+), 2+	(Co ³⁺), Co ²⁺	Co ²⁺	yes
Nickel	Ni	B	(3+), 2+	(Ni ³⁺), Ni ²⁺	Ni ²⁺	yes
Manganese	Mn	H	(4+), (3+), 2+	(4+), 2+	(3+), 2+	no ^b
Lead	Pb	B	(4+), 2+	Pb ²⁺	Pb ²⁺	yes
Silver	Ag	S	1+, (0)	Ag ⁺	Ag ⁺ /Ag(s)	yes
Copper	^c Cu	^d B/S	2+, 1+, 0	Cu ²⁺	Cu ⁺ /Cu(s)	yes
Mercury	Hg	S	2+, 1+, 0	Hg ²⁺	Hg ⁺ /Hg(l)	yes
Thallium	Tl	S	(4+), (3+), 1+	(Tl ⁴⁺), (Tl ³⁺)	Tl ₂ O(s)/Tl ⁺	yes
Arsenic	As	^d H/S	5+, 3+, 0	HAsO ₄ ²⁻	H ₃ AsO ₃ ⁰ /As(s)	yes
Antimony	Sb	H/S	5+, 3+, 0	Sb(OH) ₆ ⁻	Sb(OH) ₃ ⁰ /Sb(s)	yes
Chromium	Cr	H	6+, 3+	CrO ₄ ²⁻	Cr ³⁺ , Cr(OH) ₃ (s)	no
Molybdenum	Mo	H/S	6+, (5.33+), 5+, (4+)	HMoO ₄ ⁻	MoO ₂ ⁺ /Mo ₃ O ₈ (s)/ MoS ₂ (s)	yes
Selenium	Se	H/S	6+, 4+, (0), 2-	SeO ₄ ²⁻	SeO ₃ ²⁻ /Se(s)/ HSe ⁻	no
Vanadium	V	H	5+, 4+, 3+	H ₂ VO ₄ ⁻	VO ²⁺ , V(OH) ₃ ⁰	no

Oxidation states in parentheses are found in mineral systems only. Hard (H), soft (S), and borderline soft (B) metals are indicated.

^aCu²⁺ is borderline soft, and Cu⁺ is a soft cation.

^bB/S or H/S denotes whether the oxidized species is borderline hard or hard, and the reduced species is soft.

Other ligands that can limit maximum metal concentrations include oxygen and hydroxide, which react with the hard acid cations Al(III), Mn(III, IV), and Cr(III) to produce insoluble oxyhydroxides. Phosphate, sulfate, and carbonate also form relatively insoluble mineral precipitates when they react with divalent and trivalent metal cations. These are noted on a case by case basis below.

6.2.1 Iron and Sulfur

Although iron and sulfur are not elements of concern, their behavior needs to be discussed because it has a pivotal impact on the fate and transport of the toxic metals. Shown in Figure 13 is a solubility diagram for the Fe(III) oxyhydroxides as a function of pH. Plotted are curves showing the solubility of $\text{Fe}(\text{OH})_3(\text{am})$, which is also termed ferrihydrite or HFO, and a solubility curve for the crystalline mineral goethite. Initial precipitates of Fe(III) oxyhydroxide tend to be relatively amorphous, with a strong capacity to adsorb or coprecipitate trace metals. As they crystallize with time towards goethite, they lose surface area and adsorption capacity and tend to desorb toxic metals. Figure 13 also shows that as the pH is reduced below 7, HFO tends to dissolve, becoming quite soluble below pH 3–4. Thus, soils and sediments at low pH typically have little capacity to retain the metals of concern, whereas soils at higher pH values that contain ferric oxyhydroxides may limit the release of the toxic metals to the environment.

An Eh-pH diagram for iron in the presence of carbonate is shown in Figure 14. The ferric oxyhydroxides occupy most of the diagram for oxidizing conditions, which reflects their great stability and insolubility. The figure shows that the stability field of amorphous $\text{Fe}(\text{OH})_3$ ($\text{pK}_{\text{sp}} = 37.1$) is much smaller than that of the crystalline phase, goethite ($\text{pK}_{\text{sp}} = 44.2$), and that under strongly reducing conditions the ferric oxyhydroxides are unstable relative to dissolved ferrous iron and the mineral siderite (FeCO_3).

A sulfur Eh-pH diagram is given in Figure 15. The large size of the sulfate field is consistent with the fact that sulfate is the dominant form of sulfur in most environments. The position of the stability fields for native sulfur (S^0), hydrogen sulfide, and bisulfide ion indicate that these forms are stable only under highly reducing conditions. When we add sulfur to the iron Eh-pH diagram as shown in Figure 16, a large stability field for pyrite (FeS_2) appears at low Eh values. Acid mine drainage is produced when pyrite is exposed to atmospheric oxygen. Oxidation of the iron and sulfur in pyrite generates strong acidities and pH values as low as 1–2. This tends to dissolve any nearby HFO and solubilizes toxic metals that were present as sulfides or adsorbed to the HFO.

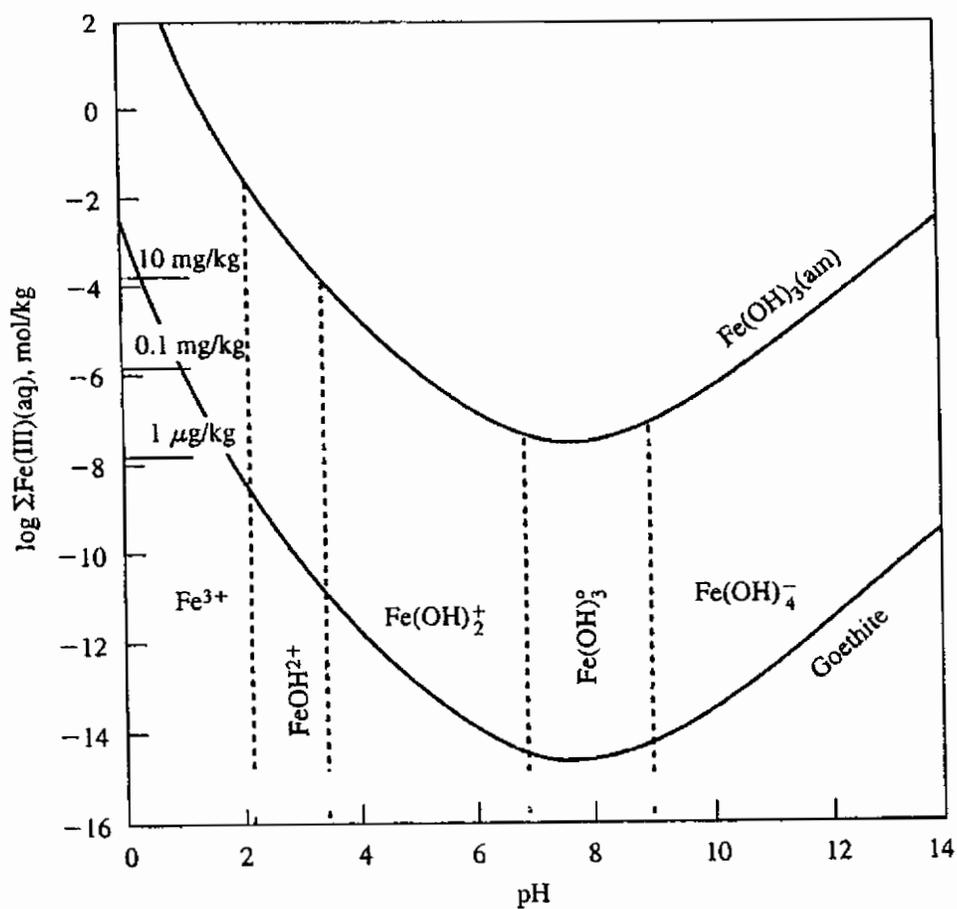


Figure 13. Solubility of amorphous Fe(OH)_3 , $\text{pK}_{\text{sp}} = 37.1$ (top curve), and goethite [α - FeOOH], $\text{pK}_{\text{sp}} = 44.2$ (bottom curve) as a function of pH at 25° C. Also shown are fields of dominance of Fe^{3+} ion and Fe^{3+} -OH complexes. After Langmuir, 1997a.

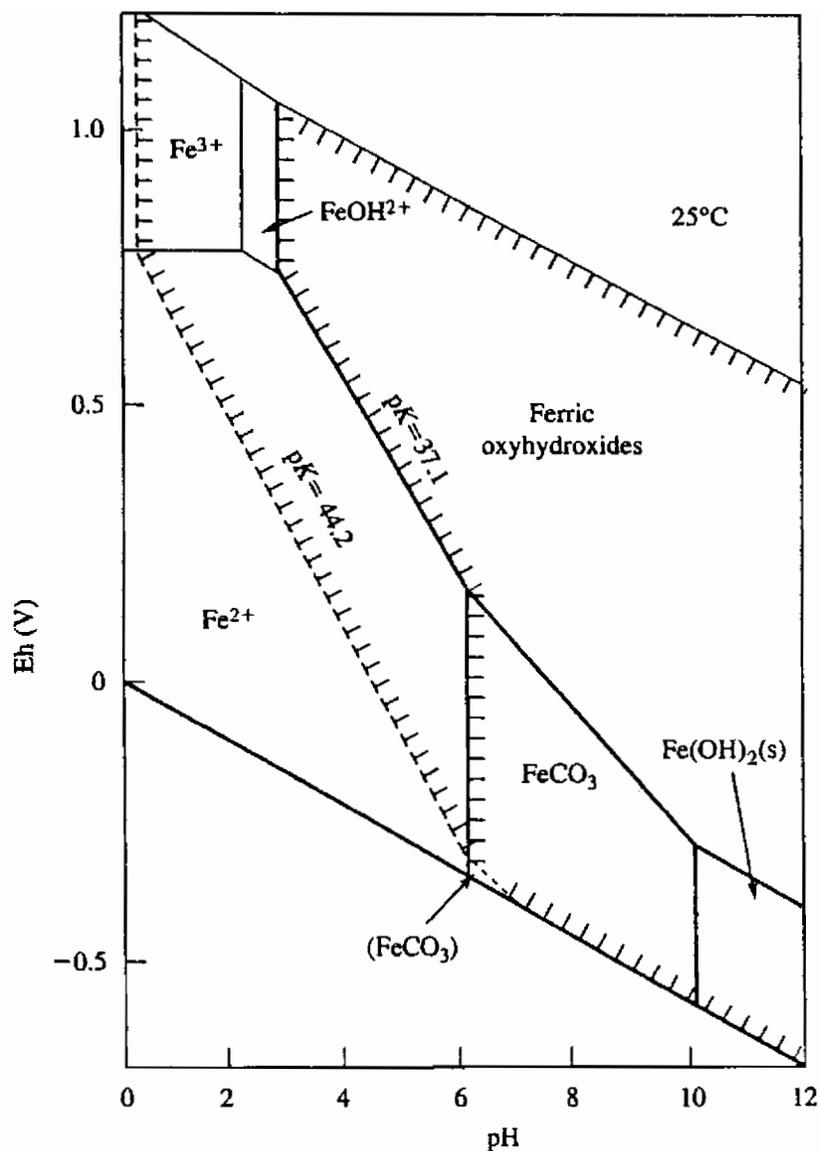


Figure 14. Eh-pH diagram for the system Fe-O₂-CO₂-H₂O, assuming that total dissolved carbonate equals 10⁻³ mol/kg and total dissolved iron is 10⁻³ mol/kg at aqueous solid boundaries. Also shown is the position of the aqueous/solid boundaries for amorphous Fe(OH)₃ with pK_{sp} = 37.1 and goethite with pK_{sp} = 44.2. The figure shows that siderite (FeCO₃) is metastable in the presence of goethite. After Whittemore and Langmuir, 1975.

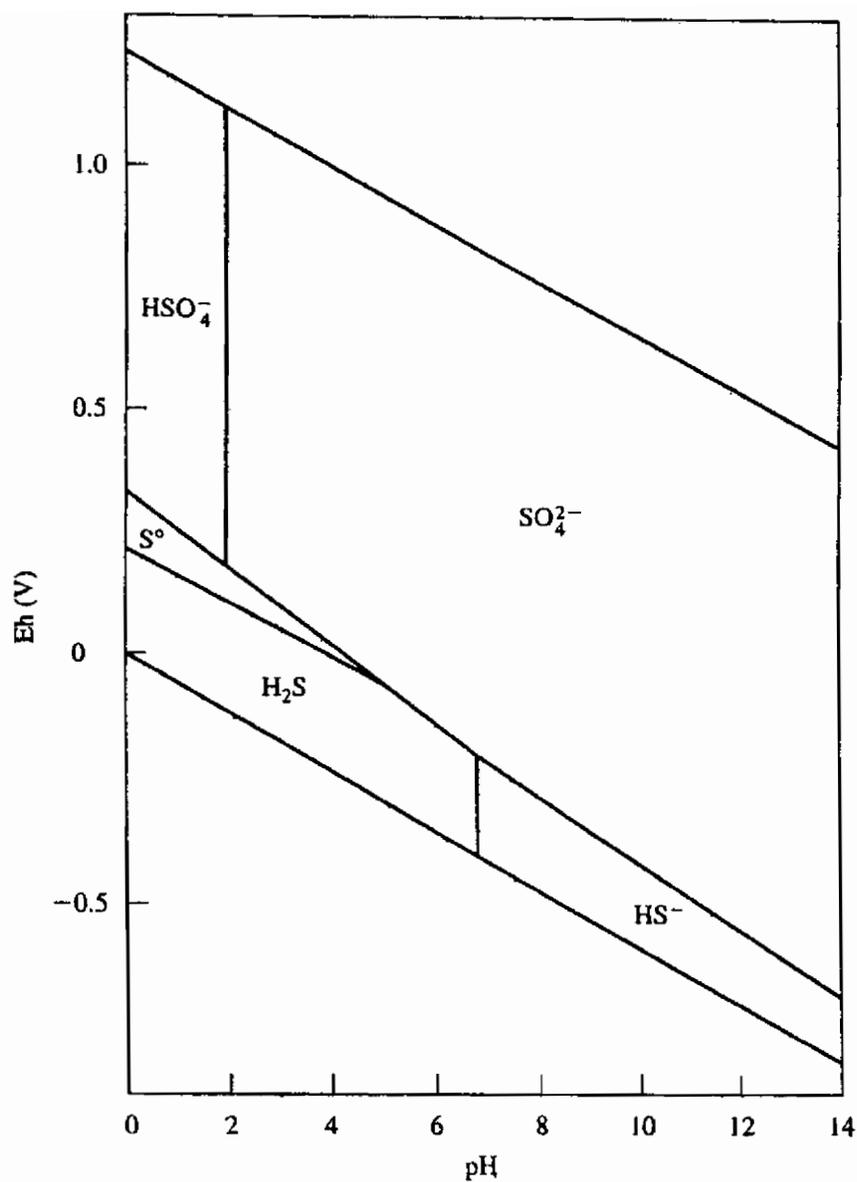


Figure 15. Eh-pH diagram for the system S-O₂-H₂O at 25° C, showing the fields of predominance of the aqueous species and of elemental sulfur (S⁰) for $\Sigma S(aq) = 10^{-3}$ mol/kg at aqueous/S⁰ boundaries. After Langmuir, 1997a.

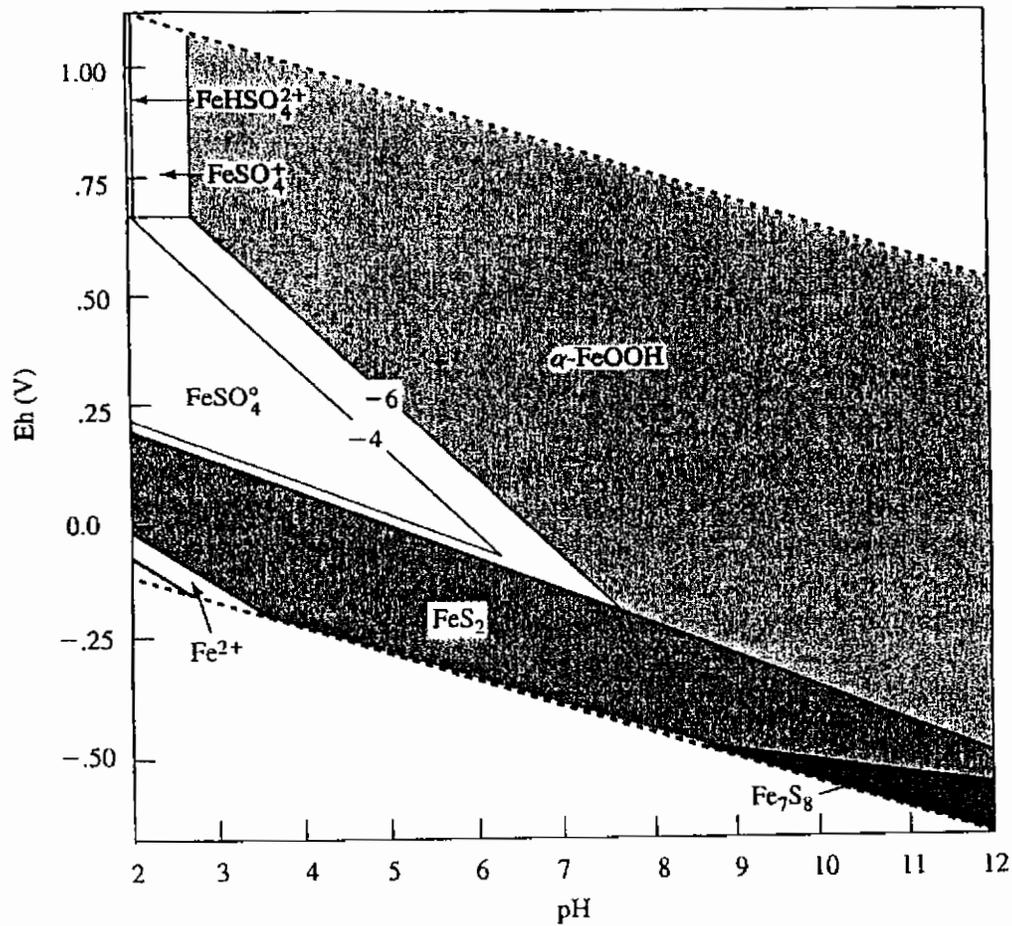


Figure 16. Eh-pH diagram for the system Fe-O₂-S-H₂O at 25° C, showing stability fields of goethite (α-FeOOH), pyrite (FeS₂), and monoclinic pyrrhotite (Fe₇S₈) for ΣS(aq) = 10⁻² mol/kg, and total carbonate 10⁻⁴ mol/kg. ΣFe(aq) = 10⁻⁶ and 10⁻⁴ mol/kg at aqueous/solid boundaries. The diagram shows that dissolved iron occurs chiefly in sulfate complexes. From Barnes and Langmuir, 1979.

6.2.2 Aluminum, Beryllium, Strontium, and Barium

As shown in Table 12, the hard acid cations, Al, Be, Sr, and Ba occur in only one oxidation state. Their least soluble solids (strongest bonds) are formed with hard bases such as OH^- , SO_4^{2-} , CO_3^{2-} , and PO_4^{3-} . Maximum Al(III) concentrations are generally limited by the solubility of aluminum oxyhydroxide solids, with dissolved Al concentrations less than the solubility of amorphous $\text{Al}(\text{OH})_3$ and more greater than the solubility of gibbsite, the least soluble form (Figure 17). The solubility of amorphous aluminum hydroxide is about 0.17 mg/L at pH 6.5, and 6 mg/L at pH 5. If the aluminum in soils or water is derived from the leaching of the more crystalline gibbsite, its equilibrium concentration is 0.34 $\mu\text{g/L}$ at pH 6.5 and 12 $\mu\text{g/L}$ at pH 5. These calculations suggest that the Al concentration of 0.07 mg/L in average world rivers (Table 3) that have a pH near 7 must be largely in suspension, probably in the colloidal size range (particles less than $\sim 10^{-5}$ m). Figure 17 also suggests that high Al concentrations in soils—concentrations toxic to many plants—will generally not be found except in acid soils.

It is unclear what solid or solids control maximum beryllium concentrations, but the least soluble Be phases for which there are such data are $\beta\text{-Be}(\text{OH})_2$ and beryllium silicate (Be_2SiO_4) (Bodek et al., 1988). The computed solubility of $\beta\text{-Be}(\text{OH})_2$ decreases from about 7.8 mg/L Be at pH 5 to 1.0 $\mu\text{g/L}$ at pH 9 (Figure 18). The silicate is considerably less soluble, with a solubility of about 7.2 $\mu\text{g/L}$ at pH 5, decreasing to 0.006 $\mu\text{g/L}$ at pH 8–9. These values may be compared to the median Be concentration in surface and ground waters, which is 5 $\mu\text{g/L}$ (Table 1).

The least soluble minerals of Sr^{2+} and Ba^{2+} are strontianite (SrCO_3), celestite (SrSO_4), and barite (BaSO_4). The solubility product of strontianite is $10^{-9.27}$, that of celestite is $10^{-6.63}$, and for barite $K_{\text{sp}} = 10^{-9.96}$ (Nordstrom et al., 1990). At a sulfate concentration of 96 mg/L, PHREEQC modeling calculations give a barite solubility of 32 $\mu\text{g/L}$ Ba. This value is not far from the median Ba concentration of 20 $\mu\text{g/L}$ in surface and ground waters (Table 1), suggesting that barite solubility must often limit maximum Ba concentrations in soils and natural waters. Modeling calculations indicate that celestite and strontianite are too soluble to limit Sr concentrations in general, so that strontium is most often limited by coprecipitation with the Ca carbonates or adsorption by clays.

