CONESTOGA-ROVERS
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May 19, 2006

Reference No. 19867

Mr. Michael Hinton, P.E.
New York Department of Environmental Conservation
Division of Environmental Remediation, Region 9
270 Michigan Avenue
Buffalo, New York 14203-2999

RECEIVED
MAY 22 2006
NYSDEC REG 9
FOIL
__REL __UNREL

Dear Mr. Hinton:

Re: RI/FS Addendum II – Work Plan
Vanadium Corporation of America Site, Town of Niagara, New York

Enclosed, please find a copy of the Work Plan for additional data collection from the Vanadium Corporation of America Site, Town of Niagara, New York. The Work Plan addresses additional sampling and study for the wetland area south of OU-1.

Should you have any questions regarding this Work Plan, please do not hesitate to contact us.

Yours truly,

CONESTOGA-ROVERS & ASSOCIATES

Jamie Puskas
JP/ck/15

Encl.
c.c. Matthew Forcucci, NYSDOH (2 copies)
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Jim Hamula, Gallagher & Kennedy
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Ed Holman, New York Power Authority
Joe Flynn, EMC^2 (2 copies)

Addendum II to Phase I Work Plan
Operable Unit 3
Vanadium Corporation of America Site
Town of Niagara

The following paragraphs describe the Scope of Work and tasks for additional data collection for Operable Unit 3 (OU-3) at the Vanadium Corporation Site (Site) in the Town of Niagara, NY. All work will be conducted in accordance with the Phase I Work Plan Operable Unit 3 dated September 2002 and the additional methods attached to this Addendum. The attached Table 1 summarizes the samples to be collected and analyses to be performed.

1.0 SEDIMENT SAMPLES FOR AVS/SEM AND PORE WATER ANALYSES

- **Purpose**
  - evaluate the bioavailability of metals in the sediments in the wetland area south of OU-1 at locations where total metals are above the NYSDEC sediment quality benchmark Severe Effects Levels (SEL) (previous sediment data are presented in Attachment A)

- **Scope of Work**
  - collect sediment samples from locations HA-7, HA-8, HA-11, HA-12, HA-15, HA-16, and HA-17 over the depth interval of 0 to 6 inches
  - analyse sediment samples for AVS/SEM metals (cadmium, chromium, copper, lead, nickel, and zinc)
  - extract pore water from sediment samples and analyse pore water for cadmium, total chromium, copper, lead, nickel and zinc
  - perform sample collection and analyses in accordance with USEPA 2005, Procedures for the Derivation of Equilibrium Partioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms Metal Mixtures (Cadmium, Copper, Lead, Nickel, Silver and Zinc EPA/600/R-02/011) (see Attachment B)
  - sample locations are shown on the attached Figure 1

2.0 SURFACE WATER SAMPLES FROM WETLAND AREA

- **Purpose**
  - obtain chemistry data for surface water in wetland to assist in evaluation of options for managing water during remediation

- **Scope of Work**
  - collect three surface water samples at locations SW-25, SW-26, and SW-27and analyze for TCL VOCs, TCL SVOCs, TAL metals (total and dissolved), total suspended solids, soluble organic carbon
  - care will be taken to avoid disturbing the bottom sediments during the sampling
  - sample locations are shown on the attached Figure 1

3.0 SEDIMENT TREATABILITY TEST

- **Purpose**
  - evaluate various options for dewatering and solidifying wetland sediments that may need to be remediated

- **Scope of Work**
  - collect representative sediment samples from the wetland in the vicinity of samples HA-11, HA-15 and HA-16 and conduct bench scale treatability testing in accordance with Attachment C

4.0 WETLAND DELINEATION AND WETLAND FUNCTION AND VALUES ASSESSMENT

- **Purpose**
  - delineate the wetland south of OU-1 and assess the function and values of the identified wetlands

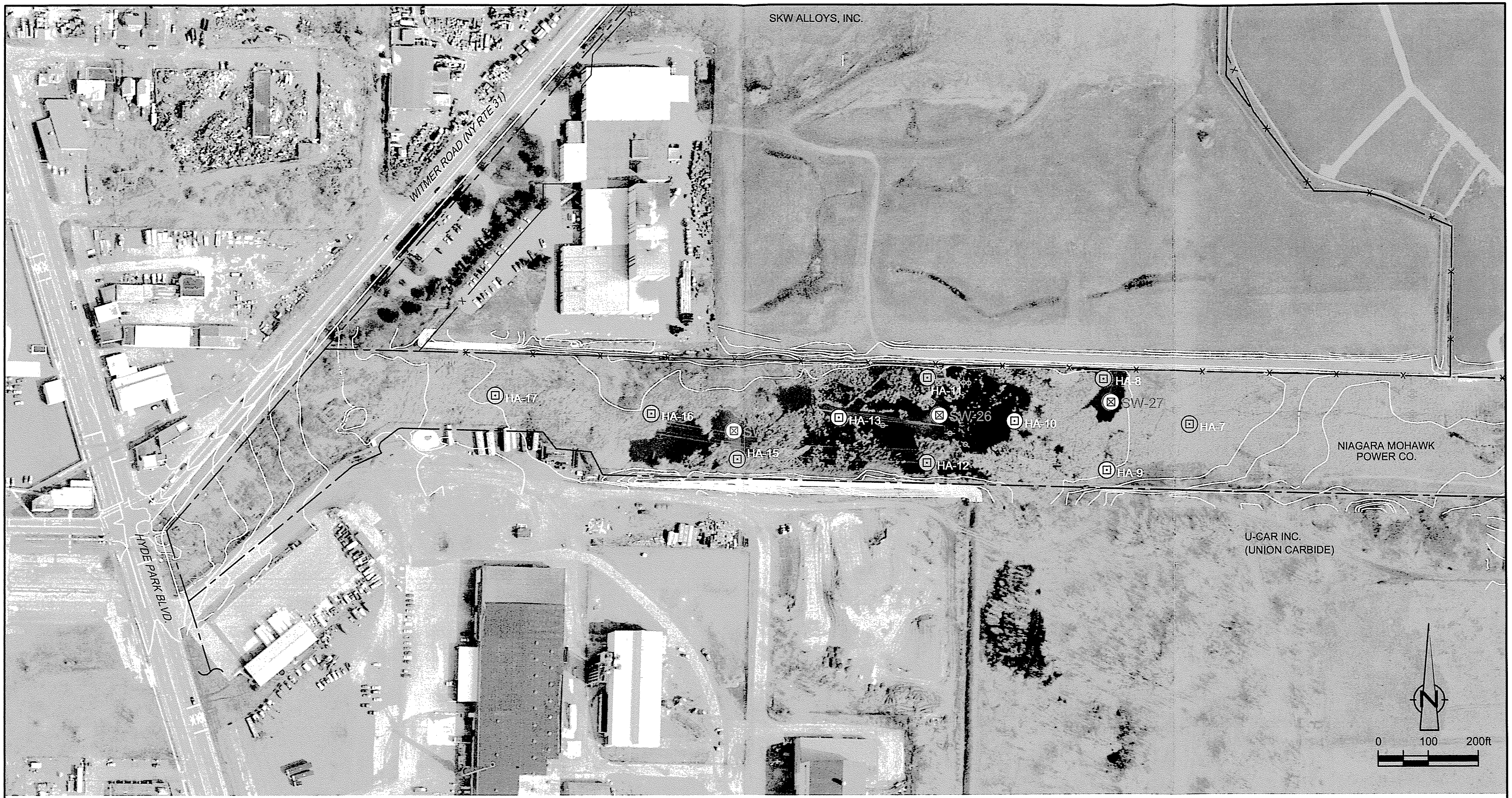
- **Scope of Work**
  - delineate the wetland area south of OU-1 in accordance with the procedures specified in the Corps of Engineers Wetland Delineation Manual produced by the Waterways Experiment Station in 1987
  - conduct functions and values assessment of the identified wetland