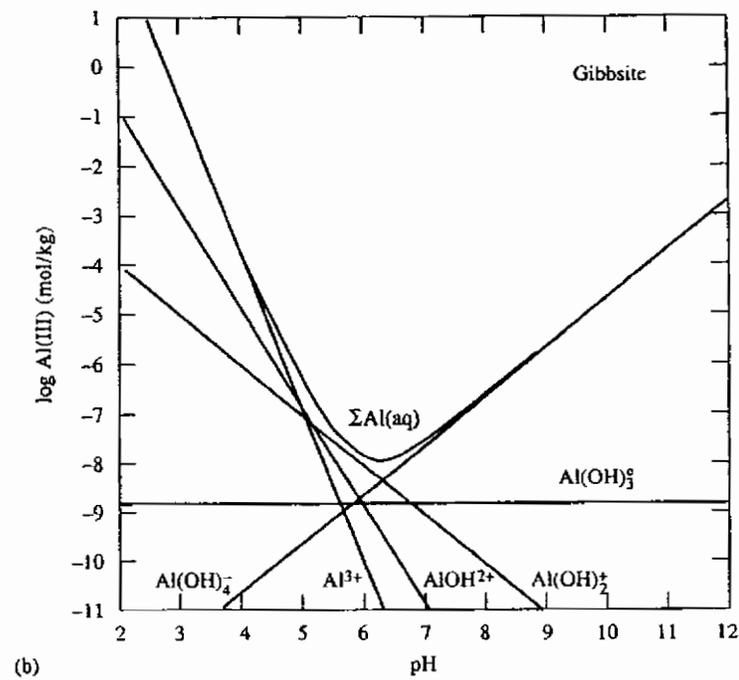
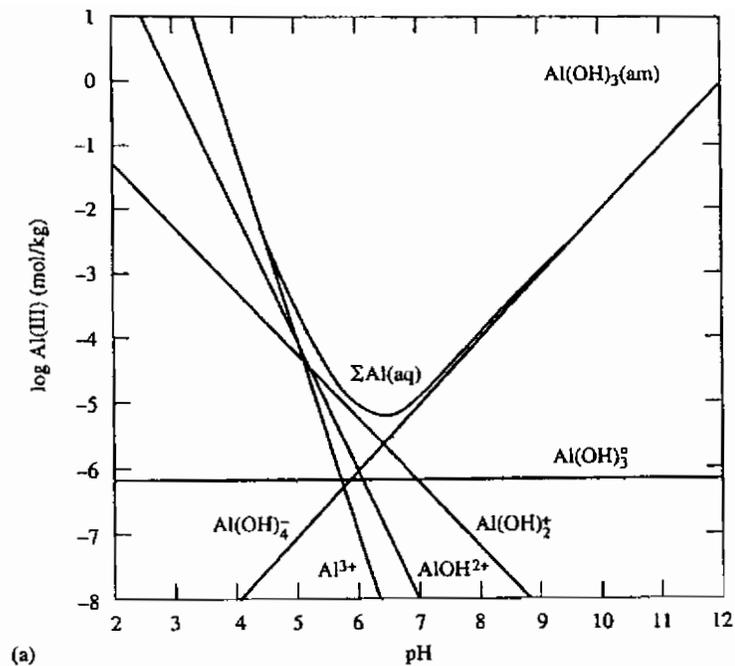


Figure 17. Solubility of (a) amorphous $\text{Al}(\text{OH})_3$, $K_{sp} = 10^{-31.2}$ and (b) gibbsite $\text{Al}(\text{OH})_3$, $K_{sp} = 10^{-33.9}$, as a function of pH at 25°C. Also shown are lines indicating the solubility contributions of Al^{3+} and individual Al-hydroxy complexes. From Langmuir, 1997a.

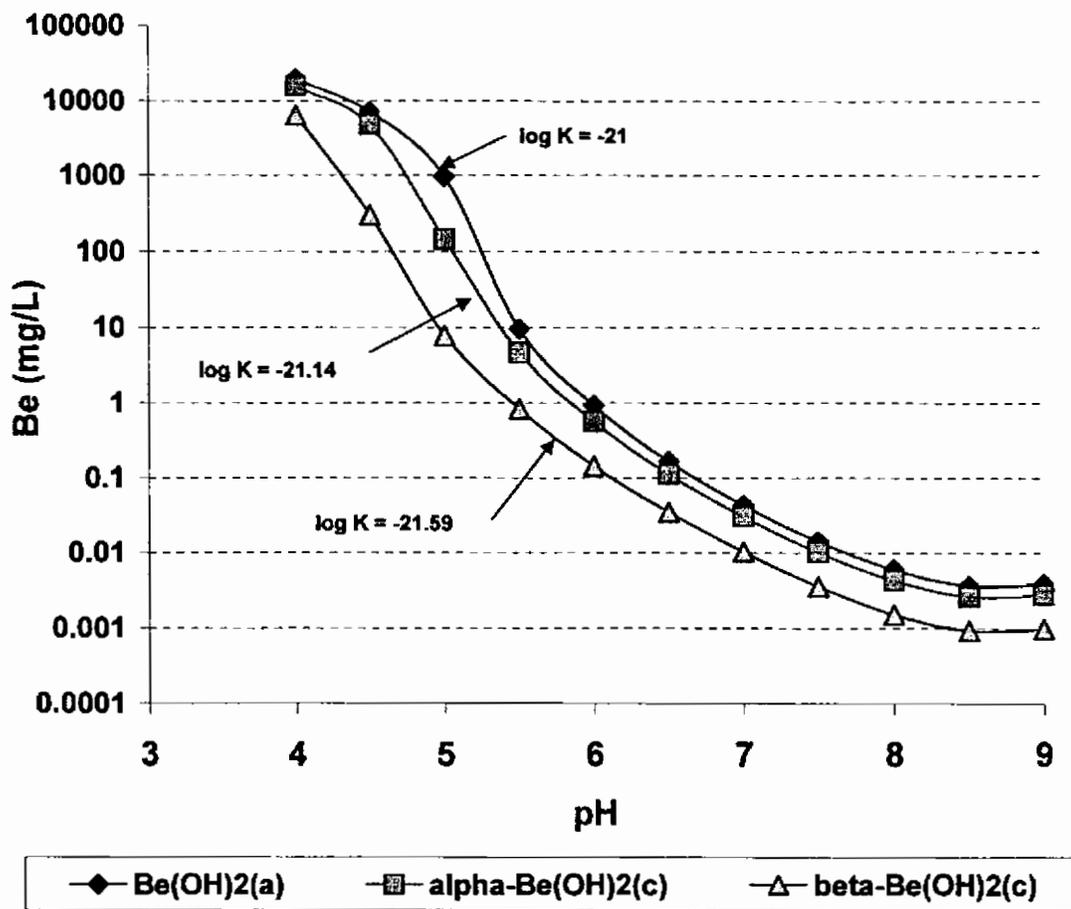


Figure 18. Solubility of three forms of $\text{Be}(\text{OH})_2$ as a function of pH. Diagram computed using the geochemical model PHREEQC (Parkhurst and Appelo, 1999).

6.2.3 Cadmium, Zinc, Cobalt, Nickel, and Lead

These metals are classified as either soft or borderline soft. Their metal sulfides are quite insoluble at low Eh, even at low metal and sulfide concentrations (Figures 19 through 24). For example, CdS (greenockite) precipitates and has a large stability field even for Cd = 11 µg/L (10^{-7} mol/kg) and total sulfur at 0.3 mg/L. The insolubility of the sulfides of Zn, Co, Ni, and Pb is similar. Other important Cd and Zn minerals include their carbonates, although the carbonates are relatively soluble at pH values below 8. Pure metal-containing mineral phases generally do not control the dissolved concentrations of Cd, Ni, or Zn in aerobic soils. These metals are more often controlled through adsorption or coprecipitation by oxyhydroxides of iron, manganese, and aluminum.

Lead is relatively immobile in soils, sediments, and ground waters. This reflects its strong tendency to be adsorbed by Fe and Mn oxides, but also the insolubility of a number of lead minerals including lead hydroxycarbonate (Figure 23), which limits lead concentrations in some public water systems, and pyromorphite (Figure 24), which controls lead concentrations in some soils adjacent to highways affected by road salt and leaded gasoline exhaust.

6.2.4 Manganese

Unlike most the other metals of concern, except aluminum, manganese is often precipitated in soils and sediments as manganese minerals. Environmentally, the most important of these minerals are the Mn(III/IV) oxides. Figure 25 shows that these phases are stable and relatively insoluble in oxidized systems above pH 6–7. The Mn oxides are often stronger sorbents of trace metals than is HFO. Suarez and Langmuir (1976) found that most of the Co, Ni, Cu, Zn, Pb, Ag, and Cd in a Pennsylvania soil were associated with Mn and Fe oxides. The Mn oxides held the highest metal amounts relative to their abundance. Rhodochrosite is an important Mn mineral, but only under reducing conditions. Manganese does form a sulfide, but it has a small stability field and is a rare mineral.

6.2.5 Silver, Copper, and Mercury

Eh-pH diagrams for these metals are shown in Figures 26 through 28. As soft metals, silver and mercury form strong complexes with borderline soft Cl ion, which may dominate the solution chemistry of these metals. Silver and mercury form even stronger complexes with the soft halogens bromide and iodide. Silver, copper, and mercury are highly insoluble in reduced environments, where they precipitate as metals or as sulfides. Copper is insoluble above pH 7–8 (because of the precipitation of tenorite, CuO) and in the presence of abundant carbonate of Cu²⁺ carbonate minerals.

Bodek et al. (1988) offer a useful summary of the behavior of mercury. Hg(II) is usually complexed—in pure water as Hg(OH)₂⁰, and at chloride concentrations typical of fresh waters (<10⁻² mol/kg) as HgCl₂⁰. Both Hg(II) and Cu(II) form strong humate complexes, so that in soils >99.9% of the metals may be complexed.

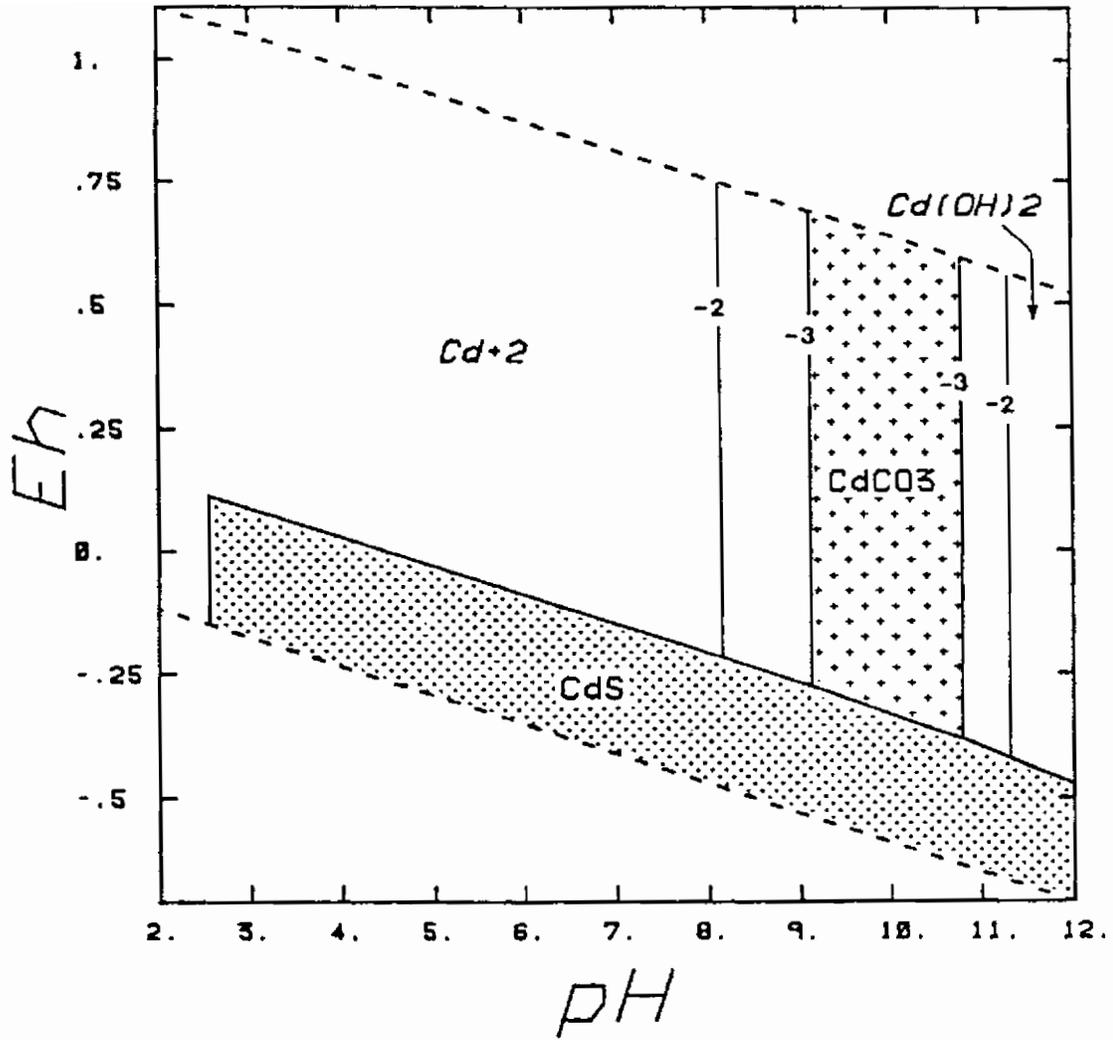


Figure 19. Eh-pH diagram for the system Cd-O₂-CO₂-S-H₂O for $\Sigma\text{Cd} = 10^{-7}$ mol/kg, $\Sigma\text{S} = 10^{-5}$ mol/kg, and total carbonate 10^{-2} and 10^{-3} mol/kg. From Barnes and Langmuir, 1978.

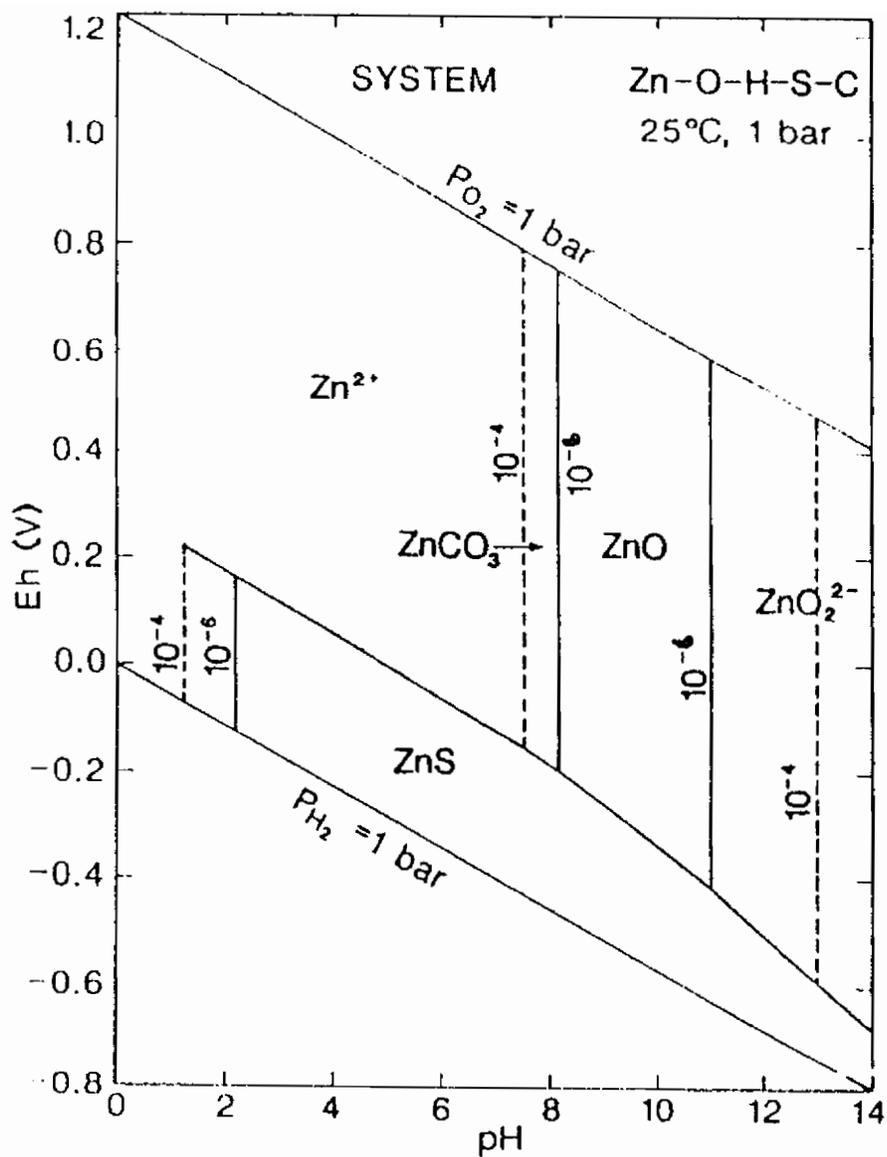


Figure 20. Eh-pH diagram for the system Zn-O₂-CO₂-S-H₂O, assuming that $\Sigma Zn = 10^{-6}$ and 10^{-4} mol/kg, $\Sigma C = 10^{-3}$ mol/kg, and $\Sigma S = 10^{-3}$ mol/kg. After Brookins, 1988.

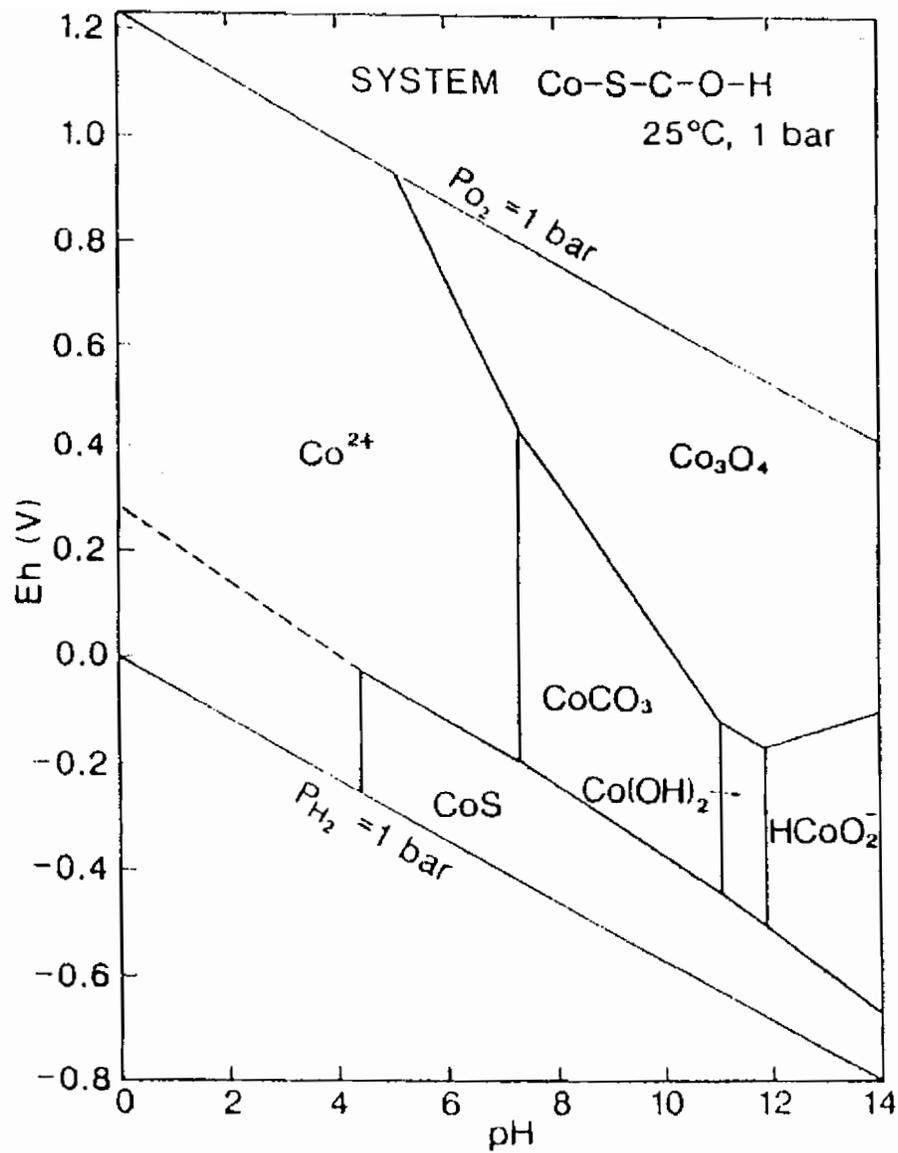


Figure 21. Eh-pH diagram for the system Co-O₂-CO₂-S-H₂O, assuming that $\Sigma Co = 10^{-6}$ mol/kg, $\Sigma C = 10^{-3}$ mol/kg, and $\Sigma S = 10^{-3}$ mol/kg. After Brookins, 1988.

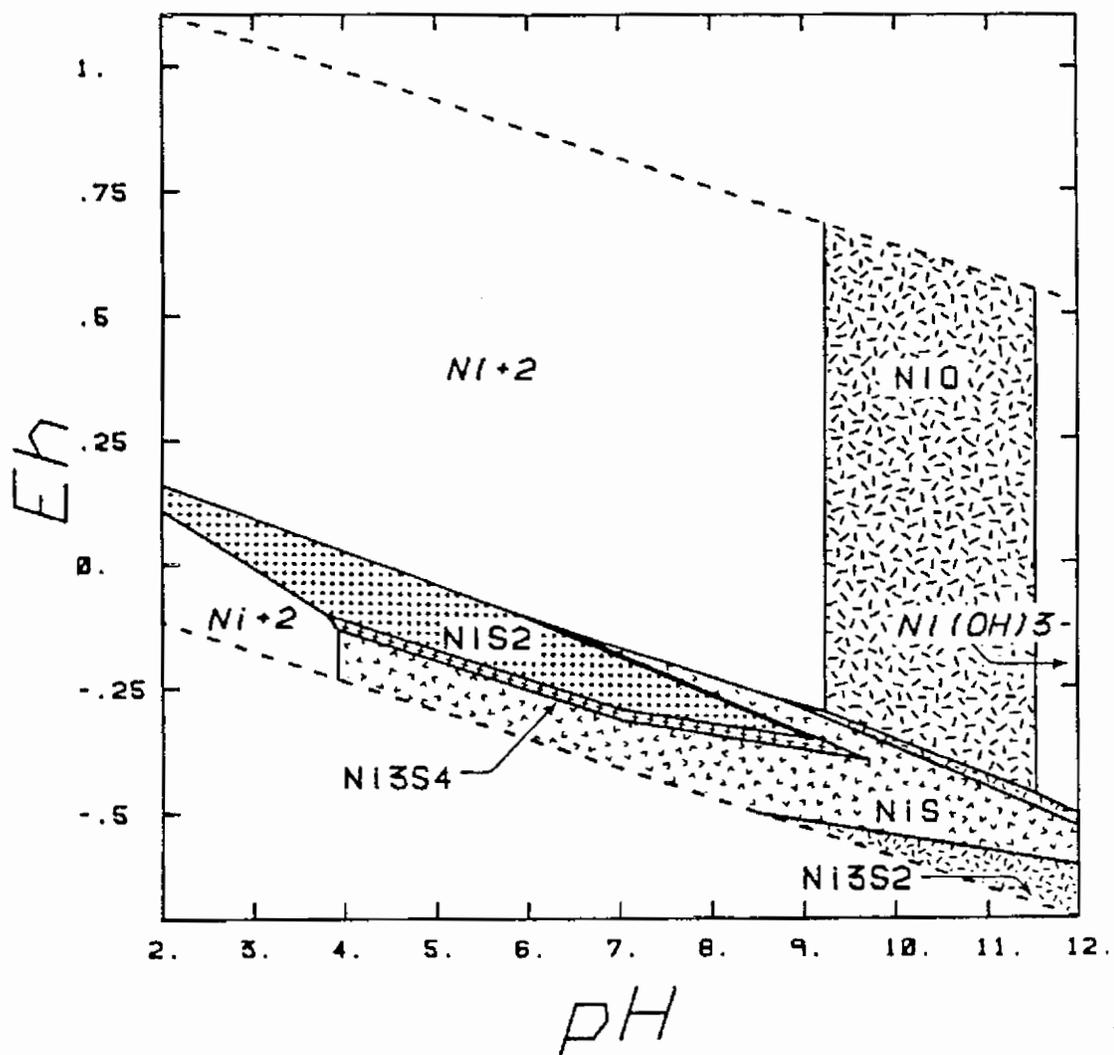


Figure 22. Eh-pH diagram for the system Ni-O₂-CO₂-S-H₂O, assuming that $\Sigma\text{Ni} = 10^{-6}$ mol/kg and $\Sigma\text{S} = 10^{-5}$ mol/kg. After Barnes and Langmuir, 1978.

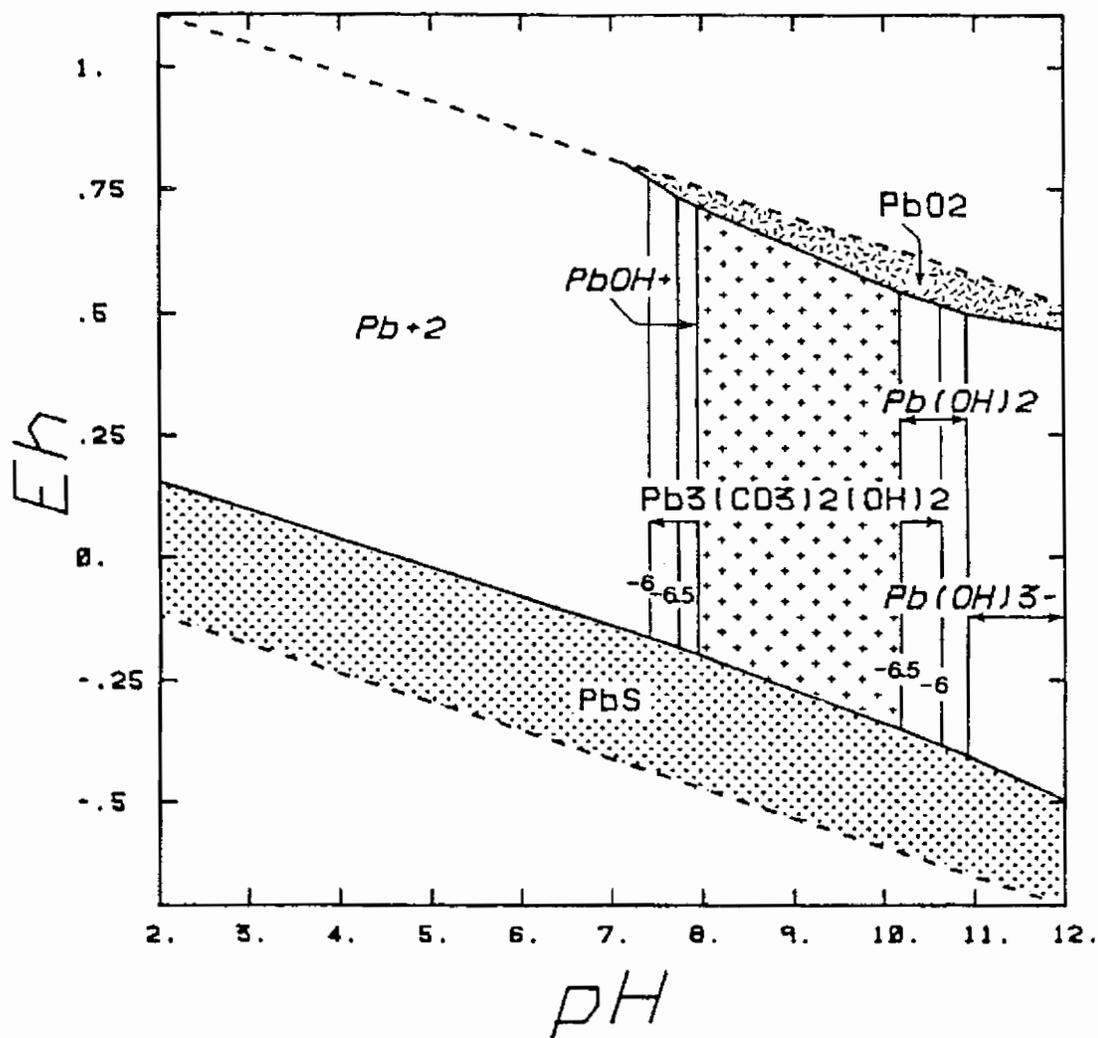


Figure 23. Eh-pH diagram for the system Pb-O₂-CO₂-S-H₂O, assuming that $\Sigma\text{Pb} = 10^{-6}$ and $10^{-6.5}$ mol/kg, $\Sigma\text{C} = 10^{-4}$ mol/kg, and $\Sigma\text{S} = 10^{-5}$ mol/kg. Diagram shows the stability fields of lead hydroxycarbonate and galena (PbS). After Barnes and Langmuir, 1978.

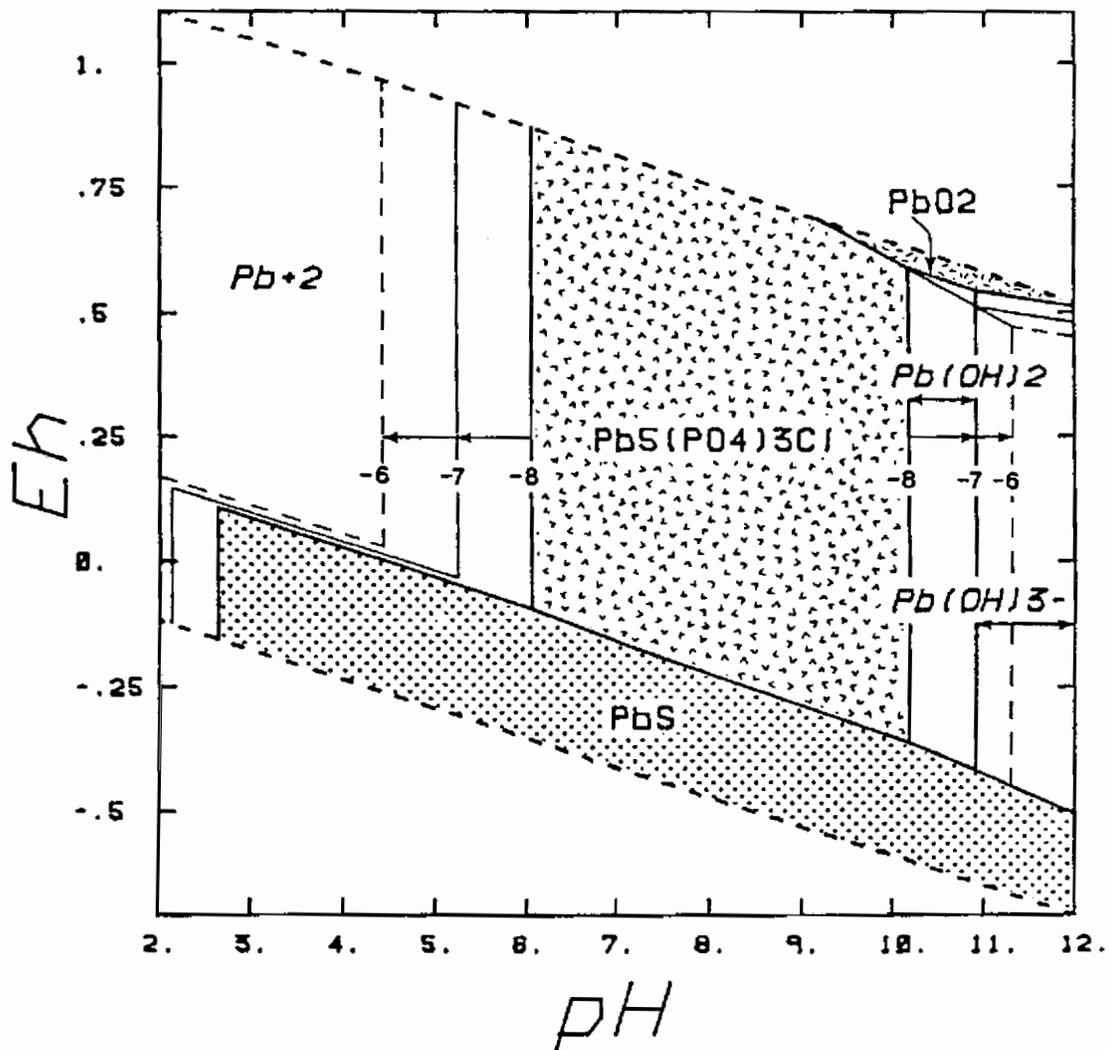


Figure 24. Eh-pH diagram for the system Pb-O₂-PO₄-S-H₂O, assuming that $\Sigma\text{Pb} = 10^{-8}$, 10^{-7} , and 10^{-6} mol/kg at solid/liquid boundaries; $\Sigma\text{S} = 10^{-5}$ mol/kg; and $\Sigma\text{PO}_4 = 10^{-6}$ mol/kg. Diagram shows the stability fields of the lead phosphate, pyromorphite, and galena (PbS). After Barnes and Langmuir, 1978.

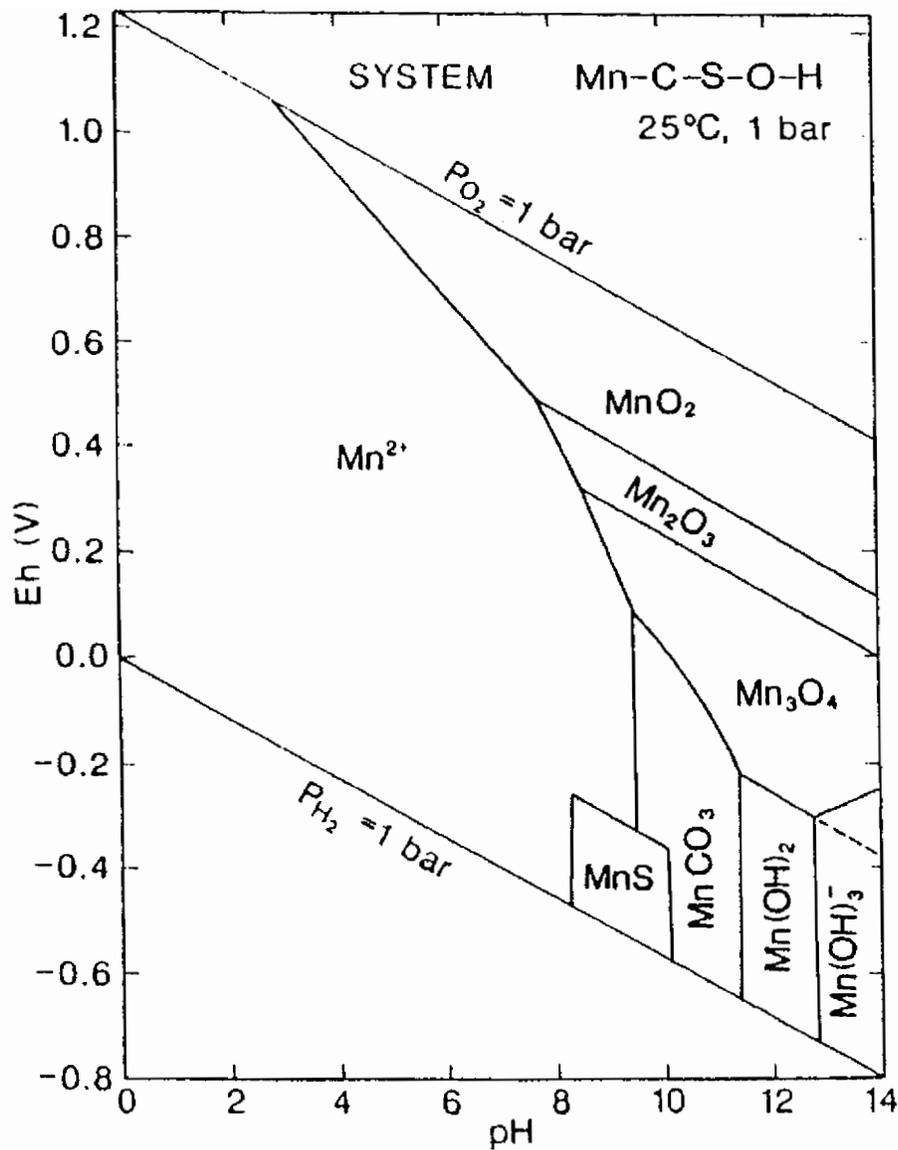


Figure 25. Eh-pH diagram for the system Mn-O₂-CO₂-S-H₂O, assuming that $\Sigma Mn = 10^{-6}$ mol/kg, $\Sigma C = 10^{-3}$ mol/kg, and $\Sigma S = 10^{-3}$ mol/kg. MnS is the very rare mineral alabandite. After Brookins, 1988.

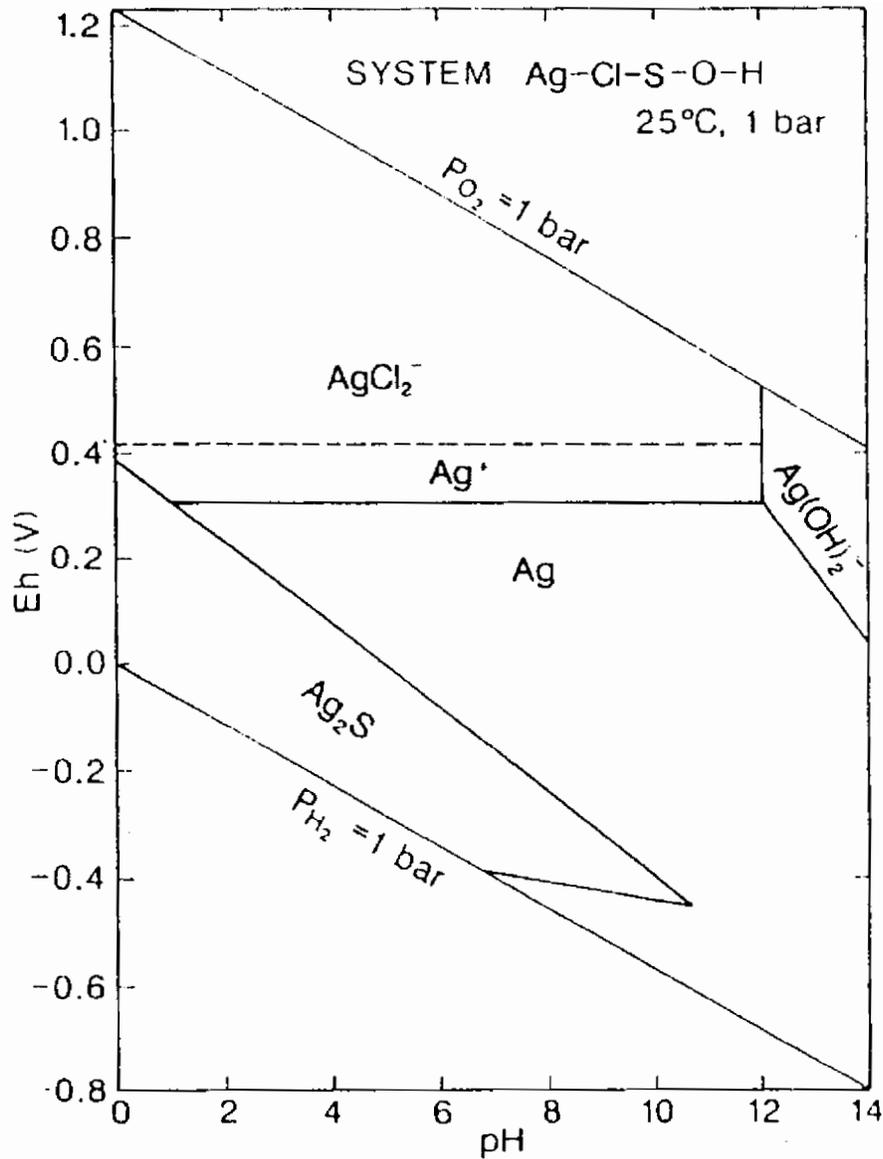


Figure 26. Eh-pH diagram for the system Ag-O₂-Cl-S-H₂O, assuming that $\Sigma Ag = 10^{-8}$ mol/kg, $\Sigma Cl = 10^{-3.5}$ mol/kg, and $\Sigma S = 10^{-3}$ mol/kg. Diagram shows the importance of Ag chloride complexing and the large stability field for metallic silver. After Brookins, 1988.

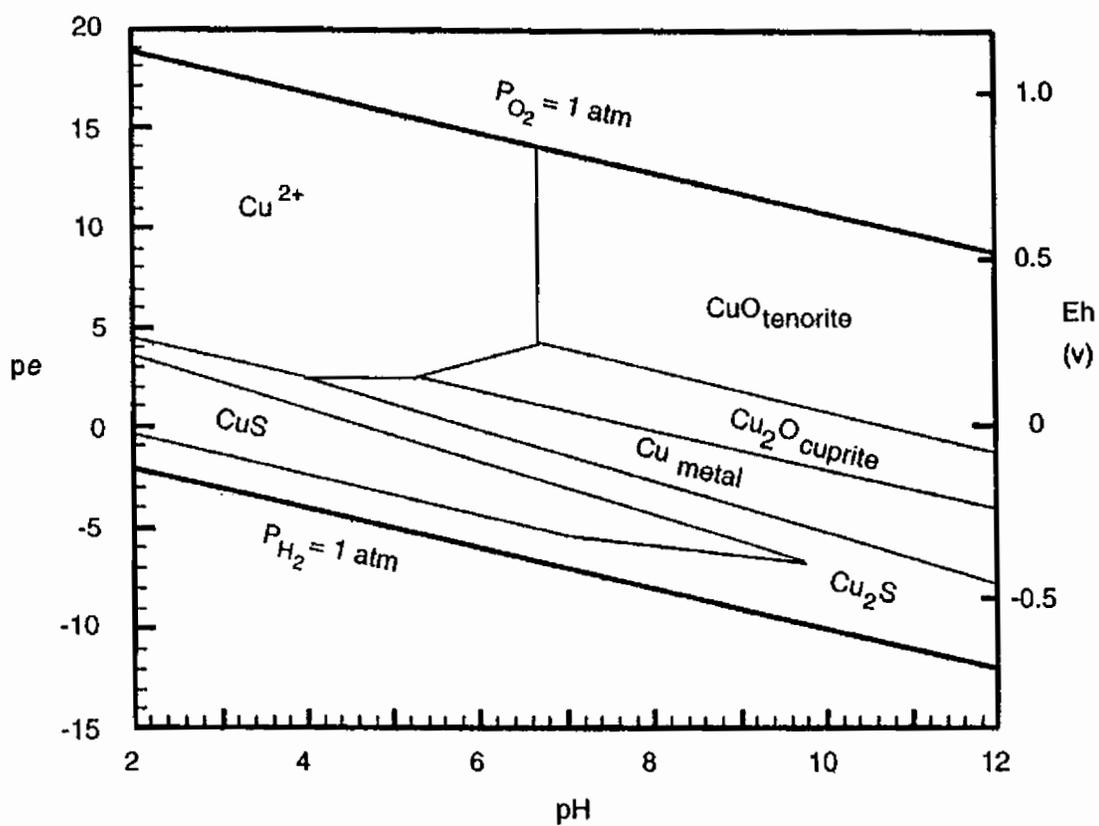


Figure 27. Eh-pH diagram for the system Cu-O₂-S-H₂O, assuming that $\Sigma\text{Cu} = 10^{-6}$ mol/kg and $\Sigma\text{S} = 10^{-2}$ mol/kg. After Drever, 1997.