5.0 ADDITIONAL PIEZOMETER INSTALLATION AND WATER LEVEL MONITORING

- **Purpose**
  - monitoring groundwater levels and surface water levels to evaluate groundwater mounding in the slag and potential discharge to surface water

- **Scope of Work**
  - install one 2″ Ø groundwater piezomete (MW-29) to the base of the slag material at the location shown on Figure 2
  - typical piezometer construction is shown on Figure 3
  - obtain water level measurements at the following locations two times per week for a period of 4weeks
    - MW-17
    - MW-18
    - MW-20
    - MW-21
    - MW-22
    - MW-23
    - MW-24
    - MW-25
    - MW-27
    - MW-28
    - MW-29
    - SG-1
    - SG-2
    - SG-3
    - SG-4
    - MW-104A
    - MW-103A
    - MW-102A
    - MW-105A

FIGURES



LEGEND

PROPERTY LINE

FENCE

RAILROAD

NYPA NEW YORK POWER AUTHORITY

SURFACE WATER/SEDIMENT SAMPLING LOCATION

HA-4 PROPOSED SEDIMENT SAMPLING LOCATION

☒ SW-25 PROPOSED SURFACE WATER SAMPLING LOCATION

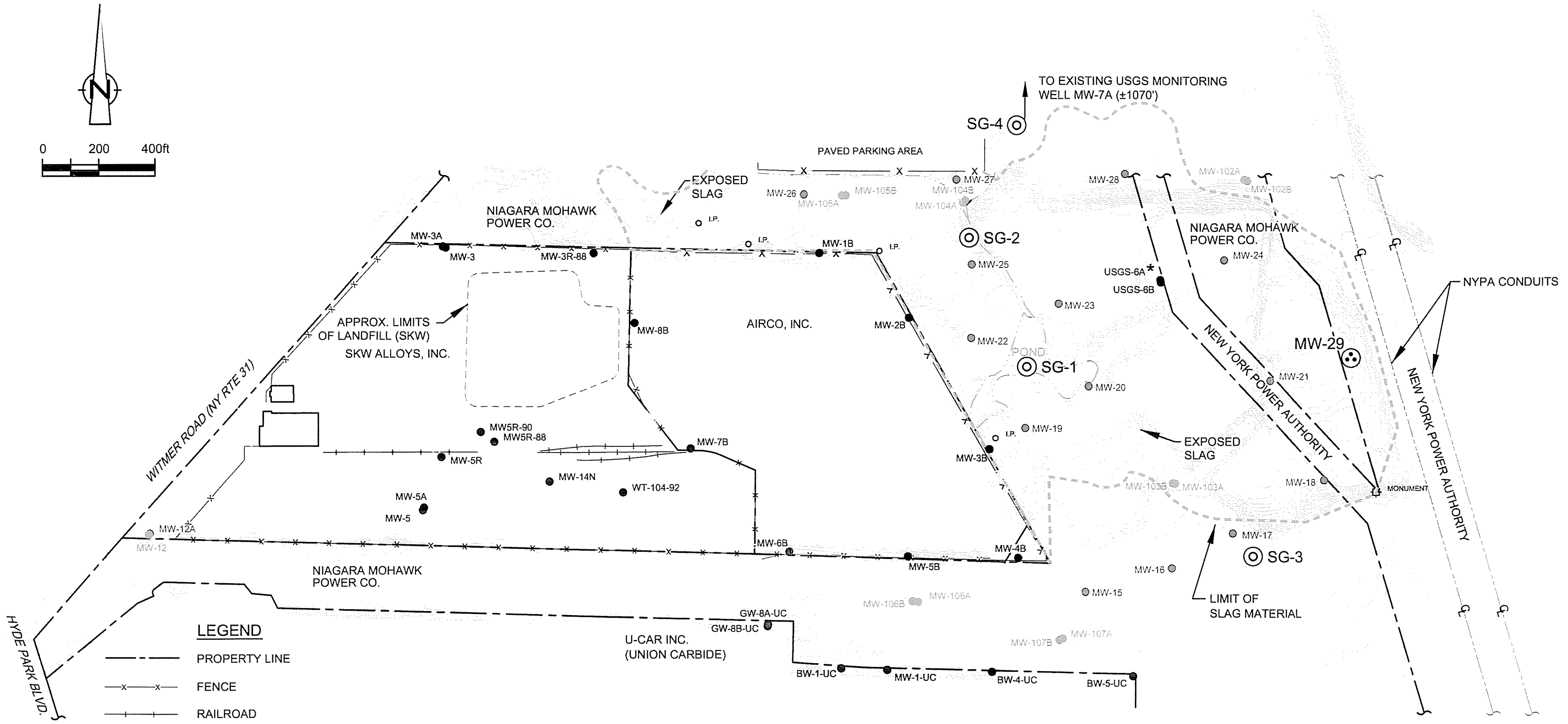
UTILITY POLE

☒ TOWER

figure 1

PROPOSED SAMPLING LOCATIONS
VANADIUM CORPORATION OF AMERICA SITE
Town of Niagara, NY

19867-00(HINT015)GN-WA001 MAY 19/2006



LEGEND

—·—·—	PROPERTY LINE
—x—x—	FENCE
—+—+—	RAILROAD
● MW-7B	OTHER EXISTING MONITORING WELL LOCATION
	MONITORING WELL NO LONGER EXISTS IN FIELD
● MW19	OU3 EXISTING SHALLOW OVERBURDEN MONITORING WELL LOCATION
● MW-105A	OU3 EXISTING DEEP OVERBURDEN MONITORING WELL LOCATION
● MW-106B	OU3 EXISTING BEDROCK MONITORING WELL LOCATION
*	MONITORING WELL NO LONGER FUNCTIONAL
⬚	LIMIT OF SLAG MATERIAL (CRA, 2003/04)
⊛ MW-29	PROPOSED PIEZOMETER LOCATION
◎ SG-1	PROPOSED SURFACE WATER ELEVATION MONITORING LOCATION

NOTES:

1. BASE MAP DIGITIZED FROM 'VANADIUM SITE NO. 932001' PROVIDED BY LU ENGINEERS, 2230 PENFIELD RD., PENFIELD, NY, (716) 377-1450. MAP DATA DIGITIZED FROM 'SITE PLAN AND SAMPLING LOCATION' PREPARED BY ABB ENVIRONMENTAL.
2. SITE FEATURES AND SAMPLE LOCATIONS ARE APPROXIMATE.

SOURCE:

NIAGARA MOHAWK POWER CORPORATION, VANADIUM CORPORATION OF AMERICA SITE, NIAGARA FALLS, NY. FIGURES 1, 2 AND 3, BBL ENGINEERS & SCIENTISTS. 12/8/2000

figure 2

PROPOSED NEW PIEZOMETER LOCATION
VANADIUM CORPORATION OF AMERICA SITE
Town of Niagara, NY

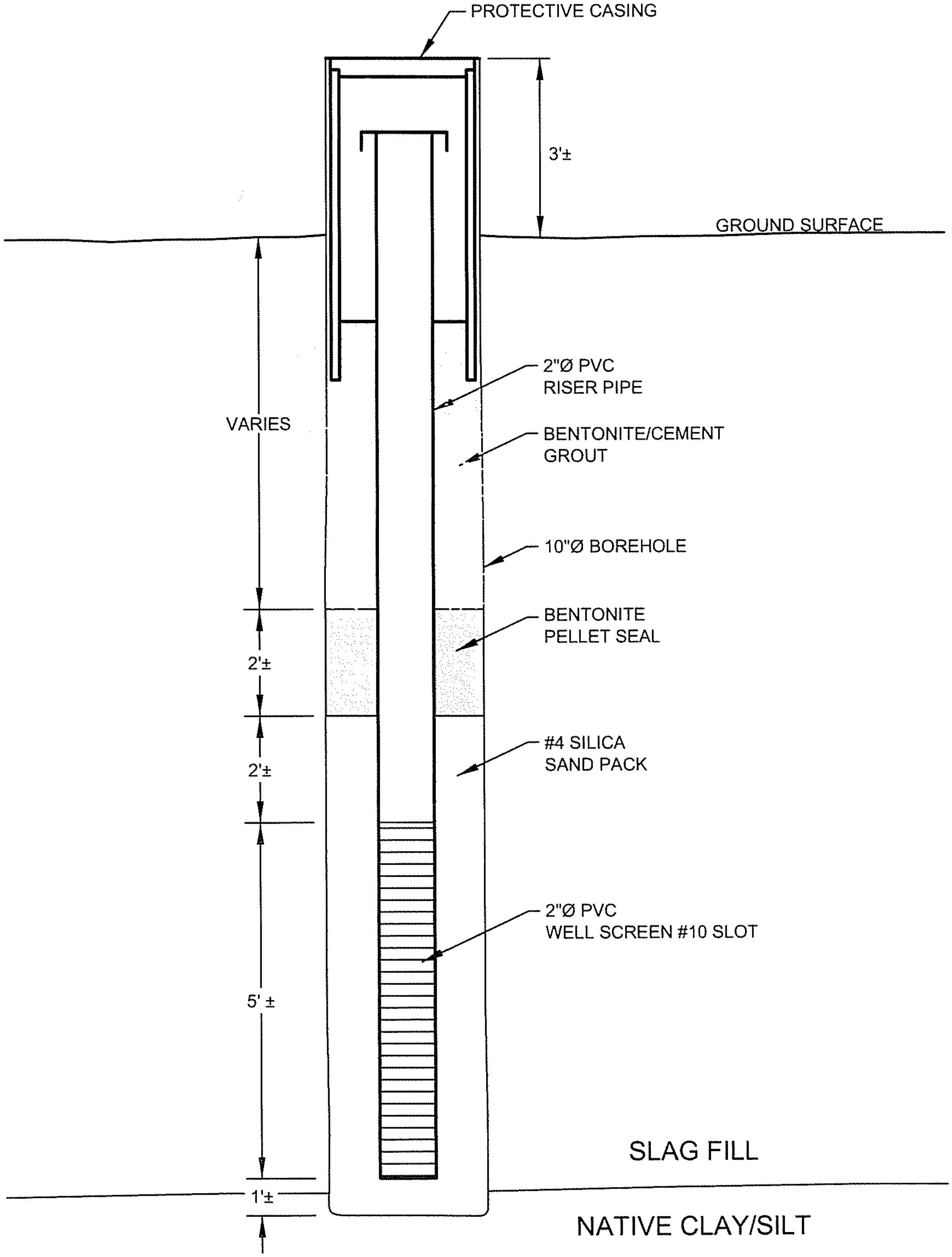


figure 3

TYPICAL SHALLOW PIEZOMETER
VANADIUM CORPORATION OF AMERICA SITE
Town of Niagara. NY

TABLES

TABLE 1

SAMPLE AND ANALYSES SUMMARY

Task	*Description*	*Material to be Sampled*	*Number of Samples*	*Analyses*
1.	Sediment Samples for AUS/SEM and Porewater Analyses	sediment from wetland (0 to 6")	7	AVS/SEM (cadmium, copper, lead, nickel, zinc, chromium), total organic carbon, and porewater (cadmium, chromium, copper, lead, nickel, zinc
2.	Surface water samples	surface water from wetland	3	TCL VOCs, TCL SVOCs, TAL metals (total and dissolved), TSS, soluble organic carbon
3.	Sediment Treatability Testing	sediment	1 representative sample	dewatering and solidification
4.	Wetland Delineation and Wetland Function and Values Assessment	NA	NA	NA
5.	Additional Piezometer Installation and water level measurements	NA	19 locations	Water level measures twice per week for 4 weeks