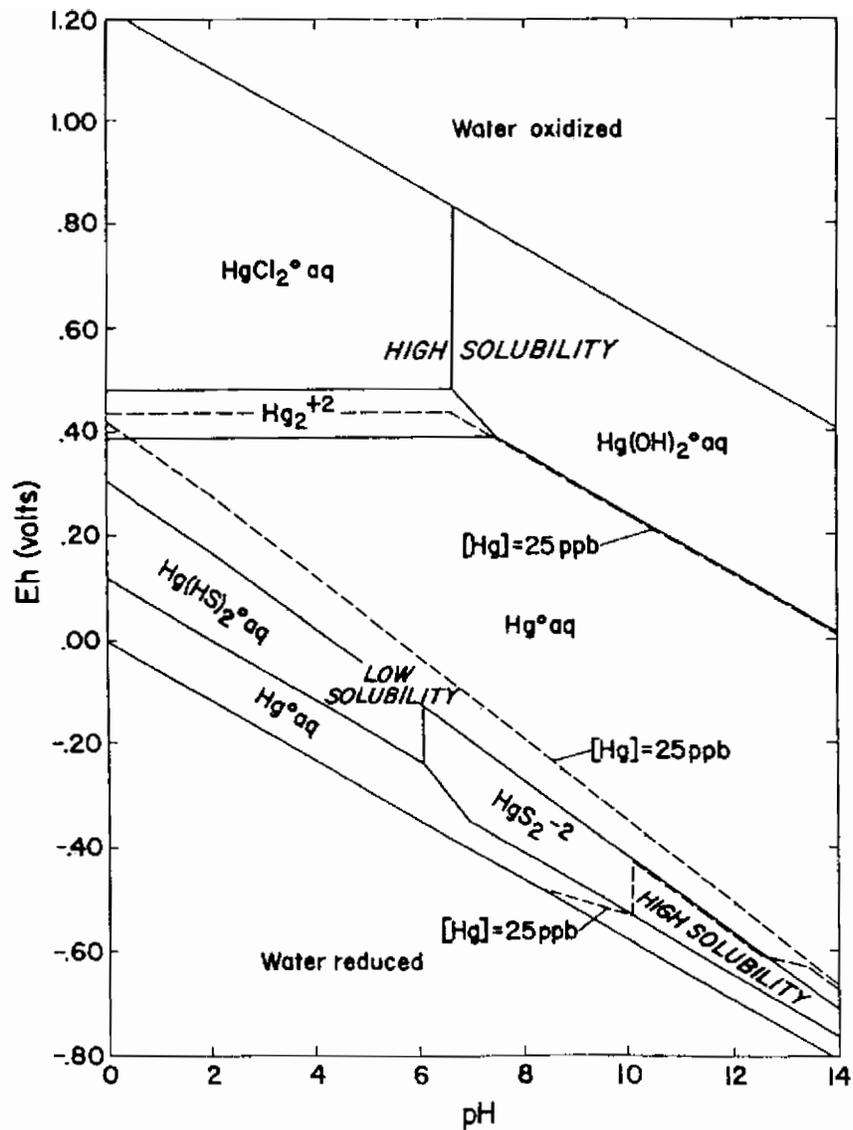


Figure 28. Eh-pH diagram for the system Hg-O₂-Cl-S-H₂O, assuming that $\Sigma\text{Hg} = 10^{-6.9}$ mol/kg, $\Sigma\text{Cl} = 10^{-3}$ mol/kg, and $\Sigma\text{S} = 10^{-3}$ mol/kg. Diagram shows the importance of Hg-Cl complexing. After Bodek et al., 1988.

Mercury is biologically methylated only in environments low in sulfide. The stable methyl mercury species in fresh waters is CH_3HgOH . The methyl mercury cation, CH_3Hg^+ , complexes with ligands containing C, P, O, N, and the halogens, and forms very stable complexes with sulfur-containing ligands. In oxidized, fresh waters the Hg(II) methyl hydroxo and methyl chloro complexes dominate. As is copper.

Mercury and copper are strongly adsorbed by organic matter. All three metals are also strongly adsorbed by Fe(III) and Mn oxides, and secondarily by clays. Sorption of mercury is very fast and practically irreversible (Bodek et al., 1988). By inhibiting mercury sorption, Hg-Cl complexing helps to mobilize the metal. Dimethyl mercury is very insoluble in water and tends to be volatilized from soils.

6.2.6 Thallium

In oxidizing environments, dissolved thallium is limited to concentrations of less than 2 $\mu\text{g/L}$ (10^{-8} mol/L) by the low solubilities of the thallium 4+, 3+ and 2+ oxides (Fig. 29). The solubility product of Tl(OH)_3 , which should be more soluble than Tl_2O_3 in Figure 29, is $10^{-45.2}$, which makes this phase highly insoluble between pH 4 and 10. Only in highly reducing systems as Tl^+ is the metal soluble. Tl^+ is a weak complex former. The sulfide of Tl^+ is stable only above pH 12. Limited data indicate that Tl is strongly adsorbed by montmorillonite clays and manganese oxides (Bodek et al., 1988).

6.2.7 Arsenic, Antimony, Chromium, Molybdenum, Selenium, and Vanadium

These six elements occur chiefly as oxyanions in oxidizing environments. As such they are relatively mobile, although they are adsorbed by ferrihydrite under acid to neutral conditions. Consistent with Figure 7, on a number of different sorbent phases, the decreasing order of adsorption is usually $\text{As} > \text{Cr} \geq \text{Mo} \geq \text{Se} \approx \text{S}$ (Bodek et al., 1988). Arsenic and phosphorus chemistry are similar under oxidizing but not reducing conditions. Figure 30 shows the stability fields of dissolved As(V) and As(III) species in pure water. With the addition of sulfur, insoluble As sulfide minerals are precipitated at low Eh (Figure 31) in the field otherwise occupied by arsenious acid species.

As suggested by the absence of a solid phase field in Figure 32, antimony may be too soluble for its concentration to be limited by mineral precipitation. The least soluble Sb phase is probably Sb(OH)_3 , which does not precipitate until ΣSb concentrations exceed about $10^{-6.67}$ mol/kg, or 26 $\mu\text{g/L}$ (Barnes and Langmuir, 1978). Antimony is a weak complex former, except for its reaction with sulfur at low Eh to form sulfide complexes.

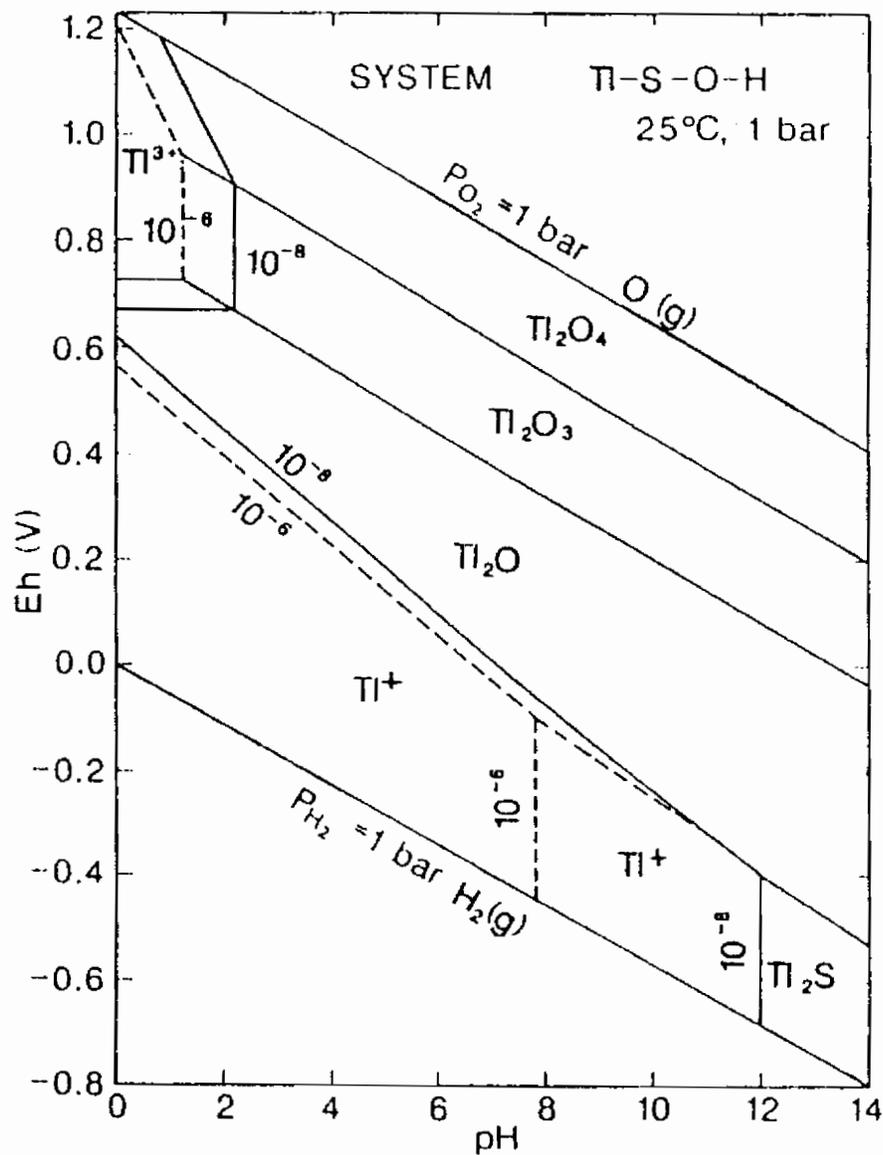


Figure 29. Eh-pH diagram for the system Ti-O₂-S-H₂O, assuming that $\Sigma Ti = 10^{-8}$ and 10^{-6} mol/kg and $\Sigma S = 10^{-3}$ mol/kg. The diagram shows the insolubility of the higher-valent Ti oxides under oxidizing conditions. After Brookins, 1988.

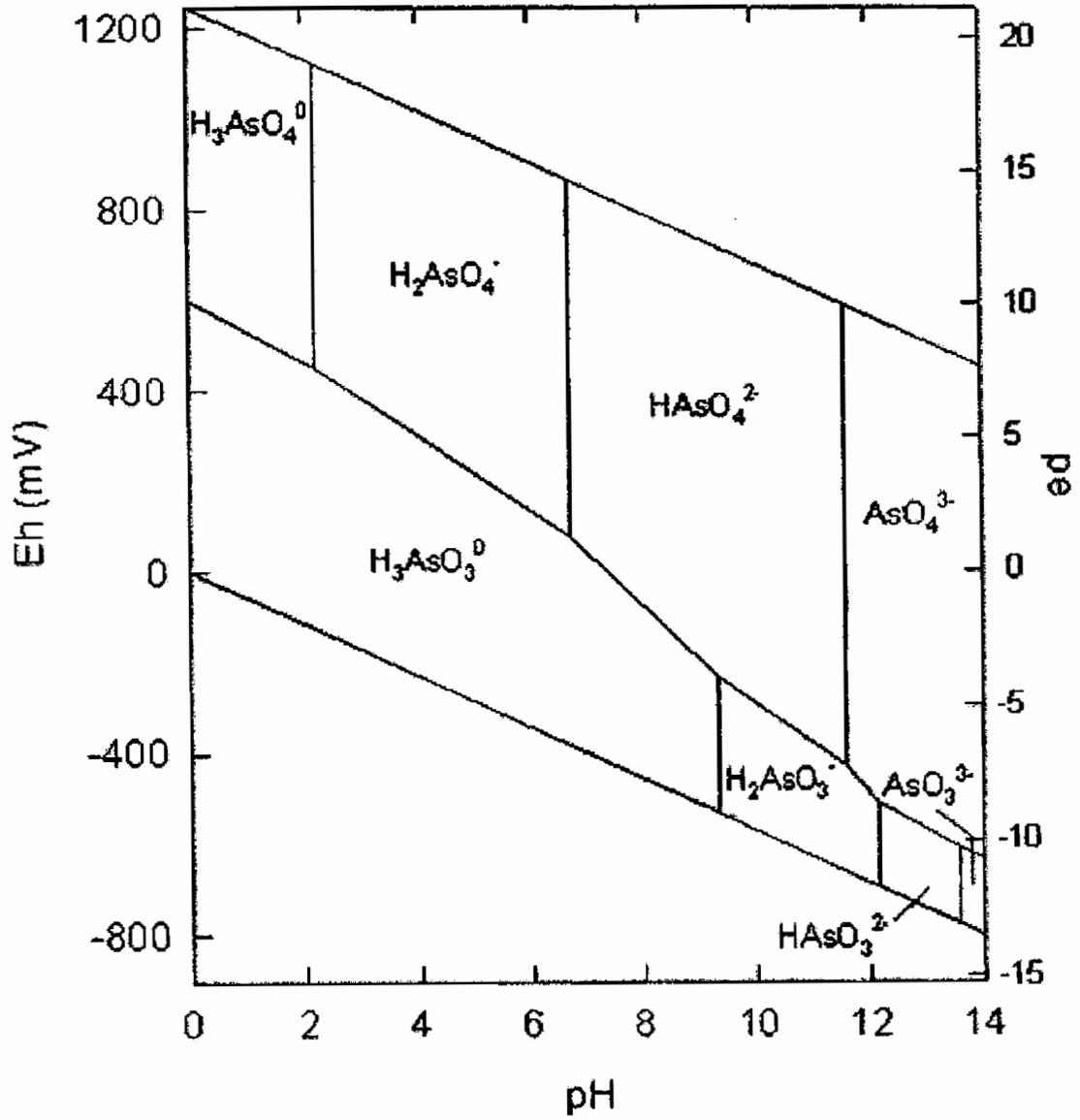


Figure 30. Eh-pH diagram for the system As-O₂-H₂O showing the relative stabilities of arsenate (arsenic acid, As[V]) and arsenite (arsenious acid, As[III]) species under oxidizing and reducing conditions.

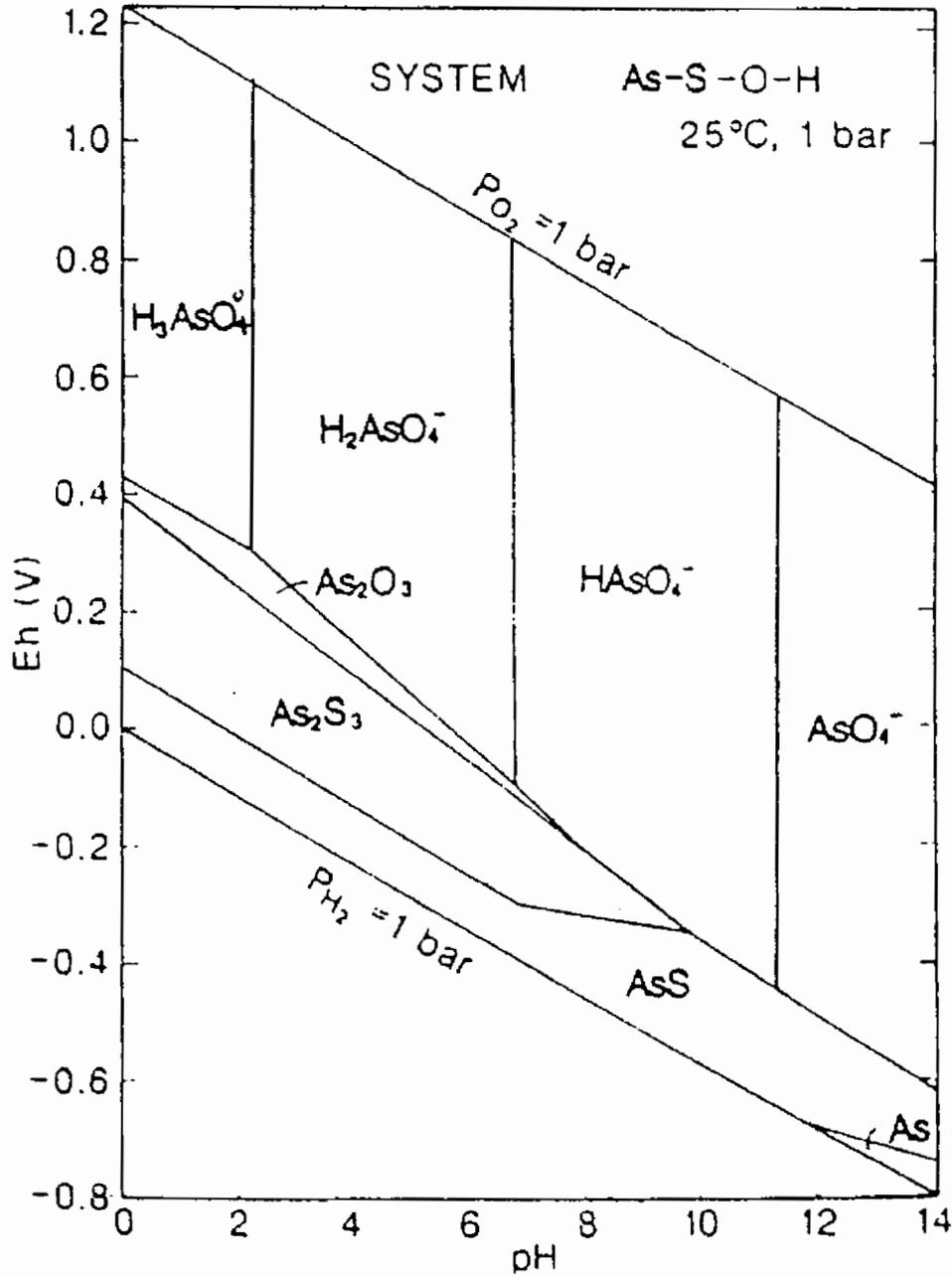


Figure 31. Eh-pH diagram for the system As-O₂-S-H₂O, assuming that $\Sigma As = 10^{-6}$ mol/kg and $\Sigma S = 10^{-3}$ mol/kg. The diagram shows that in the presence of reduced S, the As sulfides control As solubility and take over the stability field of dissolved As(III) species in Figure 26. After Brookins, 1988.

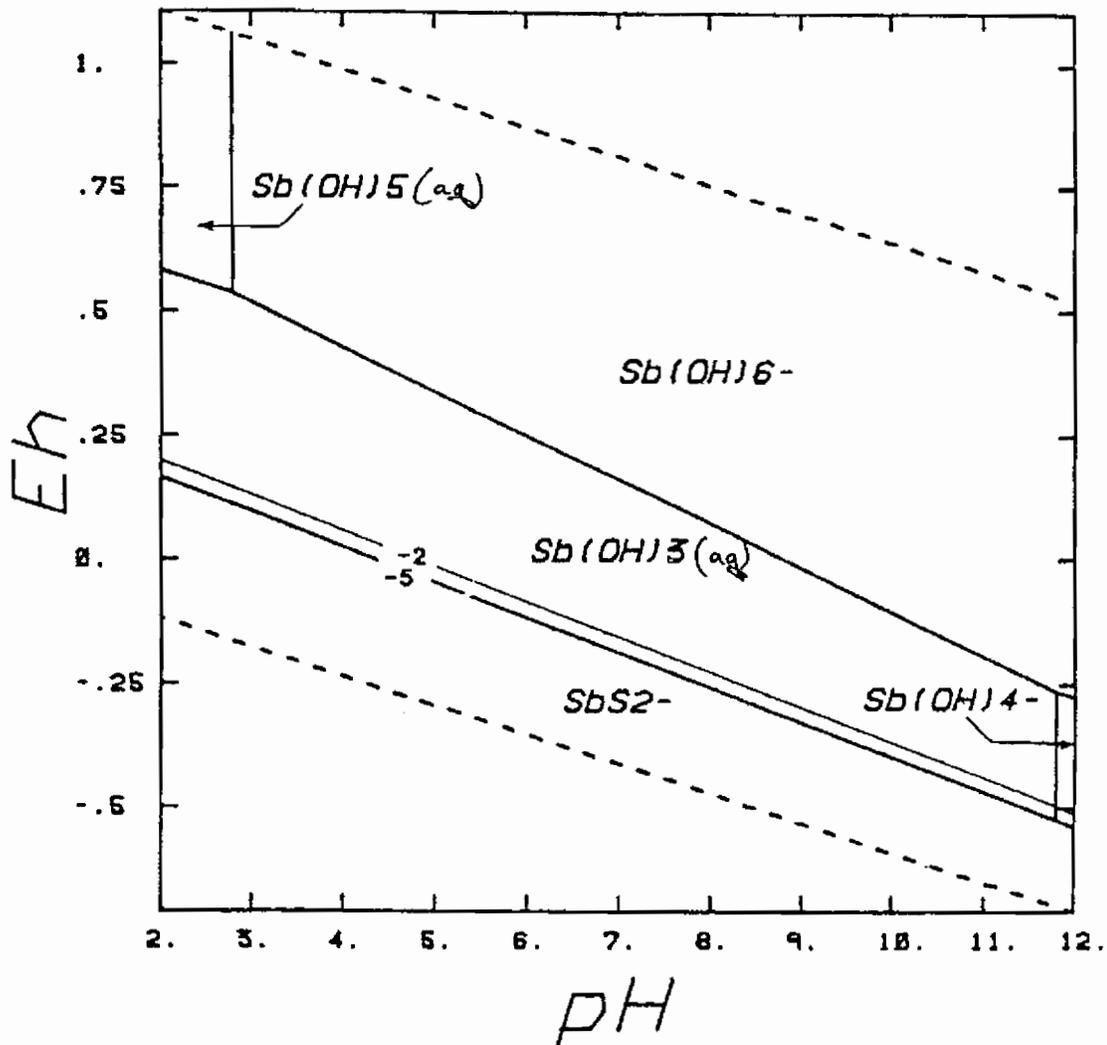


Figure 32. Eh-pH diagram for the system Sb-O₂-S-H₂O, assuming that $\Sigma\text{Sb} = 10^{-8}$ mol/kg and $\Sigma\text{S} = 10^{-2}$ and 10^{-5} mol/kg. After Barnes and Langmuir, 1978.

Chromate (Cr(VI)) species (Figure 33) predominate and are highly mobile in oxidized systems, except for their tendency to be adsorbed, particularly by Fe(III) and Mn oxides below pH 8. Chromate is in general weakly complexed. In contrast, Cr(III), which dominates in reducing environments, is a strong, hard-acid complex former. Cr(III) complexes with hydroxyl, sulfate, organic ligands, and other species, which increases its stability and thus raises the Cr(III)/Cr₂O₃ boundary to higher pH values. This increases the solubility of Cr₂O₃. Organic matter, Fe²⁺, and H₂S can reduce Cr(VI) to Cr(III). Manganese oxides in soil can adsorb Cr(III) and oxidize it to Cr(VI). As shown in Figure 7, adsorption of chromate by HFO decreases with increasing pH, whereas Cr(III) adsorption increases as the pH rises.