ATTACHMENTS

ATTACHMENT A

SEDIMENT DATA FOR WETLAND SOUTH OF OU-1

TABLE 4

ANALYTICAL RESULTS SUMMARY
HAND AUGER SEDIMENT SAMPLES
DECEMBER 2005

Sample Location:				*HA-7*	*HA-8*	*HA-9*	*HA-9*	*HA-10*	*HA-11*
Sample ID:				*S-19867-121305-JRR-005*	*S-19867-122005-KH-041*	*S-19867-121905-KH-038*	*S-19867-121905-KH-039*	*S-19867-122005-KH-043*	*S-19867-121905-KH-036*
Sample Date:				*12/13/2005*	*12/20/2005*	*12/19/2005*	*12/19/2005*	*12/20/2005*	*12/19/2005*
Sample Depth:				*0-0.5 ft*	*0-0.5 ft*	*0-0.5 ft*	*0-0.5 ft*	*0-0.5 ft*	*0-0.5 ft*
							Duplicate		
Parameters:	*Units*	*NYSDEC Sediment_Metals_Lowest_Effect_Level*	*NYSDEC Sediment_Metals_Sever_Effect_Level*						
		a	b						
Metals									
Aluminum	mg/kg	-	-	1290	14800	745 J	2540 J	20900	13400
Antimony	mg/kg	2.0	25.0	ND (2.0) UJ	ND (2.0) UJ	ND (4.3) UJ	ND (2.4) UJ	ND (1.5) UJ	ND (3.7) UJ
Arsenic	mg/kg	6.0	33.0	1.8 J	**7.0**^{a}	ND (4.3) U	2.1 J	3.4	**14.8**^{a}
Barium	mg/kg	-	-	179	104	49.0 J	85.1	126	1130
Beryllium	mg/kg	-	-	ND (0.82) U	0.82	0.31 J	0.33 J	1.3	1.2 J
Cadmium	mg/kg	0.6	9.0	0.19 J	0.50 J	0.32 J	**1.2 J**^{a}	0.42 J	**6.2**^{a}
Calcium	mg/kg	-	-	323000 J	26000	77300	149000	7250	234000
Chromium Total	mg/kg	26.0	110.0	**241**^{ab}	**291**^{ab}	**51.1**^{a}	**48.4**^{a}	**38.3**^{a}	**1340**^{ab}
Chromium VI (Hexavalent)	mg/kg	-	-	4.4 J	ND (0.80) UJ	ND (1.7) UJ	ND (0.96) UJ	ND (0.61) UJ	ND (1.5) UJ
Cobalt	mg/kg	-	-	0.62 J	8.8 J	3.5 J	6.4 J	10.1	14.9 J
Copper	mg/kg	16.0	110.0	**23.2**^{a}	**95.6**^{a}	**32.6 J**^{a}	**119 J**^{ab}	**19.9**^{a}	**693**^{ab}
Iron	mg/kg	20000	40000	2040	18100	2920	7410	**24900**^{a}	18700
Lead	mg/kg	31.0	110.0	29.8	**47.9**^{a}	12.4	24.6	10.9	**244**^{ab}
Magnesium	mg/kg	-	-	5090	5550	1420 J	2750	5590	23900
Manganese	mg/kg	460.0	1100.0	**532**^{a}	325	342 J	**2050 J**^{ab}	310	**5180**^{ab}
Mercury	mg/kg	0.15	1.3	0.033 J	0.082	0.15	**0.25**^{a}	0.064	**0.72**^{a}
Nickel	mg/kg	16.0	50.0	3.8 J	**47.0**^{a}	**21.1**^{a}	**43.2**^{a}	**20.9**^{a}	**215**^{ab}
Potassium	mg/kg	-	-	305 J	1610	349 J	528 J	2410	1760 J
Selenium	mg/kg	-	-	0.94 J	1.0	1.4 J	1.2	0.84	3.4
Silver	mg/kg	1.0	2.2	0.12 J	0.23 J	ND (2.2) U	**1.1 J**^{a}	ND (0.76) U	**4.5**^{ab}
Sodium	mg/kg	-	-	364 J	295 J	442 J	384 J	224 J	675 J
Thallium	mg/kg	-	-	ND (2.0) U	ND (2.0) U	ND (4.3) U	ND (2.4) U	ND (1.5) U	ND (3.7) U
Vanadium	mg/kg	-	-	5.9 J	30.3	5.5 J	13.3	34.1	32.8
Zinc	mg/kg	120.0	270.0	29.1	**140**^{a}	67.8 J	**204 J**^{a}	**122**^{a}	**1100 J**^{ab}
General Chemistry									
pH Field	none	-	-	7.7	7.0	7.1	7.0	6.8	6.9
Total Solids	%	-	-	48.8	50.1	23.0	41.5	65.4	27.0

Notes:

J - Estimated concentration.

ND - Non-detect at associated value.

U - Not present at or above the associated value.

UJ - Estimated reporting limit.

TABLE 4

ANALYTICAL RESULTS SUMMARY
HAND AUGER SEDIMENT SAMPLES
DECEMBER 2005

Sample Location:				*HA-12*	*HA-13*	*HA-15*	*HA-16*	*HA-17*
Sample ID:				*S-19867-122005-KH-045*	*S-19867-121905-KH-032*	*S-19867-121905-KH-034*	*S-19867-121305-JRR-009*	*S-19867-121305-JRR-011*
Sample Date:				*12/20/2005*	*12/19/2005*	*12/19/2005*	*12/13/2005*	*12/13/2005*
Sample Depth:				*0-0.5 ft*	*0-0.5 ft*	*0-0.5 ft*	*0-0.5 ft*	*0-0.5 ft*
Parameters:	*Units*	*NYSDEC Sediment_Metals_Lowest_Effect_Level* a	*NYSDEC Sediment_Metals_Sever_Effect_Level* b					
Metals								
Aluminum	mg/kg	-	-	1630	15900	2470	17800	14000
Antimony	mg/kg	2.0	25.0	ND (5.4) UJ	ND (1.5) UJ	ND (2.3) UJ	ND (2.1) UJ	ND (1.8) UJ
Arsenic	mg/kg	6.0	33.0	1.9 J	4.6	2.3	**8.2**^{a}	4.8
Barium	mg/kg	-	-	114	81.7	195	151	210
Beryllium	mg/kg	-	-	0.44 J	2.0	2.9	0.85	0.89
Cadmium	mg/kg	0.6	9.0	ND (2.7) U	0.49 J	**0.92 J**^{a}	**0.70 J**^{a}	0.60 J
Calcium	mg/kg	-	-	118000	5280	313000	13000 J	40100 J
Chromium Total	mg/kg	26.0	110.0	**173**^{ab}	**84.3**^{a}	**476**^{ab}	**658**^{ab}	**314**^{ab}
Chromium VI (Hexavalent)	mg/kg	-	-	ND (2.2) UJ	ND (0.59) UJ	ND (0.94) UJ	ND (0.85) UJ	ND (0.72) UJ
Cobalt	mg/kg	-	-	7.4 J	10.8	4.6 J	16.6	15.9
Copper	mg/kg	16.0	110.0	**98.5**^{a}	**21.1**^{a}	**48.7**^{a}	**88.0**^{a}	**65.0**^{a}
Iron	mg/kg	20000	40000	7370	**22800**^{a}	3670	**26600**^{a}	**25300**^{a}
Lead	mg/kg	31.0	110.0	**31.5**^{a}	20.2	30.7	**73.2**^{a}	**58.5**^{a}
Magnesium	mg/kg	-	-	2730	4400	4230	7650	5800
Manganese	mg/kg	460.0	1100.0	**724**^{a}	**622**^{a}	**532**^{a}	**783**^{a}	**1650**^{ab}
Mercury	mg/kg	0.15	1.3	**0.25**^{a}	0.075	0.11	**0.19**^{a}	**0.18**^{a}
Nickel	mg/kg	16.0	50.0	**40.0**^{a}	**23.0**^{a}	**16.3**^{a}	**98.7**^{ab}	**55.6**^{ab}
Potassium	mg/kg	-	-	506 J	1680	714 J	1530	2070
Selenium	mg/kg	-	-	2.0 J	0.92	4.2	3.6	4.0
Silver	mg/kg	1.0	2.2	ND (2.7) U	0.71 J	**1.5**^{a}	0.52 J	0.33 J
Sodium	mg/kg	-	-	413 J	339 J	520 J	263 J	206 J
Thallium	mg/kg	-	-	ND (5.4) U	0.97 J	ND (2.3) U	1.1 J	0.98 J
Vanadium	mg/kg	-	-	9.3 J	33.6	9.5 J	48.8	34.0
Zinc	mg/kg	120.0	270.0	75.1	75.7 J	95.6 J	**205**^{a}	**146**^{a}
General Chemistry								
pH Field	none	-	-	7.1	6.9	6.9	7.2	7.4
Total Solids	%	-	-	18.6	67.3	42.8	47.2	55.9

Notes:

J - Estimated concentration.

ND - Non-detect at associated value.

U - Not present at or above the associated value.

UJ - Estimated reporting limit.

ATTACHMENT B

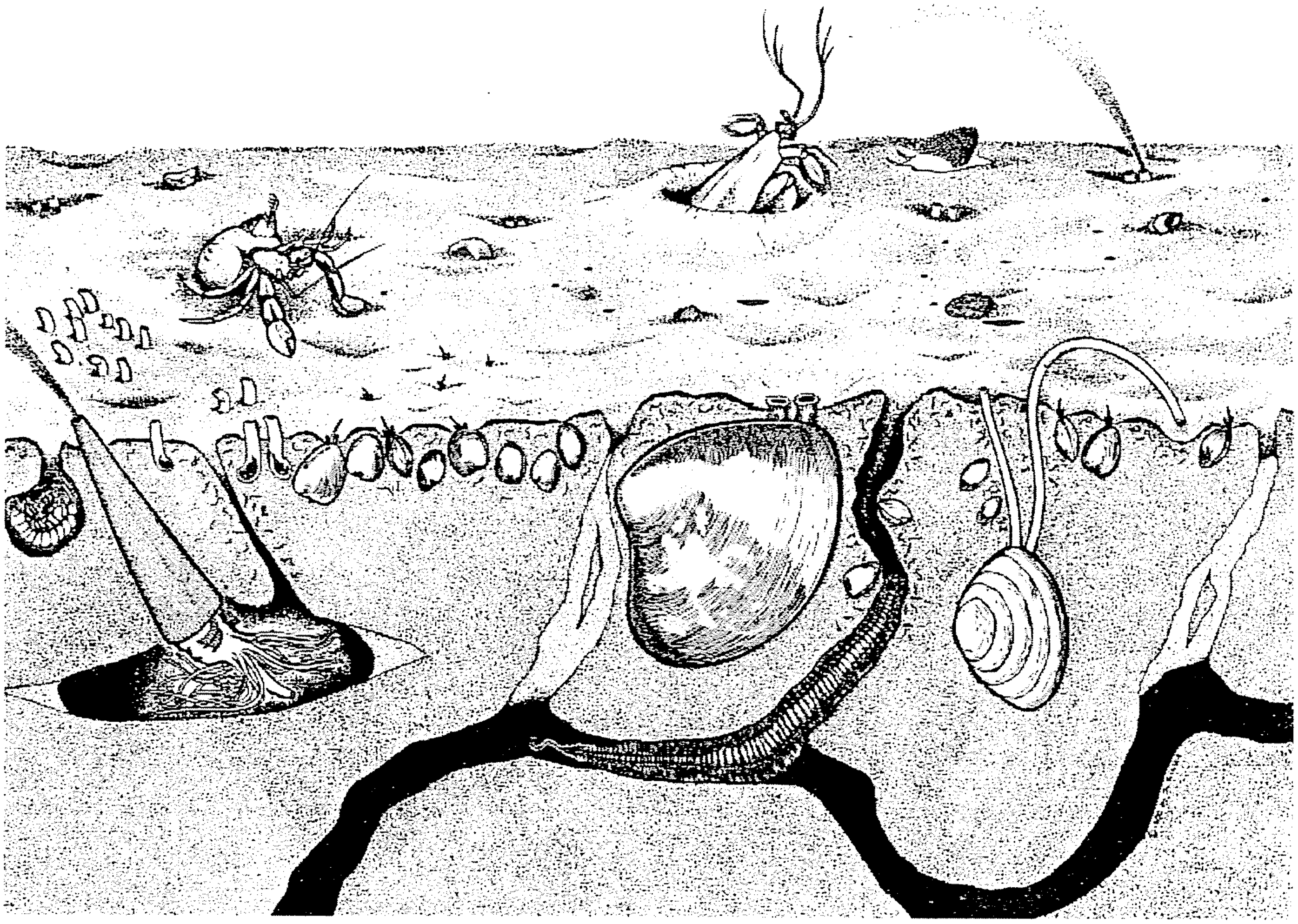
PROCEDURES FOR THE DERIVATION OF EQUILIBRIUM PARTIONING SEDIMENT BENCHMARKS (ESBs) FOR THE PROTECTION OF BENTHIC ORGANISMS: METALS MIXTURES (CADMIUM, COPPER, LEAD, NICKEL, SILVER AND ZINC)