Molybdate is highly mobile in oxidized environments (Figure 34), except for its tendency to be adsorbed by Fe(III) oxides below pH 7. Also under acid conditions, in soils and waters high in Fe(III), molybdate may precipitate as ferrimolybdite (Fe₂[MoO₄]₃[s]), which is stable up to pH 5 for $\Sigma\text{Fe(III)} = \Sigma\text{Mo} = 10^{-6}$ mol/kg (Barnes and Langmuir, 1978). Under reducing conditions, Mo is immobilized by the low solubility of the Mo oxides and MoS₂.

The redox behavior of selenium (Figure 35) is similar to that of sulfur (Figure 15) in that (1) Se(VI) oxyanions predominate under oxidizing conditions, (2) the element has a stability field under reducing conditions, and (3) metal cations react with Se(2-) to form insoluble selenides. Selenate is highly stable and not readily reduced by H₂S or Fe²⁺. The very low solubility of native Se indicates that it is an important sink for dissolved Se in reducing environments. Se(2-) forms very insoluble metal selenides with the following -log K_{sp} values: 26.0 (FeSe), 60.8 (Cu₂Se), 48.1 (CuSe), 29.4 (ZnSe), 35.2 (CdSe), 64.5 (HgSe), and 42.1 (PbSe) (Bodek et al., 1988).

Selenite salts are less soluble than selenate salts. Selenite and selenate are both strongly adsorbed by the Fe and Al oxyhydroxides. Phosphate and sulfate effectively compete with selenite and selenate for sorption sites on Fe oxides.

Like chromium, vanadium occurs as an oxyanion at high Eh values and in cationic form under reducing conditions (Figure 36). Vanadate probably forms an insoluble precipitate with Fe(III) below pH 7, although the evidence is limited. The V(III) and Fe(III) oxides are isostructural, suggesting that V(III) may substitute for Fe(III) in the iron oxides (Rai et al., 1984). A problem with this idea is the low Eh stability of V(III) versus the higher Eh stability of the Fe(III) oxides. In soils, the distribution of V closely follows that of secondary Fe(III) oxides, probably because of V adsorption by the oxides. Vanadium is readily reduced and mobilized by soil organic matter, even under oxidizing conditions.

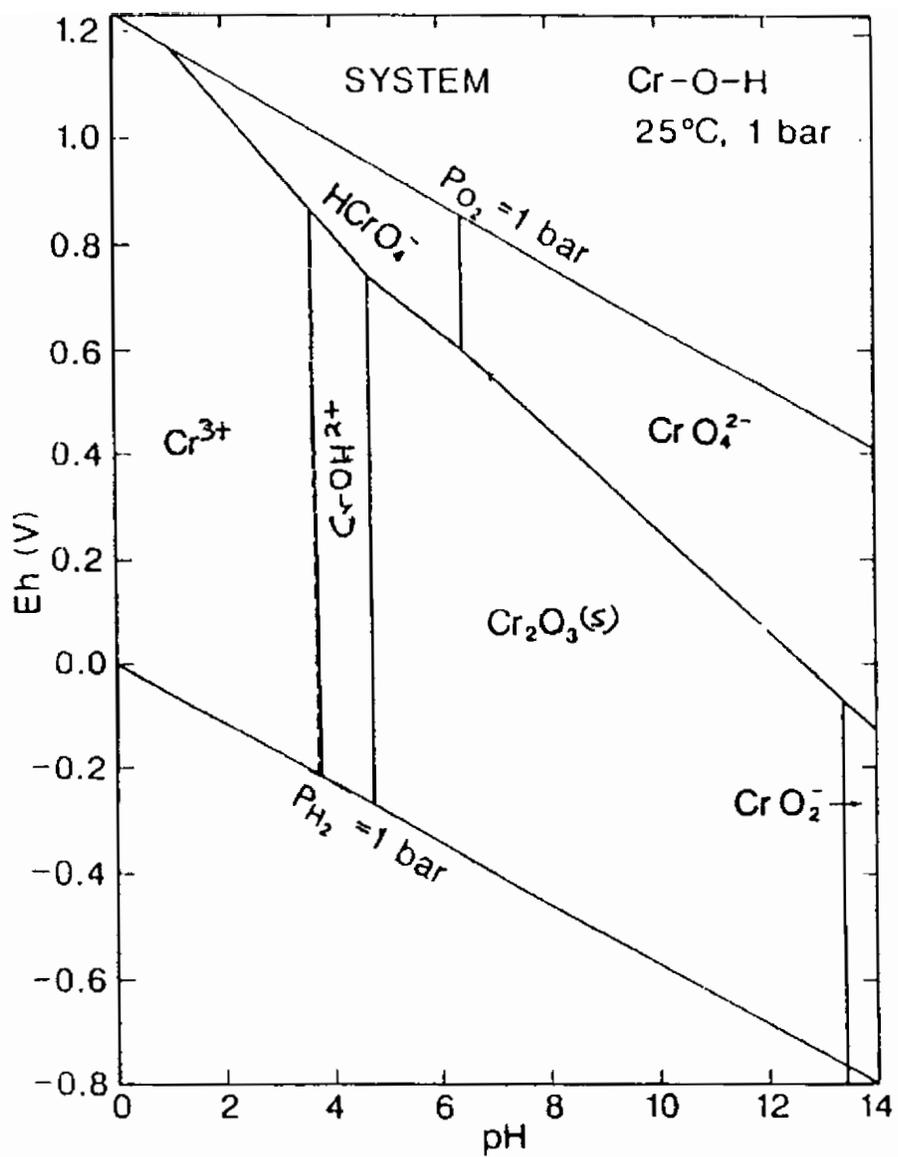


Figure 33. Eh-pH diagram for the system Cr-O₂-H₂O, assuming that the concentration of $\Sigma Cr = 10^{-6}$ mol/kg at solid/liquid boundaries. After Brookins, 1988.

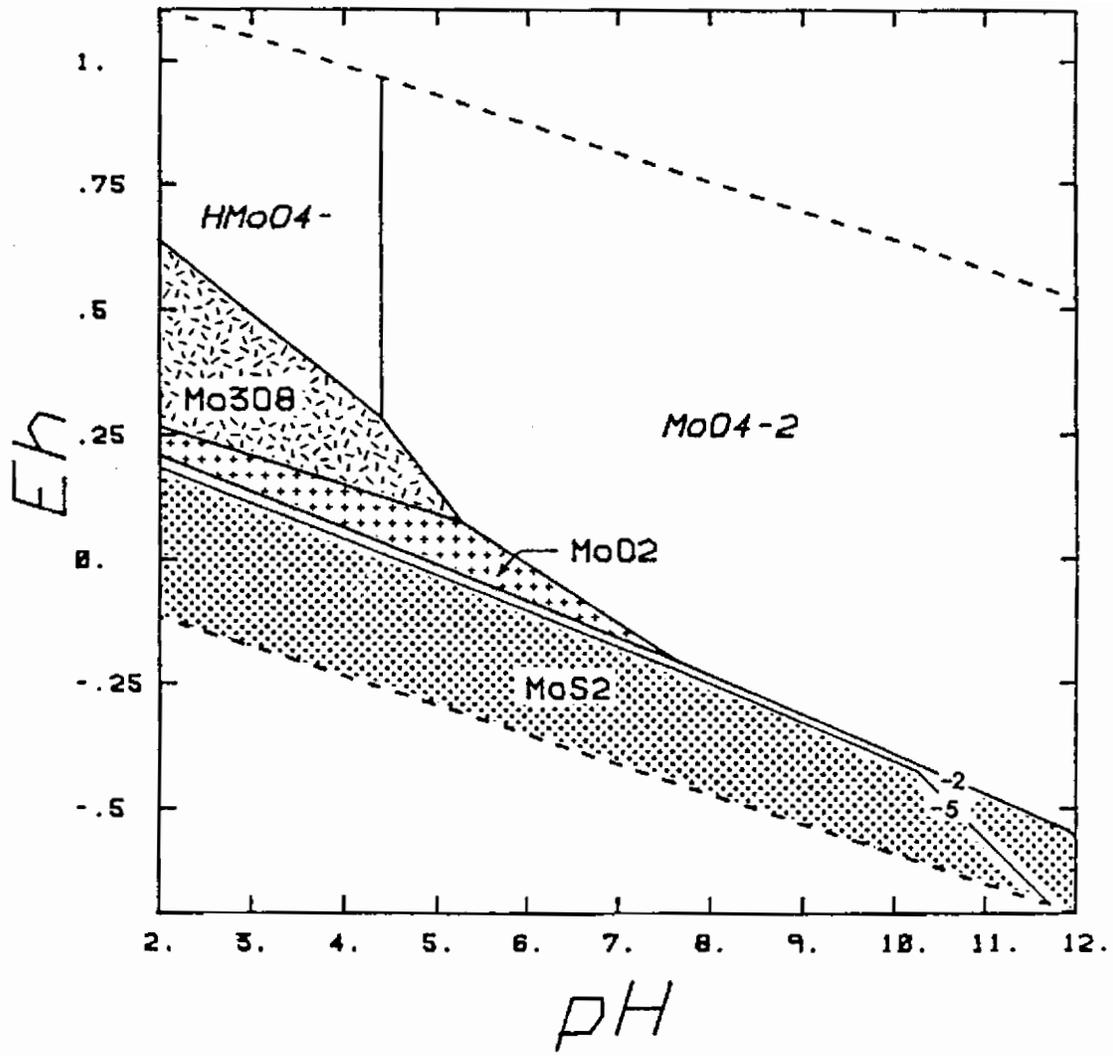


Figure 34. Eh-pH diagram for the system Mo-O₂-S-H₂O, assuming that $\Sigma\text{Mo} = 10^{-6}$ mol/kg and $\Sigma\text{S} = 10^{-2}$ and 10^{-5} mol/kg. After Barnes and Langmuir, 1978.

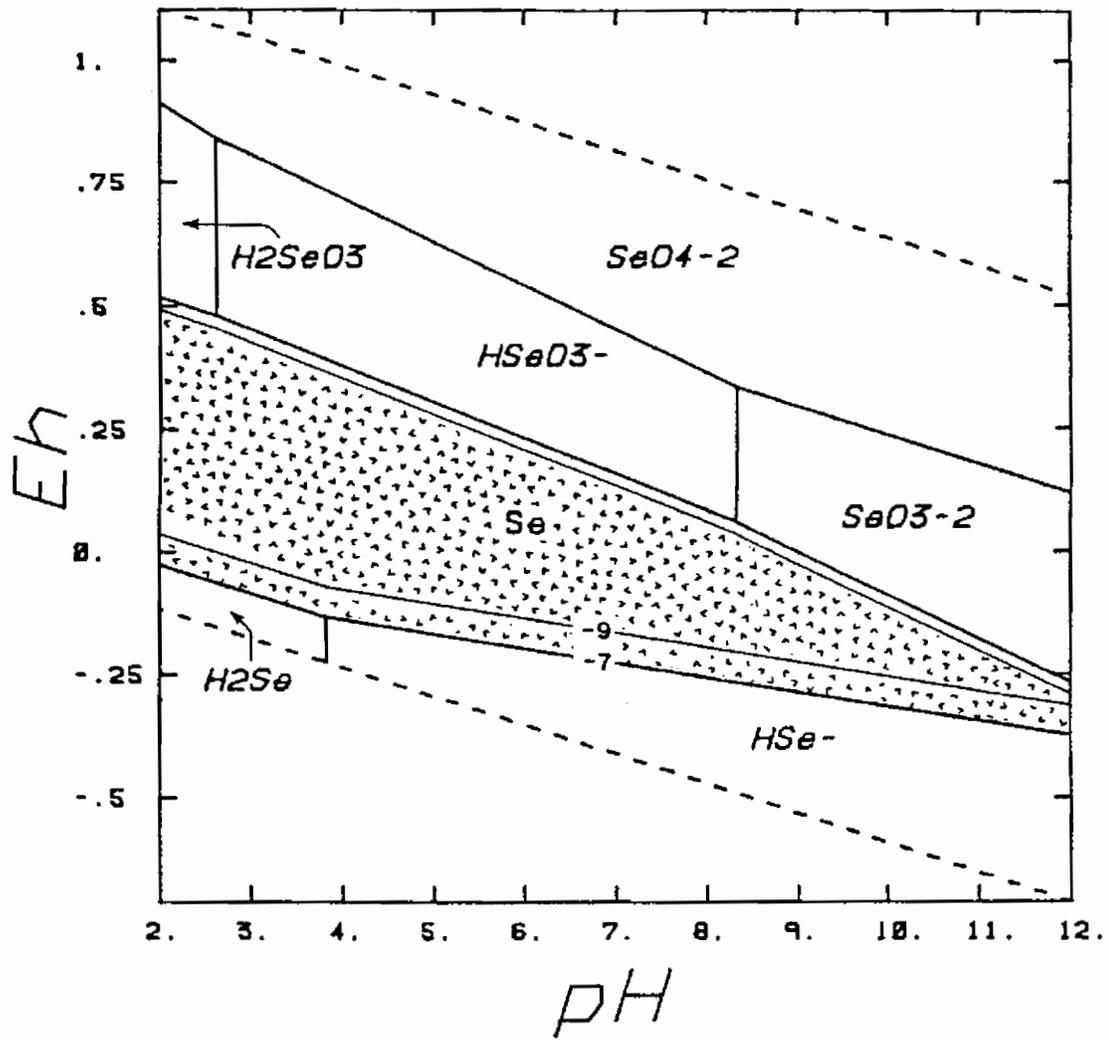


Figure 35. Eh-pH diagram for the system Se-O₂-H₂O. Solid/liquid boundaries drawn for $\Sigma\text{Se} = 10^{-7}$ and 10^{-9} mol/kg. After Barnes and Langmuir, 1978.

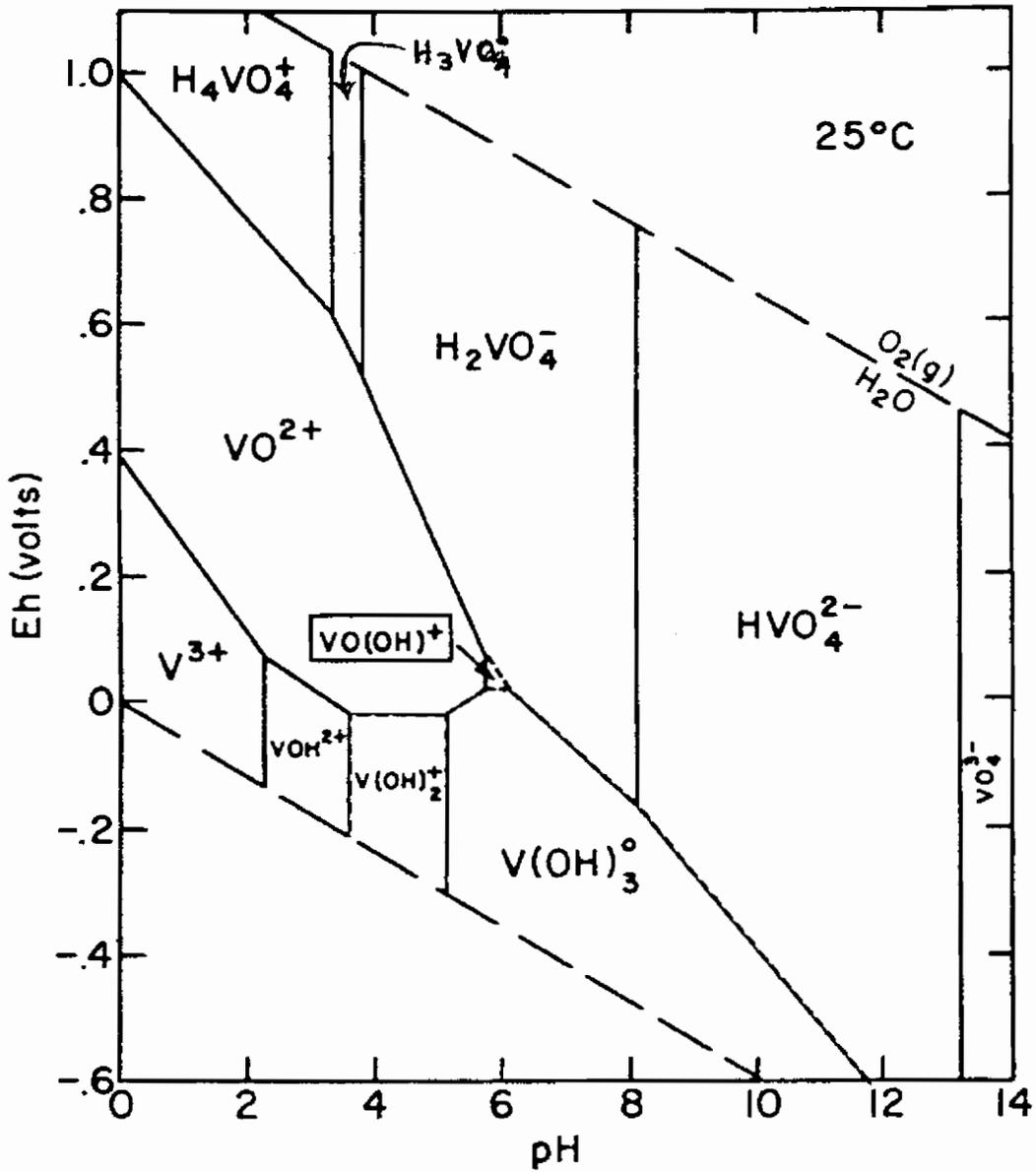


Figure 36. Eh-pH diagram for the system V-O₂-H₂O, for dissolved $\Sigma V < 10^{-4}$ mol/kg (11.5 mg/L as VO₄). After Langmuir, 1978.

7. SOIL TRACE METAL TRANSFER TO PLANTS AND THE BIOAVAILABILITY OF SOIL-METALS

The potential risk that trace elements in soils pose to the feed- and food-chain has been intensively examined during the last 35 years. One purpose of that investigation has been to understand the risk from application of biosolids (municipal sewage sludge) and other metal contamination sources to soil.

During this period, the “soil-plant barrier” concept was introduced to communicate how metal addition, soil chemistry, and plant chemistry affected the risk to animals from metals mixed in soil (Chaney, 1980). Reactions and processes that take place at the soil-plant barrier are influenced by the following: (1) solid metal sources (e.g., Fe, Al, and Mn oxyhydroxides and organic matter) may have adsorptive surfaces that influence soil chemistry; (2) adsorption or precipitation of metals in soils or in roots limits uptake-translocation of most elements to shoots; (3) the phytotoxicity of Zn, Cu, Ni, Mn, As, B, Al, F, etc., limits residues of these elements in plant shoots to levels chronically tolerated by livestock and humans; and (4) food-chain transfer of an element may not constitute a risk, but the direct ingestion of the contaminated soil may.

A summary of metal tolerances by plants and livestock is presented in Table 13. It should be noted that the NRC (1980) committee which identified the maximum levels of metals tolerated by domestic livestock based its conclusions on data from toxicological-type feeding studies in which soluble metal salts had been mixed with practical or purified diets to examine animal response to the dietary metals. If soil is incorporated into diets, metal solubility and bioavailability may be much more limited than in the tests relied on by NRC (1980). For example, it has been noted that until soil exceeds about 300 mg Pb kg⁻¹, animals show no increased body burden from ingesting the soil (Chaney and Ryan, 1993). Other metals in equilibrium with poorly soluble minerals or strongly adsorbed in soils are often much less bioavailable than they would be if they occurred in more soluble salts.

The chemistry of metals in soils is affected by the presence of ions which can cause precipitation of the metal, organic matter and sesquioxides which can adsorb metals, redox changes which affect the chemical species of the metal present, and similar factors discussed in the section about water chemistry. Soils are usually in a relatively restricted pH range of 5.5 to 8 for high-producing soils, and as wide as 4 to 9 in nearly all soils in the general environment. Industrial contamination with acids or bases can cause lower and higher pH than this practical natural pH range: as low as pH 2 and as high as pH 11. Usually, such contaminated soils are barren due to infertility or phytotoxicity of soil elements affected by extreme pH.

Many elements (e.g., Si, Ti, Fe, Pb, Hg, Al, Cr³⁺, Ag, Au, Sn, Zr, and other elements that serve as a label for soil contamination of plants and diets [Y]) are so insoluble in oxidized soils between pH 5.5 and 8 that they are not a risk even when soils with relatively high concentrations are ingested by livestock. When present at very high concentrations, elements that may pose a

risk because of absorption in the intestine when contaminated soils are ingested include F, Pb, As, and Zn. This process is also important for animals that consume soil biota such as earthworms. The earthworm is consumed without depuration on internal soil, giving exposure to high levels of dietary soil—perhaps 35% of dry weight.

Table 13. Maximum Tolerable Levels of Dietary Minerals for Domestic Livestock in Comparison With Levels in Forages

Element	“Soil-Plant Barrier”	Level in Plant Foliage ^a		Maximum Levels Chronically Tolerated ^b			
		Normal	Phytotoxic	Cattle	Sheep	Swine	Chicken
		mg/kg ⁻¹ dry foliage		mg/kg ⁻¹ dry diet			
As, inorg.	Yes	0.01-1.0	3-10	50	50	50	50
B	Yes	7-75	75	150	(150)	(150)	(150)
Cd ^c	Fails	0.1-1	5-700	0.5	0.5	0.5	0.5
Cr ³⁺	Yes	0.1-1	20	(3,000)	(3,000)	(3,000)	3,000
Co	Fail?	0.01-0.3	25-100	10	10	10	10
Cu	Yes	3-20	25-40	100	25	250	300
F	Yes?	1-5	-	40	60	150	200
Fe	Yes	30-300	-	1,000	500	3,000	1,000
Mn	?	15-150	400-2,000	1,000	1,000	400	2,000
Mo	Fails	0.1-3.0	100	10	10	20	100
Ni	Yes	0.1-5	50-100	50	(50)	(100)	(300)
Pb ^c	Yes	2-5	-	30	30	30	30
Se	Fails	0.1-2	100	(2)	(2)	2	2
V	Yes?	0.1-1	10	50	50	(10)	10
Zn	Yes	15-150	500-1,500	500	300	1,000	10,00

^aBased on literature summarized in Chaney et al., 1983.

^bBased on NRC, 1980. Continuous long-term feeding of minerals at the maximum tolerable levels may cause adverse effects. NRC estimated the levels in parentheses by extrapolating between animal species when data were not available for an animal.

^cNRC based the maximum levels tolerated of Cd or Pb in liver, kidney, and bone in foods for humans rather than simple tolerance by the animals. Because of the simultaneous presence of Zn, Cd in animal tissues is less bioavailable than Cd salts added to diets.

Freshly applied metal salts are not in equilibrium with soil and have a greater phytoavailability than they would exhibit upon equilibrating with the soil over time. The phytoavailability and bioavailability of metals may also be reduced if the metals are adsorbed, chelated, or precipitated before ingestion by children or grazing livestock.

An example of the interaction phenomenon is the toxicity of biosolids or manure-applied Cu or Zn to animals. Cu-deficiency-stressed animals are more sensitive to dietary Zn than animals fed Cu-adequate diets, but biosolids-fertilized crops are not low in Cu, so ordinarily Zn phytotoxicity protects all livestock, including the most sensitive ruminants. Similarly, Cu toxicity to sensitive ruminant animals is substantially reduced by increased dietary levels of Zn, Cd, Fe, Mo, and SO₄ or sorbents such as soil organic matter. In contrast with the predicted toxicity from Cu in ingested swine manure or biosolids, reduced Cu absorption has been observed unless ingested biosolids exceed about 1,000 milligrams Cu kg⁻¹ or manure is fed at 50% of diet.

An important interaction which reduces risk from Cd is the normal 1 Cd:100 Zn ratio of geogenic Cd. Although culture of crops in strongly acidic soils allows uptake of increased levels of Cd and Zn, the presence of Zn in the crops inhibits uptake of Cd. Because Cd and Zn are taken up from acidic soils at about the ratio of the total metals in the soil, Zn phytotoxicity (at 500 mg Zn kg⁻¹) serves as a natural maximal limit on crop Cd, and plant (intrinsic) Zn inhibits absorption of plant Cd in animals. These factors very significantly reduce soil Cd risk compared to risks observed in toxicological studies that tested risks from Cd salts.

The potential for plant uptake to allow metals to be transferred to feed- and food-chains has been extensively studied. Uptake slopes measured in pot studies are much higher than those found in the field, so greenhouse or growth chamber studies cannot be used to estimate environmentally relevant uptake slopes. Unfortunately, only a small fraction of the valid field studies were conducted under poor management conditions rather than recommended “Best Management Practices.” It is very clear that strongly acidic soils increase plant uptake of Zn, Cd, Ni, Mn, and Co, and increase the potential for phytotoxicity from Cu, Zn, and Ni. Alkaline soil pH increases uptake of Mo and Se, while Pb and Cr are not absorbed to any significant extent at any pH (Chaney and Ryan, 1993).

For the strongly adsorbed metal cations, the pattern of response for biosolids-applied metals has been found to be strongly curvilinear (plant metal concentration approaches a plateau with increasing soil metal concentration) rather than being a linear plant:soil relationship with increasing concentration—if several potential errors in the research methodology are avoided. First, comparison of application rates is only valid after the system has equilibrated for a period (e.g., during rapid biodegradation of biosolids-applied organic matter; when biosolids are applied at high rates, uptake can be increased for several years due to formation of biodegradation by-products which increase metal diffusion and convection to the roots). The effect is more significant for *Poaceae* than other species, perhaps due to the role of phytosiderophores in metal uptake. Second, soil pH levels should be equal across rates studied; co-variance of soil pH should be used to correct for unequal soil pH. Studies by Bell et al. (1988) found a strong plateau

response when pH co-variance was incorporated in the data assessment. Third, the metal concentration in the source applied affects the slope of metal uptake (or the increase above the background plant metals when the plateau is reached); higher metal concentration in the source means higher phytoavailability at equal metal applications (Jing and Logan, 1992). The presence of metal-adsorbing sesquioxides in many biosolids decreases the slope or increment at the plateau. The natural limitations on metal uptake and bioavailability, including the plateau response, prevent toxic levels of most metals being reached in plants used as food or feed.

Protection of wildlife is similar to that of livestock; wildlife's diet can consist entirely of plants grown on a contaminated site. In cases involving wildlife in unmanaged ecosystems, maximal plant residues may exceed those allowed on managed farmland—wildlife may eat sick plants which would not be harvested by a commercial grower. Evaluation of a rich literature on wildlife exposure to metal-contaminated soils indicates that animals which consume earthworms are the highly exposed individuals (Brown et al., 2002): 35% of an earthworm is soil, on a dry matter basis. But the soil in the earthworm can adsorb metals, reducing their bioavailability. Of the metals, only mercury in the methyl-mercury form is actually biomagnified, and very little of the mercury in soils is in that form. Se can be incorporated into proteins and also be biomagnified. Other metals are instead "biominified," according to many studies (Beyer et al., 1993). Nearly all of the metals ingested in forage materials or earthworms—in some cases, >99,9%—are excreted. Thus, the increase in risk with increasing trophic level seen with chlorinated hydrocarbons has not been seen with metals in soils.

Each element must be considered separately because of its unique chemistry. For example, arsenate is more strongly adsorbed than arsenite; when a soil is flooded to grow rice, soil microbes can reduce arsenate to arsenite and the higher concentration of dissolved arsenite can be phytotoxic to rice in more highly contaminated soils. Generally, for As, the most sensitive crop is rice because soils are reduced for rice production. Most elements have little potential for redox change with change in the redox status of soils. Besides forming arsenite, reduced soils also form less soluble forms of U. Reduced soils can form sulfide, and sulfide forms low-solubility compounds with most of the metals of concern in soils, including Pb, Zn, Cd, Cu, and Ni (Table 12). These low-solubility species can become deficient for rice. Upon oxidation of the soil, sulfide is quickly oxidized and the metals are returned to more normal equilibrium reactions of aerobic soils.

Much research has been conducted using multi-element analysis of plants and animals exposed to soil metals. One group of studies used neutron activation analysis of biosolids, soils, crops, and animals (e.g., Chaney et al., 1978). More recently, ICP-MS and other very sensitive analytical methods have been used to examine soil solution and soil-plant transfer of 60 elements as a function of soil pH (Tyler and Olsson, 2001a, 2001b). These studies provide evidence which further supports the concept of the soil-plant barrier. A few elements may require further evaluation in connection with industrial sources that can—despite the fact that they are normally poorly absorbed from soils—introduce them into soils at very high concentrations. When a high metal concentration source reaches soil, the soil processes that limit risk may be overwhelmed, at least for elements that are weakly accumulated by plants (e.g., Tl, Be).

8. LINKING METAL SPECIATION AND METAL TOXICITY: THE BIOTIC LIGAND MODEL APPROACH

8.1 Overview of Biotic Ligand Model Development

The biotic ligand model (BLM) approach is used to predict metal toxicity by linking chemical equilibrium models (which estimate metal speciation in solution) to metal complexation at the biological surface. The framework of the BLM approach synthesizes over 30 years of research on the geochemistry and toxicity of trace metals (Paquin et al., 2002). The first general descriptions of the approach were provided by Pagenkopf (1983), with his gill surface interaction model, and by Morel (1983), who formulated a free ion activity model. About 10 years later, Playle et al. (1992, 1993a, 1993b) provided additional information on the effect of anionic complexation and competition with other cations on trace metals binding to fish gills. These data were later integrated with toxicity data by Di Toro et al. (2001), who developed a version of the BLM model to predict the acute toxicity of copper and silver to several freshwater species.

8.2 Metal Speciation Estimation

A key component of the BLM approach is the estimation of trace metal complexation by inorganic and organic ligands in solution. While the use of chemical equilibrium models for complexation by inorganic and synthetic ligands is relatively straightforward, predicting complexation by dissolved natural organic matter is more challenging, given such matter's heterogeneous character. Basically, two different estimation approaches have been used in the BLM. The first (e.g., Di Toro et al., 2001), uses a modified CHESS speciation code (Santore and Driscoll, 1995) that includes the WHAM V (Tipping, 1994) approach to model complexation by organic matter. WHAM V is based on an extensive dataset for natural organic matter and considers mono- and bidentate complexation and the influence of electrostatic interactions on binding. Proton binding and competitive metal binding are described for two types of acid groups. Each group is assigned a range of intrinsic pKs that are given median and range values. The second approach uses the MINEQL+ (Schecher and McAvoy, 1994) speciation code, and a single binding constant measured for a natural organic matter sample (e.g., McGeer et al., 2000).

The other key component of metal speciation by BLM models is the complexation by the biotic ligand, for example by the gills of fish in the original models. Two approaches are currently used to estimate the amount of metal associated with a biological surface. The first, which is more mechanistically based, relies on measured conditional binding constants of the metals to the biological surface (e.g., MacRae et al., 1999). The second BLM approach is more empirical and uses complexing by a hypothetical biologically active surface ligand as a fitting parameter to relate metal speciation to the observed metal toxicity (e.g., De Schamphelaere and Janssen, 2002). In the later approach, in addition to the free metal ion, binding of metal complexes such as CuOH^+ (De Schamphelaere and Janssen, 2002) and AgCl^0 (Paquin et al., 1999) may also be considered.

In toxicity testing at relatively high metal concentrations, the measured or estimated binding constants are often roughly constant for different biological ligands. This is presumably because surface complexation is associated with similar low-affinity chemical moieties in each case. For example, Heijerick et al. (2002a) noted the similarity of published binding constants for zinc: experimentally derived $\log K_{ZnBL}$ values of 5.3 to 5.6 (Alsop and Wood, 2000) and 5.1 (Galvez et al., 1998) for rainbow trout, and estimated values of 5.4 for steelhead trout (Cusimano et al., 1986) and 5.3 for *Daphnia magna* (Heijerick et al., 2002b). Conditional stability constants for copper are also almost constant for fish gills, with experimentally derived $\log K_{CuBL}$ values of 7.5 for rainbow trout and 7.3 for brook trout (MacRae et al., 1999) and 7.4 for fathead minnows (Playle et al., 1993a). But the binding constants are different for other organisms, with an estimated $\log K_{CuBL}$ of 8.0 for *Daphnia magna* (de Schamphelaere et al., 2002) and expected differences for non-chitinous invertebrates such as *Lumbriculus variegatus* (Meyer et al., 2002). Some of these differences may also be due to differences in experimental and model design, as there are no standardized methodologies and procedures for deriving data for conditional stability constants.

The effects of pH on metal toxicity can be illustrated with the BLM model, which can consider changes in aqueous metal speciation and competition of H^+ with metals for binding sites at the biological surface. For example, using the BLM approach (Di Toro et al., 2001), we estimated the competitive effect of H^+ from pH 5 to pH 9 on copper and silver binding to the gills of fathead minnows in Lake Superior water (Figure 37). The effect shown in the figure only relates to competition for binding to the gill surface, not to changes in copper or silver speciation in solution. This is because total dissolved metal concentrations were increased with pH so that free metal concentrations remained constant. In a toxicologically relevant metal concentration range and pH, the direct competition of protons for binding to the gill surface is weak due to the higher affinity of Cu^{2+} and Ag^+ ions for binding sites. Neither copper nor silver is completely displaced from the surface even at pH 5. Copper associated with the gills almost doubles from pH 5 to pH 7, and competition between Cu^{2+} and $CuOH^+$ becomes significant at pH 8 and above. In contrast to copper, there is almost no predicted competition of H^+ with silver. In fact, no experimental data support competition of H^+ with silver; the small reduction of Ag^+ bound to the gill at pH below 6 is presumably an artifact related to the use of an empirically derived lower proton binding constant for the silver BLM (Paquin et al., 1999).

8.3 Validation Studies

While the toxicity of trace metals can vary by several orders of magnitude, studies that have validated the BLM approach with independent datasets indicate that BLM-predicted toxicity is generally within 2 times the observed toxicity. De Schamphelaere et al. (2002) validated their BLM model for predicting acute copper toxicity to *Daphnia magna* using independent toxicity test data conducted with 25 reconstituted media representative of European natural waters and with 19 spiked European natural waters. Heijerick et al. (2002b) conducted a similar validation using 17 reconstituted media to predict zinc acute toxicity to *Daphnia magna*. Santore et al. (2001) have also tested their BLM model for acute copper toxicity to fathead minnows by comparing their prediction to the toxicity test results for two effluent-impacted

streams in the United States. Finally, the model developed by McGeer et al. (2000) to predict acute silver toxicity to rainbow trout also accurately predicted the toxicity measured in 31 toxicity test results obtained from 10 different independent studies. The BLM approach has thus been validated and shown to be mechanistically based for the prediction of trace metal acute toxicity to certain indicator species.

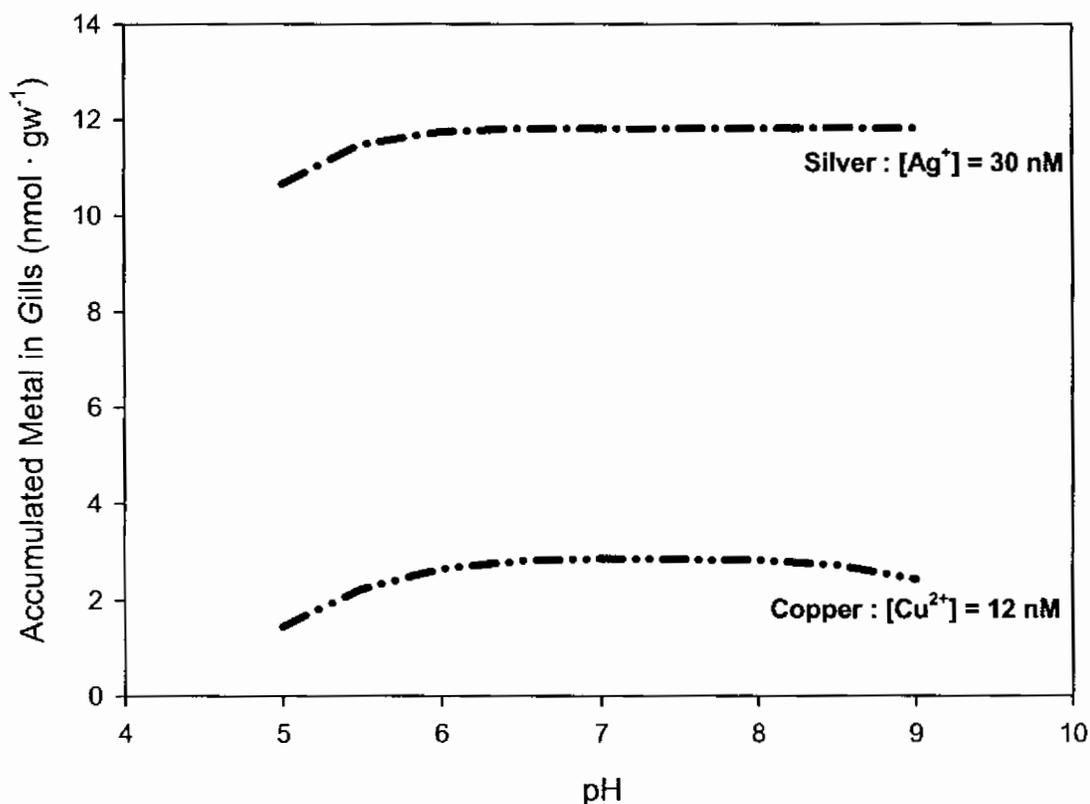


Figure 37. Effect of pH on the BLM-predicted (HydroQual, 2002) Cu^{2+} and Ag^+ accumulation in the gills of *Pimephales promelas*. Lake Superior average composition (Erickson et al., 1996) and freshwater criteria maximum total dissolved concentrations (U.S. EPA, 2002c) of 205 nM for copper and 32 nM for silver assumed at pH 5. Total dissolved concentrations were increased with increasing pH so that free copper and free silver concentrations would remain constant. Silver BLM: $\text{Log } K_{\text{H}^+-\text{gills}} = 4.3$ and $\text{Log } K_{\text{Ag}^+-\text{gills}} = 7.3$. Copper BLM: $\text{Log } K_{\text{H}^+-\text{gills}} = 5.4$ and $\text{Log } K_{\text{Cu}^{2+}-\text{gills}} = 7.4$.

8.4 Current Limitations and Future Research

The BLM approach's limits are mostly related to its inherent assumption that (1) trace metal speciation and metal uptake are in chemical equilibrium and (2) the biotic ligand remains unmodified through exposure. The model also assumes that metal uptake or expression of the biological response is the rate-limiting step. Trace metals in surface waters and exposure media are not always in chemical equilibria, especially with natural organic matter. Campbell (1995) reviewed other exceptions to the BLM's assumptions, such as direct uptake through passive diffusion of lipophilic complexes or kinetically controlled uptake of some trace metals because of their fast uptake. The assumption that the affinity of the biotic ligand is constant has also been challenged. There are physiological responses to metal exposures that might affect metal uptake. In addition, prior sublethal exposures to metal or the quality of the diet have been shown to affect the binding of metal to fish gills (e.g., Alsop and Wood, 2000; Szebedinszky et al., 2001). Variation in the affinity of the biotic ligand for metals will be especially important for the prediction of chronic toxicity.

Extensive current research is focused on predicting chronic toxicity and metal mixture toxicity. Applying the BLM model to chronic toxicity is not straightforward, since the physiological mechanisms involved are likely to be much different. Similarly, predicting the toxicity of metal mixtures that have different modes of action is difficult. For example, Cu and Ag affect ionoregulation, whereas metals such as Ni have respiratory effects. Accounting for such differences will require further refinement of the BLM model. However, it can be expected that the toxicity of metal mixtures in which the metals have the same mode of action can be predicted using the current BLM framework.

9. ATMOSPHERIC CHEMISTRY OF THE METALS

Metals are ubiquitous components of particulate matter in ambient air and are emitted by numerous natural and anthropogenic sources. Richardson (2002) included volcanic eruptions and emissions, entrainment of soil and dust, entrainment of sea salt spray, and natural forest fires as significant metals emission sources. Most metals are removed from the atmosphere by deposition and have relatively short atmospheric half-lives. Table 14, abstracted from Seinfeld and Pandis (1998), presents average atmospheric residence time and airborne concentrations for some metals in California.

Table 14. Atmospheric Metals

Metal	Residence Time (days)	Average Concentration (ng/m³)
Arsenic	Unknown	2.4
Cadmium	7	1-2.5
Nickel	Unknown	7.3
Beryllium	10	0.11-0.22
Lead	7-30	270-820
Mercury	0.3-2 years	0.37-0.49 ppb

A substantial part of the atmospheric chemistry of metals takes place in the aqueous phase, where it is not significantly different from aqueous chemistry in other media. Constructs described elsewhere in this report (e.g., pH-Eh diagrams and geochemical computer models) may be used to determine metal speciation in atmospheric aquatic aerosols. However, the application of such diagrams and models, which assume that metal species are in chemical equilibrium, must be limited to describing metal speciation reactions that can equilibrate in seconds or less. These include many acid/base and metal complex formation reactions, but not most reactions involving adsorption, oxidation/reduction, or mineral precipitation. Atmospheric metal reactions that take longer to equilibrate must be studied in terms of their reaction kinetics rather than equilibrium chemistry.

Seinfeld and Pandis (1998) present a detailed discussion of the acid-base chemistry of atmospheric water that may be useful in modeling metal speciation. In addition, sorption to particles, deposition, and gas phase redox chemistry may be important for some metals (Bodek et al., 1988). Deposition is largely a function of the properties of particulates, not the sorbed or incorporated metals. Redox chemistry takes place through oxidation with free radicals such as OH or through direct photolysis of metal complexes (Finlayson-Pitts and Pitts, 1986). Due to the oxidizing nature of the atmosphere, metals are often converted to their most oxidized stable forms.

Metals have not been a major component of EPA air programs. Lead is listed as a criteria pollutant under the Clean Air Act. A group of metals including antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium are listed as hazardous air pollutants under the Clean Air Act. Of these only a few have concerns related to speciation. Arsenic is listed for "inorganic" and arsine forms; the listing for chromium makes a distinction between Cr(III) and Cr(VI); mercury is listed for elemental, inorganic (apparently divalent), and methyl forms; and nickel is listed as salts, refinery dust or subsulfide, and carbonyl (U.S. EPA, 1994). Deposition of metals from the atmosphere is under consideration by the Office of Water (U.S. EPA, 2003). This latter program is primarily concerned with deposition, speciation, and transformation after deposition of mercury, although lead and cadmium are involved to a lesser extent. The State of California has a comprehensive program for monitoring airborne metals through its air toxics monitoring network.

With very few exceptions (e.g., hexavalent chromium, nickel refinery dust, mercury), EPA does not consider bioavailability or speciation in risk assessment of atmospheric metals; rather, risks are assessed on the basis of total or respirable airborne metal concentrations (U.S. EPA, 1998). EPA assesses risks for lead with a set of pharmacokinetic models known as the integrated uptake biokinetic (IEUBK) and Adult Lead models. Although these models explicitly consider oral bioavailability of lead, they do not consider inhalation bioavailability.

Most sampling and analytical techniques published by EPA for metals in air are oriented toward evaluation of particulate-phase total metals rather than metal species (U.S. EPA, 1999a). These methods involve collection of either total or respirable particulate fractions with subsequent analysis by X-ray fluorescence, atomic absorption, inductively coupled plasma, proton-induced x-ray emission, or neutron activation analysis gamma spectroscopy techniques. The one notable exception is a method for mercury (Method IO-5) that speciates vapor and particulate forms. To the extent that metals are sorbed to particulate phases, analysis of individual metal species can, at least theoretically, be accomplished by the same techniques used to analyze those species in other solid media.