United States
Environmental Protection
Agency

Office of Research and Development
Washington, DC 20460

EPA-600-R-02-011
www.epa.gov

Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Metal Mixtures (Cadmium, Copper, Lead, Nickel, Silver, and Zinc)



EPA/600/R-02/011
January 2005

Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Metal Mixtures (Cadmium, Copper, Lead, Nickel, Silver and Zinc)

David J. Hansen
(formerly with U.S. EPA)

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Office of Research and Development
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Mid-Continent Ecology Division, Duluth, MN

Notice

The Office of Research and Development (ORD) has produced this document to provide procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for metal mixtures. ESBs may be useful as a complement to existing sediment assessment tools. This document should be cited as:

> U.S. EPA. 2005. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Metal Mixtures (Cadmium, Copper, Lead, Nickel, Silver and Zinc). EPA-600-R-02-011. Office of Research and Development. Washington, DC 20460

This document can also be found in electronic format at the following web address:

http://www.epa.gov/nheerl/publications/

The information in this document has been funded wholly by the U.S. Environmental Protection Agency. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document.

Abstract

This equilibrium partitioning sediment benchmark (ESB) document describes procedures to derive concentrations of metal mixtures in sediment which are protective of the presence of benthic organisms. The equilibrium partitioning (EqP) approach was chosen because it accounts for the varying biological availability of chemicals in different sediments and allows for the incorporation of the appropriate biological effects concentration. This provides for the derivation of benchmarks that are causally linked to the specific chemical, applicable across sediments, and appropriately protective of benthic organisms.

EqP can be used to calculate ESBs for any toxicity endpoint for which there are water-only toxicity data; it is not limited to any single effect endpoint. For the purposes of this document, the ESB for mixtures of the metals cadmium, copper, lead, nickel, silver, and zinc, the $\text{ESB}_{\text{AVS:WQC}}$, is derived based on two complementary approaches. In the first approach, the $\text{ESB}_{\text{AVS:WQC}}$ is based on the solid phase and interstitial water phase of sediments. In sediments, these metals should not cause direct toxicity to benthic organisms if the ΣSEM-AVS is ≤ 0.0. In the second approach, sediments containing these metals should not cause direct toxicity to benthic organisms if the sum of the dissolved interstitial water concentrations for each of the metals ($\Sigma M_{i,d}$) divided by their respective Water Quality Criteria (WQC) Final Chronic Value (FCV) is ≤ 1.0. Uncertainty bounds on ΣSEM-AVS and (ΣSEM-AVS)/f_{OC} can be used to identify sediments where toxicity, because of these metals, is unlikely, uncertain, or likely. If the ΣSEM-AVS is > 0.0 or $\Sigma M_{i,d}$ divided by their respective FCVs is >1.0, effects may occur with increasing severity as the degree of exceedance increases. A procedure for addressing chromium toxicity in sediments is also included in an appendix.

The ESBs do not consider the antagonistic, additive or synergistic effects of other sediment contaminants in combination with metal mixtures or the potential for bioaccumulation and trophic transfer of metal mixtures to aquatic life, wildlife or humans.

Foreword

Under the Clean Water Act (CWA), the U.S. Environmental Protection Agency (EPA) and the States develop programs for protecting the chemical, physical, and biological integrity of the nation's waters. To support the scientific and technical foundations of the programs, EPA's Office of Research and Development has conducted efforts to develop and publish equilibrium partitioning sediment benchmarks (ESBs) for some of the 65 toxic pollutants or toxic pollutant categories. Toxic contaminants in bottom sediments of the nation's lakes, rivers, wetlands, and coastal waters create the potential for continued environmental degradation even where water column contaminant levels meet applicable water quality standards. In addition, contaminated sediments can lead to water quality impacts, even when direct discharges to the receiving water have ceased.

The ESBs and associated methodology presented in this document provide a means to estimate the concentrations of a substance that may be present in sediment while still protecting benthic organisms from the effects of that substance. These benchmarks are applicable to a variety of freshwater and marine sediments because they are based on the biologically available concentration of the substance in the sediments. These ESBs are intended to provide protection to benthic organisms from direct toxicity due to this substance. In some cases, the additive toxicity for specific classes of toxicants (e.g., metal mixtures or polycyclic aromatic hydrocarbon mixtures) is addressed. The ESBs do not consider the antagonistic, additive or synergistic effects of other sediment contaminants in combination with metal mixtures or the potential for bioaccumulation and trophic transfer of metal mixtures to aquatic life, wildlife or humans.

ESBs may be useful as a complement to existing sediment assessment tools, to help assess the extent of sediment contamination, to help identify chemicals causing toxicity, and to serve as targets for pollutant loading control measures.