Of all the metals of interest, mercury has the most complex and best understood atmospheric chemistry (Lindqvist, 1994; Munthe, 1994). In the gas phase, mercury is oxidized by O_3 and NO_2 ; aqueous-phase chemistry includes oxidation of elemental mercury by free radicals such as OH and HO_2 . Both vapor phase and aqueous atmospheric chemistry may involve heterogeneous-phase components. EPA has made a substantial effort to evaluate the atmospheric fate of mercury due to the requirements of the Clean Air Act. The *Mercury Study Report to Congress* (RTC) (U.S. EPA, 1997) contains a complete qualitative and quantitative evaluation of mercury's atmospheric fate based on the state of knowledge when the report was written. EPA is also working with the University of Wisconsin to quantify mercury transformations in the atmosphere, including depositional behavior.⁶

9.1 Discussion and Recommendations About Atmospheric Metal Chemistry

Metal speciation and chemistry have not been significant components of EPA's evaluation and assessment of environmental metals. The impetus toward a more comprehensive evaluation of metals must start with qualitative and quantitative toxicology. If there is a significant difference among the various atmospheric metal species with respect to toxicology (as is the case with divalent and elemental mercury), then expenditure of resources on environmental fate models, development of analytical techniques, and monitoring may be warranted. To some extent, the Mercury RTC (U.S. EPA, 1997) is a paradigm for a complete multimedia exposure and risk assessment for metal species. The resources and management of the development of the RTC may be used as a benchmark by EPA for the development of similar efforts for other metals.

⁶ EPA Grant R829798. Project officer: Bill Stelz, NCER.

10. DETERMINATION OF METAL SPECIATION IN WATERS AND SOILS

10.1 Unfiltered Versus Filtered Water Samples

The metals transported by surface and ground waters are present in true solution as ionic or molecular species, and in suspended particles (cf. Stumm and Morgan, 1996; Langmuir, 1997a). The suspended particles can be colloidal in size and as small as 10 to 100 Angstroms (10^{-9} to 10^{-8} m). By definition, metals that pass through a $0.45\ \mu\text{m}$ (4.5×10^{-7} m) filter are usually assumed to be dissolved. Because colloidal particles range in size from less than 10^{-8} m to about 10^{-5} m, a significant fraction of particulate metal concentrations can pass through a $0.45\ \mu\text{m}$ filter and be listed as dissolved. For example, Kennedy et al. (1974) found that the concentration of colloidal-sized particles of Al, Fe, Mn, and Ti passing through a $0.45\ \mu\text{m}$ filter could exceed the dissolved concentration of these metals by an order of magnitude or more. (See also Bergseth, 1983; Puls and Barcelona, 1989; Pohlmann et al., 1994). Clark et al. (1992) reported that the type of pump used to sample ground waters had a major effect on total concentrations of Mn, Pb, and Zn, with higher turbidity and particulate metal concentrations collected from centrifugal pumps than from slower-flow-rate bladder pumps.

Usually the metals of concern are associated with the smallest particle size fractions (especially colloidal-sized) in soils and sediments which have the largest surface areas per weight, rather than with larger particle sizes on a weight basis. A variety of methods are available for separating dissolved and suspended metals. These include centrifugation, filtration, ultrafiltration, ion-exchange chromatography, and organic extraction. These methods are discussed in some detail by Salbu and Steinnes (1994).

The distinction between dissolved and particulate metal concentrations is important, because reactions such as adsorption, precipitation, oxidation/reduction and, complexation control metal amounts in true solution, but not the amounts in suspension. The latter are limited, if at all, by chemical coagulation and/or filtration in porous media, or, if the particles are large enough (larger than about 10^{-5} m), by gravitational settling. Metals in suspension are usually adsorbed or coprecipitated with suspended Fe, Al, or Mn oxyhydroxides or adsorbed by suspended organic matter or clays. Only rarely, as in streams affected by acid rock drainage or at sources of metal contamination, do the metals of concern occur as pure metal oxyhydroxides or metal salts.

In public water supplies that are subject to pH control by lime addition, the addition of flocculants, and/or filtration, suspended metal concentrations may be largely eliminated. But measurable amounts of dissolved and suspended metals may be contributed to drinking water by the plumbing in distribution systems that connect the utilities and their customers.

10.2 Unstable Parameters or Species Including Metal Redox Pairs

The reactions that control the mobility of the metals of concern in porous media are usually strong functions of pH, and—except for Al, Ba, Be and Sr—also depend on the oxygen

content or Eh of the media (See Baedecker and Cozzarelli, 1992). An accurate assessment of metals mobility at a specific site requires that the values of these parameters used in any modeling calculation be the same as in the medium involved. Values of pH and Eh, temperature, and gas pressures (e.g., the partial pressures of O₂, CO₂, H₂, CH₄, and H₂S) must be measured immediately upon collection, or when possible fixed in the field for later analysis. Otherwise their values will usually change rapidly due to temperature change, loss or gain of gases to or from the atmosphere, and the growth of organisms such as bacteria and algae. For such reasons, the pH of a water measured in the laboratory after a few weeks of sample storage at ambient temperature will usually differ from its value in the field by ±0.2 to ±1 pH units (Langmuir, 1971, 1997a).

Methods of field analysis of pH and Eh are discussed in detail by Langmuir (1971) and Wood (1976). (See also USGS, 1998.) Modern, battery-operated solid-state pH/millivolt meters for field use have greatly improved the ease of pH and Eh measurement. If pH meters and electrodes are properly calibrated using a double pH buffer check, field-measured values can be accurate to ±0.02 to ±0.05 pH units. Accurate and meaningful Eh measurements are usually far more difficult to obtain. In fact the U.S. Geological Survey (1998) states that Eh measurement “is not recommended in general because of the difficulties inherent in its theoretical concept and its practical measurement.” An accurate Eh measurement using a platinum (or other noble metal) or glassy carbon electrode depends upon the presence of significant concentrations (usually greater than 10⁻⁵ m) of a pair of electroactive redox species that can attain rapid chemical equilibrium and greatly exceed the concentrations of the non-electroactive species also present. Most often the species that control an Eh measurement are species of iron, manganese, or sulfide and native sulfur (Langmuir, 1997a). This tends to limit thermodynamically meaningful Eh measurements to acid mine waters and iron-, manganese-, or sulfide-rich stagnant surface waters or ground waters. In other waters, which include most surface waters in contact with the atmosphere, Eh measurements are of qualitative value only. In such waters, a measurement of dissolved oxygen (DO) is the most reliable indication of the oxidation state. In fact field DO measurements should be performed any time redox sensitive metals of concern are of interest. DO is measurable in the field at concentrations as low as 0.03 μM using modern analytical methods (cf. Kent et al., 1994).

Lovely et al. (1994) and others have suggested that instead of Eh, field measurements of dissolved H₂ be performed to define the redox state of surface-water bottom sediments and ground waters. This reflects the fact that bacteria employ H₂ in the reduction of nitrate Mn(IV), Fe(III), sulfate, and carbon dioxide.

Geochemical models such as MINTEQA2 (U.S. EPA, 1991), PHREEQC (Parkhurst and Apello, 1999) and WHAM 6 (Tipping, 1994) can compute the relative amounts of redox sensitive species of As, Se, Mo, Cr, N, C, and other metals of concern from the total metal concentration and measured Eh (at a given pH). This assumes of course that this Eh represents the overall oxidation state of the system (which is usually questionable), and that the redox pairs of these elements are electroactive and in equilibrium with the measured Eh, which they usually are not.

The only way to determine accurate relative amounts of redox pairs of As, Cr, N, C, or Se, for example, is to fix them upon collection and measure them directly (cf. Baedecker and Cozzarelli, 1992; Sule and Ingle, 1996). For example, Tretner et al. (2001) have shown that for non-sulfidic waters, the As(V)/As(III) ratio and As concentrations could be maintained for two weeks by first filtering samples, then acidifying them with HCl to pH 1.5–1.8 and refrigerating them to below 4°C. In general, the accurate measurement of concentrations of individual redox pairs is difficult and costly, and not recommended for routine studies.

10.3 Determination of Individual Species Concentrations in Water

There are various methods for directly measuring the aqueous activity or concentration of individual metals, including specific ion electrodes and voltammetric techniques (cf. Salbu and Steinnes, 1994). Most of these methods, though, have interference problems and require the addition of reagents to the natural water, which may itself change the metal speciation. The simplest approach is to compute metal ion activities from a geochemical model calculation, based on a chemical analysis of concentrations of dissolved metal and related species in the water.

11. SOILS

11.1 Sampling of Soil Moisture

A major challenge when sampling soil moisture for chemical analysis is to avoid changing metal speciation in the sampling process. This means that methods involving the application of gas pressure should be avoided, in that they will change ambient gas pressures and so change the pH, for example. The most appropriate moisture sampling methods use either negative pressure as in suction lysimeters (cf. Knight et al., 1998; Davis et al., 1999; Tye et al., 2003), or positive pressure without contact between air or other foreign gases and the soil. The latter devices include gas pressure membrane extractors and pressure plate extractors (cf. SoilMoisture Equipment Corp., 1997).

11.2 Sequential Extractions To Determine the Nature of Metal/Soil Associations

The purpose of sequential extractions is to define the speciation of individual metals in the soil through a series of soil leaching steps. Using sequential extractions, Tessier et al (1979) have categorized metals as exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter, or residual. The extractions often involve (1) addition of a MgCl₂ solution at pH 7 to define the exchangeable metals fraction; (2) addition of a pH 5 sodium acetate/acetic acid solution to selectively dissolve carbonates (the acid extractable fraction) and release their metals; (3) addition of an acidic hydroxylamine hydrochloride (NH₂OH.HCl) solution, which is a reductant, to dissolve the amorphous Fe-Mn oxyhydroxides and release their metals; (4) addition of a hydrogen peroxide extraction at pH 2 and 85°C to determine organic matter content and the metals associated with it; and (5) aqua regia destruction of remaining minerals to obtain the residual metal concentration. Typical extraction results show minor to

below-detection concentrations of trace metals associated with the exchangeable fraction, and major metal concentrations released by both the acid extractable and reductant leaching steps (cf. Tack and Verloo, 1999). In another sequential extraction study, Tye et al. (2003) found that the behavior of Cd^{2+} and Zn^{2+} in a variety of contaminated soils was best explained by assuming they were adsorbed by soil humus.

Tack and Verloo (1999) list some of the problems associated with sequential extractions, which include problems due to sample handling and preparation, the non-selectivity of the extractants, and the redistribution of trace metals among remaining solids during extraction. It has long been known that the five extraction steps do not clearly distinguish the forms of metal association and speciation identified above (cf. Suarez and Langmuir, 1975). Tye et al. (2003) point out further that “single or sequential chemical soil extraction schemes provide a comparative classification system for soil metals but do not predict (metal) the bioavailability.”

The free metal ion activity in the soil solution phase has been shown to be a better indicator of bioavailability and toxic response than is the total soil metal content (cf. Tye et al., 2003). Most of the soil equilibrium models assume that the labile (bioavailable) metal content of a soil can be predicted from the total or extractable soil metal content (e.g., NICA, Goody et al., 1995; SCAMP, Lofts and Tipping, 1998; Tipping et al., 2000). Such an approach will generally overestimate the labile metal fraction. More directly, the soil moisture may be sampled and chemically analyzed, and the solution speciated, using a model such as WHAM 6 (Tipping, 1998) to determine metal ion activities in the soil solution.

12. APPLICATION IN A REGULATORY CONTEXT

EPA needs to use the tools of environmental chemistry to determine metal speciation for use in risk assessments. In addition, EPA needs to be able to assess the mobility of metals in the environment, especially the subsurface. Each of these applications will be discussed in turn.

13. APPLICATIONS TO SPECIATION

Metal speciation may be required for risk assessment. If so, it is desirable to know the identity and form of a metal at the exposure point. If information regarding bioavailability, pharmacokinetics, and toxicology is also known, speciation information may be used in risk assessment. EPA has developed bioavailability and toxicological data for very few metal species. A review of the Integrated Risk Information System (IRIS) shows that, disregarding organometallics and cyano complexes, EPA has developed toxicological information for the following metals:

- Arsenic—inorganic, arsine
- Chromium—Cr(III), Cr(VI)
- Mercury—elemental, mercuric chloride

- Thallium—oxide, acetate, carbonate, chloride, nitrate, selenite, sulfate
- Vanadium—pentoxide
- Uranium—soluble, natural
- Zinc—phosphide

EPA has not formalized toxicity reference values (TRVs) for ecological risk assessment, but there is little consideration currently given to metal speciation (with the possible exceptions of chromium oxidation state and organometallic forms of mercury) in contemporary ecological risk assessment. A limited number of Ambient Water Quality Criteria (Table 5) also exist for metal species.

It is useful to hypothesize a future condition, however, in which there are no limits on toxicological information and a real need exists to determine metal species. The exact information required and questions to be asked of the environmental chemist will depend on the nature of the assessment in the context of the framework:

- **Site-Specific Risk Assessment**—What are the existing metal species at the exposure points? Is there likely to be a change in speciation over the exposure duration? Can normal human behavior alter the speciation? If there is a strong likelihood of more than one species, should different species be selected for risk assessment (i.e., a common, but possibly less toxic species for a central tendency risk and a rarer but possibly more toxic species for a high-end risk)?
- **National Regulatory Assessment**—What generalized information is available to determine the species of a receptor at any exposure point in the United States? Is it possible to generalize speciation across the U.S. or is it necessary to develop regional (e.g., physiographic province) or water-body type (stream, lake, estuary) speciation? How do metals species change when traveling from a potentially regulated source to an exposure point?
- **National Hazard or Risk Ranking**—Is there a property of metals analogous to organic persistence that can be used to generalize across metals? How can chemical information be developed to perform the generalization? What degree of stability is required to determine if the property will persist?

Many of these questions need to be addressed by risk managers within their specific context. From a chemistry standpoint, there are several levels of information that can be used to answer these questions: regulatory defaults, literature information based on limited measurement, analytical chemistry, geochemical modeling, and chemical-specific modeling.

13.1 Regulatory Defaults

Current regulatory practice is to use total metal concentrations in risk assessments, with a few exceptions. Assumptions made about the bioavailability of a metal are often based on the toxicologic or epidemiologic studies that form the basis of derivation of the appropriate dose-response values. This practice is conservative from an environmental health standpoint and is likely to continue as a default into the future. In a tiered risk assessment approach, the production of an unacceptable risk or exceedence of a standard or criterion by a total metal concentration could trigger a more refined approach to evaluate the speciation of the metal. An alternative approach is to use the most toxic species from Table 6, for example. This is predicated on the availability of dose-response information for that species.

13.2 Literature/Limited Measurement

Obtaining speciation data at this level involves a combination of limited environmental measurements along with literature information. This technique is already in use for determining water quality criteria for metals as a function of hardness.⁷ A more sophisticated use of combined analytical and literature information is the determination of metal speciation using look-up diagrams such as the pH-Eh diagrams presented in this paper. This requires reliable measurements of pH and Eh for the system under evaluation. For example, Figure 19 presents an Eh-pH diagram for cadmium. At neutral pH in a mildly reducing environment, this diagram tells us, cadmium will exist as the slightly soluble cadmium sulfide, while under oxidizing conditions it will exist as the soluble divalent cadmium ion. This conclusion would, of course, depend on the availability of sufficient sulfide in the system. There are limitations to this approach which include the need to be aware of assumptions that were used in producing the diagrams and interactions from other chemicals. The analyst also needs to be aware of the fact that, especially in natural waters, pH and Eh are not static concepts. The values selected should be representative of both the current status of the system and reasonable future geochemical changes.

13.3 Analytical Chemistry

Most site-specific risk assessments, some ranking assessments (e.g., HRS), and many waste characterizations currently depend on analytical chemistry. With rare exceptions, the metals are treated as total metals or some subset of total metals such as total recoverable metals. EPA compendia of analytical methods such as SW-846 have traditionally focused on methods for total metal analyses such as atomic absorption or inductively coupled plasma. The primary exception is chromium. Several EPA methods currently exist to quantify Cr(III) and Cr(VI), including ion chromatography (0218.6), differential pulse polarography (7198) and speciated isotope dilution mass spectrometry (6800). EPA has also published methods for differentiating As(III) from As(V) by anodic stripping voltometry.

⁷ The assumed inverse relationship between metal toxicity and hardness can be questioned for metals—such as Cu and Hg—that form strong organic complexes.

Analytical methods for identifying and quantifying chemical species have been discussed earlier in this paper. Most of these methods are used by academic or private research laboratories and are not currently amenable to routine use in a regulatory context. Before being used for site-specific risk assessment or waste characterization, for example, these methods require robust evaluations to determine if they are capable of meeting data quality objectives. This would include (but not be limited to) evaluations of accuracy, precision, and sensitivity when used on a routine basis by a contract laboratory.

Another class of analytical methods could be termed “adjunct” methods. These methods do not measure the metal of concern directly, but measure other aspects of environmental chemistry that are useful in determining metal speciation. DO, Eh, pH, and hardness are examples of adjunct measurements. If a metal species is to be determined by means of a look-up table, for example, system measurements of pH, Eh (or a surrogate), and DO are required. The quantification of major anions (chloride, bromide, nitrate, sulfate, carbonate) and cations (Na, K, Ca, and Mg) is necessary to compute metal speciation using a chemical equilibrium modeling approach. EPA has published methods for routine determination of these adjunct parameters.

13.4 Geochemical Modeling

Geochemical modeling probably has the most utility for regulatory application for metal chemistry of all the techniques discussed here. There are numerous geochemical models available in the literature. EPA (1999) has reviewed many of these models and should be consulted for a more detailed discussion (see also Langmuir, 1997a). In general, geochemical models are classified as “speciation-solubility” or “reaction path” models. Speciation-solubility models may be used to calculate aqueous speciation/complexation and the degree of saturation with respect to the solids in the model’s database. Some specialization-solubility models also include limited mass transfer capabilities. Examples of refined speciation-solubility models include WATEQ, REDEQL, GEOCHEM, MINEQL, MINTEQ (see EPA, 1999, for detailed references) and their subsequent versions. Reaction path models have more advanced mass transfer capabilities. At each step of a process (e.g., travel of an ion through an aquifer) reaction path models calculate masses of minerals precipitated or dissolved and the resulting composition of the solution. Reaction path models include PHREEQC, PATHCALC, and EQ3/EQ6.

MINTEQ2 (U.S. EPA, 1991; HydroGeologic, 1998; HydroGeologic and Allison, 1999a) has been widely used in a national regulatory context by EPA. Typically MINTEQ is used to calculate partition coefficients that are used in a subsequent national regulatory analysis (U.S. EPA, 1996b; HydroGeologic and Allison 1999b) or a site-specific risk assessment (U.S. EPA, 1998). This usage is discussed in more detail in a subsequent section of this paper. There is no technical reason why MINTEQ2 could not be used on a routine basis to determine chemical speciation for site-specific risk assessments.

13.5 Chemical-Specific Modeling

Chemical-specific modeling involves the construction of a mathematical model that is capable of predicting all of the significant fate and transport processes of a given chemical. It should be capable of tracing a chemical from a source to an exposure point and predicting both concentration and speciation at the exposure point with a sufficient degree of accuracy to reflect the objectives of the assessment.

The only model of this type for a metal is the modeling reflected in the *Mercury Study Report to Congress* (RTC) (U.S. EPA, 1997). In general, the RTC evaluates the behavior of three mercury species (divalent, elemental, and methyl). In the atmosphere, fate and transport in both particulate and vapor phases are assessed for long range and local behavior using established atmospheric transport models. Terrestrial and aquatic modeling is accomplished by application of the IEM-2M model, which was specifically developed for the RTC.⁸ This model simulates the behavior of mercury in watershed soils and water bodies using a mass balance approach. The RTC was a National Regulatory Assessment in the context of the framework. It generalized environments to the eastern and western United States and evaluated mercury behavior in these environments. The models may be applied on a site-specific basis (Foster and Chrostowski, 2003) if sufficient environmental information is available. The IEM-2M model is data intensive. Each mercury species evaluated with the model required input values for molecular weight, Henry's law constant, soil, bed sediment and suspended sediment partition coefficients, air diffusivity, chemical reaction rate constants for six processes in three media and biotransfer factors for all biota of concern. Inputs of concentrations or emission rates of the various mercury species are also required, but in practice, default assumptions of speciation were used by EPA. The development and application of this type of model for other metals is limited by the amount of resources and scientific information required.

14. APPLICATIONS TO MOBILITY

Quantification of the mobility of metals in the unsaturated zone or ground water is a significant regulatory application of speciation information. For example, metals criteria for the toxicity characteristic in RCRA depend on the development of a generic soil-to-groundwater dilution attenuation factor (DAF), as do the Soil Screening Levels (SSLs) for metals. Site-specific risk assessments for all programs need to be able to predict the rate of movement of metals through soils and subsequent movement and concentrations in groundwater. The primary processes governing the environmental fate and transport of metals in the subsurface are advection, dispersion, matrix diffusion, and retardation (U.S. EPA, 1994). Advection and dispersion are functions of the system rather than the contaminant. Matrix diffusion, which is a function of the contaminant, is relatively unimportant and omitted in most model transport algorithms. Retardation depends on a number of factors (U.S. EPA, 1994; Langmuir, 1997a) and may involve or be affected by the following:

⁸ The IEM-2M was also used by EPA to support development of mercury emissions limitations for hazardous waste combustors.