This document provides technical information to EPA Program Offices, including Superfund, Regions, States, the regulated community, and the public. For example, ESBs when used in the Superfund process, would serve for screening purposes only, not as regulatory criteria, site specific clean-up standards, or remedial goals. The ESBs do not substitute for the CWA or EPA's regulations, nor is it a regulation itself. Thus, it cannot impose legally binding requirements on EPA, States, or the regulated community. EPA and State decision makers retain the discretion to adopt approaches on a case-by-case basis that differ from this technical information where appropriate. EPA may change this technical information in the future. This document has been reviewed by EPA's Office of Research and Development (Mid-Continent Ecology Division, Duluth, MN; Atlantic Ecology Division, Narragansett, RI), and approved for publication.

Mention of trade names or commercial products does not constitute endorsement or recommendation of use.

This is contribution AED-02-048 of the Office of Research and Development National Health and Environmental Effects Research Laboratory's Atlantic Ecology Division.

Front cover image provided by Wayne R. Davis and Virginia Lee.

Contents

Tables

Figures

Acknowledgments

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Mary C. Reiley	U.S. EPA, Office of Water, Washington, DC
Christopher S. Zarba	U.S. EPA, Office of Research and Development, Washington, DC

Significant Contributors to the Development of the Approach and Supporting Science

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Executive Summary

This equilibrium partitioning sediment benchmark (ESB) document describes procedures to derive concentrations of metal mixtures in sediment which are protective of the presence of benthic organisms. The equilibrium partitioning (EqP) approach was chosen because it accounts for the varying biological availability of chemicals in different sediments and allows for the incorporation of the appropriate biological effects concentration U.S. EPA (2003a). This provides for the derivation of benchmarks that are causally linked to the specific chemical, applicable across sediments, and appropriately protective of benthic organisms.

Equilibrium partitioning theory predicts that these metals partition in sediment between acid volatile sulfide (AVS, principally iron monosulfide), interstitial (pore) water, benthic organisms, and other sediment phases such as organic carbon. Biological responses of benthic organisms to these metals in sediments are different across sediments when the sediment concentrations are expressed on a dry weight basis, but similar when expressed on a ΣSEM-AVS or interstitial water basis. The difference between the sum of the molar concentrations of simultaneously extracted metal (ΣSEM, the metal extracted in the AVS extraction procedure) minus the molar concentration of AVS accurately predicts which sediments are not toxic because of these metals. The use of (ΣSEM-AVS)/f_{OC} reduces variability associated with prediction of when sediments will be toxic.

EqP can be used to calculate ESBs for any toxicity endpoint for which there are water-only toxicity data; it is not limited to any single effect endpoint. For the purposes of this document, the ESB for mixtures of the metals cadmium, copper, lead, nickel, silver, and zinc is based on the solid phase and interstitial water phase of sediments. In sediments, these metals should not cause direct toxicity to benthic organisms if the ΣSEM-AVS is ≤ 0.0. Alternatively, sediments containing these metals should not cause direct toxicity to benthic organisms if the sum of the dissolved interstitial water concentrations for each of the metals ($\Sigma M_{i,d}$) divided by their respective water quality criteria final chronic value (FCV) is ≤ 1.0. Uncertainty bounds on ΣSEM-AVS and (ΣSEM-AVS)/f_{OC} can be used to identify sediments where toxicity, because of these metals, is unlikely, uncertain, or likely. If an FCV is not available, a secondary chronic value (SCV) can be substituted. Ancillary analyses conducted as part of this derivation suggest that the sensitivity of benthic/epibenthic organisms is not significantly different from pelagic organisms; for this reason, the FCV and the resulting $\text{ESB}_{\text{AVS:WQC}}$ should be fully applicable to benthic organisms. The $\text{ESB}_{\text{AVS:WQC}}$s should be interpreted as chemical concentrations below which adverse effects are not expected. At concentrations above the $\text{ESB}_{\text{AVS:WQC}}$s, effects may occur with increasing severity as the degree of exceedance increases. In principle, above the upper confidence limit effects are expected if the chemical is bioavailable as predicted by EqP theory. A sediment-specific site assessment would provide further information on chemical bioavailability and the expectation of toxicity relative to the $\text{ESB}_{\text{AVS:WQC}}$s and associated uncertainty limits. An appendix addresing chromium toxicity in sediments is also included in this document.

As discussed, while this document uses the WQC or AVS values, the EqP methodology can be used by environmental managers to derive a benchmark with any desired level of protection, so long as the water-only concentration affording that level of protection is known. Therefore, the resulting benchmark can be species or site-specific if the corresponding water-only information is available. For example, if a certain water-only effects concentration is known to be

economically important benthic species, the FCV or SCV for that benthic species could be used to derive the benchmark. Such a benchmark might be considered as providing "site-specific protection" for a species or endpoint, if the goal is to derive a benchmark for that particular site or species. Another way to make an ESB site-specific would be to incorporate information on unusual partitioning, if suspected, at the site (see U.S. EPA 2003b).

The ESBs do not consider the antagonistic, additive or synergistic effects of other sediment contaminants in combination with metal mixtures or the potential for bioaccumulation and trophic transfer of metal mixtures to aquatic life, wildlife or humans. Consistent with the recommendations of EPA's Science Advisory Board, publication of these documents does not imply the use of ESBs as stand-alone, pass-fail criteria for all applications; rather, ESB exceedances could be used to trigger the collection of additional assessment data. When using the AVS approach, the $ESB_{AVS:WQC}$ applies to sediments having AVS concentrations $\geq$ 0.1 μmol/g.

Tier 1 and Tier 2 ESB values were developed to reflect differing degrees of data availability and uncertainty. Tier 1 ESBs have been derived for metal mixtures in this document, and for the nonionic organic insecticides endrin and dieldrin, and polycyclic aromatic hydrocarbon (PAH) mixtures in U.S. EPA (2003c, d, e). Tier 2 ESBs are reported in U.S. EPA (2003f).