- Sorption—the attachment of chemical species to mineral surfaces or other surfaces.
- Ion exchange—competitive adsorption of ionic species, including ionic contaminants and major ions, onto oppositely charged surfaces of geologic materials.
- Speciation—the distribution of a given constituent among its possible chemical forms, including metal complexes, which have differing tendencies to be adsorbed or desorbed.
- Precipitation—the process by which dissolved species exceed the solubility limits of their solids, so that some of the species precipitate from solution. When a metal species reaches mineral saturation, addition of further amounts of the species to solution are precipitated, not adsorbed.
- Colloid formation—the process of forming colloids and the association of metal species with them. The metals may be sorbed or coprecipitated with colloidal-sized particles.
- Biofixation—the binding of metals to solid materials due to the interactions of microorganisms or plants.
- Natural organic matter interactions.
- Anion exclusion—negatively charged mineral or other surfaces repelling anions and so preventing their sorption by those surfaces.
- Other importance processes—changes in pH, oxidation potential, salinity, concentrations of competing ions, the nature of sorbent phases and their surface areas, and surface site densities

Due to the complexity and multiplicity of the processes involved, recourse is often made to the use of a single partition or distribution coefficient that describes the degree to which the contaminant's transport is retarded relative to water. This approach starts with defining the retardation factor:

$$R_f = \frac{v_p}{v_c} \quad (7)$$

where R_f is the retardation factor, v_p the velocity of water through a control volume, and v_c the velocity of contaminant through a control volume. The retardation factor is related to the distribution coefficient through the expression:

$$R_f = 1 + \frac{\rho_b}{n_e} K_d \quad (8)$$

where ρ_b is the porous media bulk density and n_e is the effective porosity at saturation given as a volume fraction (cf. Langmuir, 1997a). This model only applies if fluid flow in the porous media is isotropic and adsorption is fast, reversible, and linear (cf. Freeze and Cherry, 1979). These assumptions are often not valid, particularly for metal adsorption. As discussed above, the distribution coefficient approach can provide accurate modeling results for organic contaminants, but is likely to be in serious error when applied to the transport of metals through porous media at specific sites. This is because, as emphasized previously, the reactions and processes that control metal sorption are in general far greater in number than is the case for the adsorption of organic substances. Some transport models assume a constant partition coefficient, or assume linearity of the partition coefficient over all concentration ranges. To the extent that sorption is not constant and follows a non-linear isotherm—which is the usual case for metals—these models will be inaccurate and should be avoided. The best that can be hoped for when single partition coefficients are used to describe metal adsorption is that they represent bounding values in a given application.

Laboratory adsorption studies often find that, in simple systems, the value of $\log K_d$ for metal adsorption increases linearly with pH. For example, for Zn^{2+} adsorption by HFO, Langmuir (1997a) noted that adsorption followed the equation $\log K_d = -5.48 + 1.77 \text{ pH}$.

EPA (1999b) presents a comprehensive review of the properties and applications of partition or distribution coefficients for metals. These coefficients may be obtained from the literature, estimated using mathematical models, or measured. Partition coefficients tabulated as a function of pH by EPA (1998) are listed in Table 15 for several important elements of potential concern. EPA (1999b) has also presented non-pH-dependent values for lead (900), mercuric chloride (58,000) and elemental mercury (1,000), which for reasons just discussed should be used with considerable caution.

Table 15. Partition Coefficients as a Function of pH for Several Important Elements of Potential Concern (U.S. EPA, 1998)

Element	pH 4.9	pH 6.8	pH 8.0
Arsenic(V)	25	29	31
Barium	11	41	52
Beryllium	23	790	1E+5
Cadmium	15	73	4.3E+3
Chromium (III)	1.2E+3	1.8E+6	4.3E+6
Chromium (VI)	31	19	14
Nickel	16	65	1,900
Selenium (VI)	18	5.0	2.2
Silver	0.1	8.3	110
Thallium (I)	44	71	96
Zinc		62	

EPA (1999) discusses the advantages and disadvantages of several methods for measuring partition coefficients, including laboratory batch testing, in situ field batch testing, flow-through testing, and field modeling. In many national assessments, EPA has used MINTEQA2 and its subsequent versions to generate generic partition coefficients that may be applied to regional or national mobility evaluations.

The application of single partition coefficient values for individual metals should be limited to regional and national scale studies where accuracy is not required, and bounding or representative values are adequate. As noted previously in the discussion of adsorption, metal partition coefficients can vary by several orders of magnitude over short distances (meters or less) in porous media because of changes not only in pH, but also in metal complex formation, metal adsorption competition, the solid/solution ratio, the relative abundances, the surface areas, and the surface charge densities of the different metal-sorbing phases.

A number of papers have measured adsorption of radionuclide elements by a variety of minerals (including oxyhydroxides, clays, and other silicates), and have developed diffuse layer adsorption parameters which allow the prediction of radionuclide adsorption by these minerals (cf. Langmuir, 1997b). A similar effort has not been made for most of the metals of concern, for which diffuse layer modeling of adsorption is largely limited to their adsorption by Fe(III), Mn, and Al oxyhydroxides.

It may be possible to estimate metal adsorption with some accuracy without having to measure it, depending on the information available on a specific soil, surface water, or ground water system. What is needed minimally is the amounts of potentially sorbing materials (e.g., metal oxides, clays and organic matter) in a soil or sediment or in suspension in a stream. Literature information such as given in Table 10 can then be used to estimate the sorption properties of these materials for use in a sorption model. For example, as noted above in discussion of the diffuse layer adsorption model, where ferric oxyhydroxide (HFO) is the

dominant sorbent, and the amount of it suspended in a stream is known, estimation of metal adsorption can be accurate to within 10–20%, as shown in Table 11 (Smith et al., 1998). As a general observation, other things being equal, it has been found that the surface charge density and thus the metal adsorption capacity of most minerals is largely a function of their surface areas exposed to water (cf. Pabalan et al., 1998). Thus, the adsorption of metals by Al and Fe(III) oxyhydroxides in a system at a given pH may be assumed the same if they have the same surface areas.

If greater accuracy or site-specificity is required, it may be necessary to measure metal adsorption in laboratory experiments. Such measurements can be performed on pure minerals or on whole (usually sieved) soils. The sorption results may be used to develop diffuse layer model parameters for metal adsorption (cf. Dzombak and Morel, 1990; Stumm, 1992). Model results may then be used to compute partition or distribution coefficients as a function of pH, for example.

Several chemical mass transport codes are available that can model metal transport through porous media using the more accurate diffuse layer adsorption model for metals. These models include PHREEQC (Parkhurst and Appelo, 1999) and CHMTRNS (Noorishad et al., 1987), and—for transport by streams—OTIS/OTEQ (Runkel et al., 1999). Even if model parameters are estimated based on literature values, such models will generally predict metal adsorption and retardation more accurately than is possible when using single or linearly varying distribution coefficient values.

15. RESEARCH RECOMMENDATIONS

In general, environmental chemistry of metals research could benefit from the development of more routine chemical-species-specific analytical methods, the development of extraction techniques that have general utility in assessing bioavailability and/or mobility, and the validation of geochemical and chemical-specific environmental fate and transport models. The quality of EPA's use of environmental chemistry could benefit from the training of risk managers and other decision-makers in inorganic environmental chemical science.

The environmental chemistry of metals occupies a key position in the regulatory understanding of mobility, exposure, toxicity, and waste characterization. However interesting in its own right, EPA-sponsored research into the environmental chemistry of metals should be structured to answer specific environmental problems. Typically, these problems are associated with particular instances in which mobility, bioavailability, bioaccumulation, or toxicity are important. Rather than environmental chemistry driving the research agenda, it is probably more important for risk assessment to drive the research agenda.

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COMPARISON OF TOTAL COST OF REMEDIAL SOLUTIONS			
Site:	Charleston Naval Complex	Base Year:	2003
Location:	SWMU 65	Date:	11/25/03
Phase:	Corrective Measures Study		
	Alternative Number 1	Alternative Number 2	Alternative Number 3
Total Project Duration (Years)	10	5	5
Capital Cost	\$24,900	\$67,000	\$63,000
Annual O&M Cost	\$5,000	\$5,000 Yr 2-5	\$35,000 Yr 1 \$14,000 Yr 2-5
Total Present Value of Solution	\$63,000	\$90,000	\$180,000
<p>Disclaimer: The information in this cost estimate is based on the best available information regarding the anticipated scope of the remedial alternatives. Changes in the cost elements are likely to occur as a result of new information and data collected during the engineering design of the remedial alternative. This is an order-of-magnitude cost estimate that is expected to be within -50 to +100 percent of the actual project costs.</p>			

Alternative: Number 1		COST ESTIMATE SUMMARY				
Elements: Monitored Natural Attenuation with Land Use Controls						
Site:	Charleston Naval Complex	Description:	Implementation of base-wide land use management plan to put deed restrictions in place to prevent ingestion of groundwater.			
Location:	SWMU 65					
Phase:	Corrective Measures Study					
Base Year:	2003					
Date:	11/25/03					
ANNUAL CAPITAL COSTS						
DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES	
Initial Round of Water Levels	1	EA	\$1,300	\$1,300	See Water Levels Worksheet	
Annual Groundwater Monitoring of 4 wells	4	EA	\$600	\$2,400	See Laboratory Worksheet	
SUBTOTAL				\$3,700		
Contingency	20%		\$3,700	\$740		
SUBTOTAL				\$4,440		
Project Management	10%		\$4,440	\$444		
Remedial Design	0%		\$4,440	\$0	Not applicable.	
Construction Management	0%		\$4,440	\$0	Not applicable.	
SUBTOTAL				\$444		
TOTAL CAPITAL COST				\$4,900		
OPERATIONS AND MAINTENANCE COST						
DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES	
Annual Groundwater Monitoring of 4 wells	4	EA	\$600	\$2,400		
Reporting	1	EA	\$1,500	\$1,500		
SUBTOTAL				\$3,900		
Allowance for Misc. Items	20%		\$3,900	\$780		
SUBTOTAL				\$4,680		
TOTAL ANNUAL O&M COST				\$5,000		
PRESENT VALUE ANALYSIS						
			Discount Rate =	3.2%		
End Year	COST TYPE	TOTAL COST	TOTAL COST PER YEAR	DISCOUNT FACTOR (3.2%)	PRESENT VALUE	NOTES
1	FIRST YEAR CAPITAL COST	\$4,900	\$4,900	1.000	\$4,900	
10	ANNUAL COST	\$5,000	\$5,000	7.714	\$38,570	
	LUCs				\$20,000	
					\$63,470	
TOTAL PRESENT VALUE OF ALTERNATIVE					\$63,000	
SOURCE INFORMATION						
1. United States Environmental Protection Agency. July 2000. A Guide to Preparing and Documenting Cost Estimates During the Feasibility Study. EPA 540-R-00-002. (USEPA, 2000).						

Alternative: Number 2		COST ESTIMATE SUMMARY				
Elements: In-Situ Stabilization						
Site:	Charleston Naval Complex	Description: Ferrous sulfate injection into shallow groundwater zone (5-10 ft bgs); effect will be to bring pH into optimal zone for lead and antimony precipitation.				
Location:	SWMU 65					
Phase:	Corrective Measures Study					
Base Year:	2003					
Date:	11/25/03					
CAPITAL COSTS						
DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES	
Initial Round of Water Levels	1	EA	\$1,300	\$1,300	See Water Levels Worksheet	
Groundwater monitoring: quarterly of 1 well for first year; annually for the other 3 wells	7	EA	\$600	\$4,200	See Laboratory Worksheet	
Bench-scale study to select in-situ reagent	1	EA	\$8,000	\$8,000	CH2M estimate	
Injection Work Plan	1	EA	\$8,000	\$8,000	CH2M estimate	
Injection well	1	EA	\$2,000	\$2,000	CH2M estimate	
Initial Ferrous Sulfate injection	1	EA	\$10,000	\$10,000	CH2M estimate	
SUBTOTAL				\$33,500		
Contingency	20%		\$33,500	\$6,700		
SUBTOTAL				\$40,200		
				\$3,216	USEPA 2000, p. 5-13, \$100K \$500K	
Project Management	8%		\$40,200			
Remedial Design	0%		\$40,200	\$0	Included in work plan	
Construction Management	10%		\$40,200	\$4,020		
LUCs			\$20,000	\$20,000		
SUBTOTAL				\$27,236		
TOTAL CAPITAL COST				\$67,000		
OPERATIONS AND MAINTENANCE COST						
DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES	
GW Monitoring: Annual sampling of 4 wells for 4 years	4	EA	\$600	\$2,400	See Laboratory Worksheet	
Reporting	1	EA	\$1,500	\$1,500		
SUBTOTAL				\$3,900		
Allowance for Misc. Items	20%		\$3,900	\$780		
SUBTOTAL				\$4,680		
TOTAL ANNUAL O&M COST				\$5,000		
PRESENT VALUE ANALYSIS						
			Discount Rate =	3.2%		
End Year	COST TYPE	TOTAL COST	TOTAL COST PER YEAR	DISCOUNT FACTOR (3.2%)	PRESENT VALUE	NOTES
1	CAPITAL COST	\$67,000	\$67,000	1.000	\$67,000	
5	ANNUAL O&M COST (Yr 1-5)	\$5,000	\$5,000	3.699	\$18,497	
					\$85,497	
	TOTAL PRESENT VALUE OF ALTERNATIVE				\$90,000	
SOURCE INFORMATION						
1. United States Environmental Protection Agency. July 2000. A Guide to Preparing and Documenting Cost Estimates During the Feasibility Study. EPA 540-R-00-002. (USEPA, 2000).						

Alternative: **Number 3**
 Elements: **Groundwater Extraction with Treatment and Discharge**

COST ESTIMATE SUMMARY

Site: Charleston Naval Complex

Description: Groundwater extraction and treatment with discharge to sanitary sewer

Location: SWMU 65
 Phase: Corrective Measures Study
 Base Year: 2003
 Date: 11/25/03

CAPITAL COSTS

DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES
Initial Round of Water Levels	1	EA	\$1,300	\$1,300	See Water Levels Worksheet
Laboratory-first year: quarterly influent and effluent samples; monthly discharge analy.for lead	20	EA	\$50	\$1,000	
Recovery Well	1	EA	\$2,000	\$2,000	Engineers estimate
Pump test	1	EA	\$5,000	\$5,000	
Pump Equipment	1	EA	\$2,800	\$2,800	See Pump Worksheet
Electrical	1	EA	\$2,000	\$2,000	See Electrical Worksheet
Precipitation Treatment	1	EA	\$13,000	\$13,000	See Precip./Filtration Sheet
Groundwater monitoring - 4 wells once during first year	4	EA	\$600	\$2,400	See Laboratory work sheet
SUBTOTAL				\$27,100	
Contingency	20%		\$27,100	\$5,420	10% Scope + 10% Bid
SUBTOTAL				\$32,520	
Project Management	8%		\$32,520	\$4,878	USEPA 2000, p. 5-13, \$100K-\$500K
Remedial Design	15%		\$32,520	\$3,252	USEPA 2000, p. 5-13, \$100K-\$500K
Construction Management	10%		\$32,520	\$3,252	USEPA 2000, p. 5-13, \$100K-\$500K
LUCs			\$20,000	\$20,000	
SUBTOTAL				\$30,732	
TOTAL CAPITAL COST				\$63,000	

OPERATIONS AND MAINTENANCE COST

DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES
Laboratory (Annual Yr 2-5)	4	EA	\$600	\$2,400	
Monthly discharge analysis	12	EA	\$50	\$600	
Operation/labor	1	EA	\$4,200	\$4,200	
Electrical	1	EA	\$1,000	\$1,000	
Precipitation/filtration treatment (first year only)	1	EA	\$37,666	\$37,666	
SUBTOTAL				\$45,866	
Allowance for Misc. Items	20%		\$45,866	\$9,173	
SUBTOTAL				\$55,039	
TOTAL ANNUAL O&M COST				\$55,000	

PRESENT VALUE ANALYSIS

Discount Rate =

3.2%

End Year	COST TYPE	TOTAL COST	TOTAL COST PER YEAR	DISCOUNT FACTOR (3.2%)	PRESENT VALUE	NOTES
1	CAPITAL COST	\$63,000	\$63,000	1.000	\$63,000	
1	ANNUAL O&M COST-FIRST YR	\$55,000	\$55,000	0.969	\$53,295	
5	ANNUAL O&M COST-Yr 2-5	\$16,734	\$16,734	3.585	\$59,993	
					\$176,287	
	TOTAL PRESENT VALUE OF ALTERNATIVE				\$180,000	

SOURCE INFORMATION

1. United States Environmental Protection Agency. July 2000. A Guide to Preparing and Documenting Cost Estimates During the Feasibility Study. EPA 540-R-00-002. (USEPA, 2000).

Alternative:	Number 3					
Element:	Pump Installation					
Site:	Charleston Naval Complex	Prepared By:	RLC	Checked By:		
Location:	SWMU 65	Date:		Date:		
Phase:	Corrective Measures Study					
Base Year:	2003					
WORK STATEMENT						
Pump groundwater to surface for treatment.						
CAPITAL COSTS						
	DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES
	Pump	1	EA	\$1,550	\$1,550	CH2M-Jones Est.
	Install pump and secure	4	HR	\$68	\$272	CH2M-Jones Est.
	Controller	1	EA	\$200	\$200	CH2M-Jones Est.
	Tubing	20	LF	\$5	\$100	CH2M-Jones Est.
	Connections	1	EA	\$50	\$50	CH2M-Jones Est.
	Other Consumables	1	EA	\$200	\$200	CH2M-Jones Est.
	SUBTOTAL				\$2,372	
	Allowance for Misc Items	20%		\$2,372	\$474	
	SUBTOTAL				\$2,846	
	TOTAL UNIT COST				\$2,800	
OPERATIONS AND MAINTENANCE COST						
	DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES
	Site Operator	52	HR	\$68	\$3,536	1 hr/week for one year
	SUBTOTAL				\$3,536	
	Allowance for Misc. Items	20%		\$3,536	\$707	
	SUBTOTAL				\$4,243	
	TOTAL ANNUAL O&M COST				\$4,200	
Source of Cost Data						
1. Sources are as noted in cost table.						

Alternative: **Numbers 1,2,3**
 Element: **Water Levels**

Site: Charleston Naval Complex
 Location: SWMU 65
 Phase: Corrective Measures Study
 Base Year: 2003

Prepared By: DFW
 Date: 11/25/03

Checked By:
 Date:

WORK STATEMENT

Costs associated with a one-time collection of water levels

CAPITAL COSTS

DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES
Collection of water levels	6	HR	\$40	\$240	CH2M-Jones Est.
Potentiometric contour maps	8	HR	\$110	\$880	
SUBTOTAL				\$1,120	
Allowance for Misc. Items	20%		\$1,120	\$224	
SUBTOTAL				\$1,344	
TOTAL UNIT COST				\$1,300	

OPERATION AND MAINTENANCE COSTS

DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES
SUBTOTAL				\$0	
Allowance for Misc. Items	20%		\$0	\$0	
SUBTOTAL				\$0	
TOTAL O&M COST				\$0	

Alternative: Numbers 1,2,3					
Element: Laboratory Costs					
Site: Charleston Naval Complex	Prepared By: DFW	Checked By:			
Location: SWMU 65	Date: 11/25/03	Date:			
Phase: Corrective Measures Study					
Base Year: 2003					
WORK STATEMENT					
Costs associated with water sample collection, shipment and analysis on a per event and per well basis.					
CAPITAL COSTS					
DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES
Equipment & Labor per Event					
1 Liter Polypropylene	1	EA	\$1	\$1	CH2M-Jones Est.
Coolers	1	EA	\$10	\$10	CH2M-Jones Est.
Disposable Gloves	1	BOX	\$20	\$20	CH2M-Jones Est.
Collection of samples	2	HR	\$68	\$136	CH2M-Jones Est.
Sample Shipment	1	EA	\$20	\$20	CH2M-Jones Est.
Field Instruments	1	EA	\$50	\$50	CH2M-Jones Est.
Sample Analysis (metals)	1	SAMPLE	\$140	\$140	GEL, PEL, STL average
Analysis of data	1	HR	\$100	\$100	CH2M-Jones Est.
SUBTOTAL				<u>\$477</u>	
Allowance for Misc. Items	20%		\$477	<u>\$95.40</u>	
SUBTOTAL				<u>\$572</u>	
TOTAL UNIT COST				\$600	
OPERATION AND MAINTENANCE COSTS					
DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES
SUBTOTAL				\$0	
Allowance for Misc. Items	20%		\$0	<u>\$0</u>	
SUBTOTAL				<u>\$0</u>	
TOTAL O&M COST				\$0	
Source of Cost Data					
1 Analytical Bid Form - Charleston Naval Complex - Level II					

Alternative: **Number 1,3**
 Element: **Precipitation/Filtration System**

Site: Charleston Naval Complex
 Location: SWMU 65
 Phase: Corrective Measures Study
 Base Year: 2003

Prepared By: DFW
 Date: 11/25/03

Checked By:
 Date:

WORK STATEMENT

Use a precipitation/filtering system for remediation of lead in groundwater

CAPITAL COSTS

DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES
Capital Costs					
System: Tanks/Filters Feed system Mixer Associated Piping	1	EA	\$10,000	\$10,000	CH2M HILL
Piping: Tank to Treatment	10	FT	\$100	\$1,000	CH2M JonesEst.
SUBTOTAL				\$11,000	
Allowance for Misc Items	20%		\$11,000	\$2,200	
SUBTOTAL				\$13,200	
TOTAL COST				\$13,000	

OPERATION AND MAINTENANCE COSTS

DESCRIPTION	QTY	UNIT	UNIT COST	TOTAL	NOTES
Site Operator	416	HR	\$68	\$28,288	CH2M Jones Est. 8 hrs every week for first year
Chemicals/Filters Non-Hazardous Precipitate Disposal	26	EA	\$100	\$2,600	CH2M JonesEst.
	1	EA	\$500	\$500	CH2M JonesEst.
SUBTOTAL				\$31,388	
Allowance for Misc Items	20%		\$31,388	\$6,278	
SUBTOTAL				\$37,666	
TOTAL ANNUAL O&M COST				\$38,000	

Source of Cost Data

1. R.S. Means Company. 2000. Environmental Remediation Cost Data - Unit Price, 6th Edition. R.S. Means Company and Talisman Partners, Ltd. Kingston, MA. (Means(a)).
2. R.S. Means Company. 1999. Site Work and Cost Data, 18th Edition. R.S. Means Company. Kingston, MA. (Means(b)).
3. R.S. Means Company. 1999. Heavy Construction Cost Data, 13th Edition. R.S. Means Company. Kingston, MA. (Means(c)).

Cost Adjustment Checklist

FACTOR:

- H&S Productivity
- Escalation to Base Year
- Area Cost Factor
- Subcontractor Overhead and Profit
- Prime Contractor Overhead and Profit

NOTES:

Assume work conducted in Level D
 Current year (2001) is base year
 Adjusted Unit Costs for Charleston, South Carolina where applicable
 Assumed included in unit prices (15% Overhead + 10% Profit)
 Included in Solution Set Cost Estimates only.