Glossary of Abbreviations

Ag	Silver
Ag_2S	Silver monosulfide
AVS	Acid volatile sulfide
CCC	Criteria continuous concentration
Cd	Cadmium
$\{Cd^{2+}\}$	Activity of ionic cadmium (mol/L)
$[Cd^{2+}]$	Concentration of ionic cadmium (mol/L)
$[Cd]_A$	Concentration of added cadmium (mol/L)
$[Cd]_B$	Concentration of bound cadmium (mol/L)
$[CdS(s)]$	Concentration of solid-phase cadmium sulfide (mol/L)
Cr	Chromium
C_S	Concentration of contaminant in sediment
C_s^*	Sediment LC50 Concentration
Cu	Copper
CWA	Clean Water Act
DOC	Dissolved organic carbon
EDTA	Ethlyenediaminetetra-acetic acid
EMAP	Environmental Monitoring and Assessment Program
EPA	U.S. Environmental Protection Agency
EqP	Equilibrium partitioning
ESB(s)	Equilibrium partitioning sediment benchmark(s)
$ESB_{AVS:WQC}$	Equilibrium partitioning sediment benchmark(s) for metal mixtures based on the Water Quality Criteria Final Chronic Values or Acid Volatile Sulfide
f_{OC}	Fraction of organic carbon in sediment
FCV	Final chronic value
Fe	Iron
$\{Fe^{2+}\}$	Activity of ionic iron (mol/L)
$[Fe^{2+}]$	Concentration of ionic iron (mol/L)
$[FeS(s)]$	Concentration of solid-phase iron sulfide (mol/L)

$[FeS(s)]_i$	Concentration of initial solid-phase iron sulfide (mol/L)
FeS	Iron monosulfide
GFAA	Gas Furnace Atomic Absorption Spectrophotometry
HECD	U.S. EPA, Health and Ecological Criteria Division
IW	Interstitial water
IWBU	Interstitial water benchmarks unit
IWTU	Interstitial water toxic unit
K_{FeS}	Solubility product for FeS(s) $[(mol/L)^2]$
K_{MS}	Solubility product for MS(s) $[(mol/L)^2]$
K_{OC}	Organic carbon–water partition coefficient
K_P	Sediment–interstitial water partition coefficient
K_{SP}	Solubility product constant
LC50	Concentration estimated to be lethal to 50% of the test organisms within a specified time period
M^{2+}	Divalent metal—cadmium, copper, lead, nickel, silver, or zinc
MOH^+	Metal hydroxide
MS	Metal sulfide
Mn	Manganese
$\{M^{2+}\}$	Divalent metal activity (mol/L)
$[M^{2+}]$	Concentration of ionic metal (mol/L)
$[M]_A$	Concentration of added metal (mol/L)
$[M]_B$	Concentration of bound metal (mol/L)
$[M_d]$	Dissolved metal concentration in the interstitial water
[MS(s)]	Concentration of solid-phase metal sulfide (mol/L)
$[M_T]$	Total cold extractable metal (mol/L)
NA	Not applicable, not available
NAS	National Academy of Sciences
Ni	Nickel
NOAA	National Oceanographic and Atmospheric Administration
NOEC	No observed effect concentration
NST	National Status and Trends monitoring program
NTA	Nitrilotriacetic acid

NTIS	National Technical Information Service
Pb	Lead
OEC	Observed effect concentration
ORD	U.S. EPA, Office of Research and Development
OST	U.S. EPA, Office of Science and Technology
POC	Particulate organic carbon
REMAP	Regional Environmental Monitoring and Assessment Program
S^{2-}	Sulfide ion
$\{S^{2-}\}$	Activity of sulfide (mol/L)
$[S^{2-}]$	Concentration of sulfide (mol/L)
SAB	U.S. EPA Science Advisory Board
SD	Standard deviation
SEM	Simultaneously extracted metals
$[SEM_T]$	Simultaneously extracted metals, concentration of the combined metals (μmol/g)
$[SEM_{Cd}]$	Simultaneously extracted metals, Cd concentration (μmol/g)
$[SEM_{Cu}]$	Simultaneously extracted metals, Cu concentration (μmol/g)
$[SEM_{Pb}]$	Simultaneously extracted metals, Pb concentration (μmol/g)
$[SEM_{Ni}]$	Simultaneously extracted metals, Ni concentration (μmol/g)
$[SEM_{Ag}]$	Simultaneously extracted metals, Ag concentration (μmol/g)
$[SEM_{Zn}]$	Simultaneously extracted metals, Zn concentration (μmol/g)
TIE	Toxicity identification evaluation
TOC	Total organic carbon
WQC	Water quality criteria
Zn	Zinc
$[\Sigma Cd(aq)]$	Concentration of total dissolved Cd^{2+} (mol/L)
$[\Sigma Fe(aq)]$	Concentration of total dissolved Fe^{2+} (mol/L)
$[\Sigma M(aq)]$	Concentration of total dissolved M^{2+} (mol/L)
$[\Sigma S(aq)]$	Concentration of total dissolved S^{2-} (mol/L)

Section 1

Introduction

1.1 General Information

Toxic pollutants in bottom sediments of the Nation's lakes, rivers, wetlands, estuaries, and marine coastal waters create the potential for continued environmental degradation even where water column concentrations comply with established WQC. In addition, contaminated sediments can be a significant pollutant source that may cause water quality degradation to persist, even when other pollutant sources are stopped (Larsson, 1985; Salomons et al., 1987; Burgess and Scott, 1992). The absence of defensible equilibrium partitioning sediment benchmarks (ESBs) make it difficult to accurately assess the extent of the ecological risks of contaminated sediments and to identify, prioritize, and implement appropriate cleanup activities and source controls (U.S. EPA 1997a, b, c).

As a result of the need for a procedure to assist regulatory agencies in making decisions concerning contaminated sediment problems, the U.S. Environmental Protection Agency (EPA) Office of Science and Technology, Health and Ecological Criteria Division (OST/HECD) and Office of Research and Development National Health and Environmental Effects Research Laboratory (ORD/NHEERL) established a research team to review alternative approaches (Chapman, 1987). All of the approaches reviewed had both strengths and weaknesses, and no single approach was found to be applicable for the derivation of benchmarks in all situations (U.S. EPA, 1989, 1992). The equilibrium partitioning (EqP) approach was selected for nonionic organic chemicals because it presented the greatest promise for generating defensible, national, numeric chemical-specific benchmarks applicable across a broad range of sediment types. The three principal observations that underlie the EqP approach to establishing sediment benchmarks are as follows:

1. The concentrations of nonionic organic chemicals in sediments, expressed on an organic carbon basis, and in interstitial waters correlate to observed biological effects on sediment-dwelling organisms across a range of sediments.

2. Partitioning models can relate sediment concentrations for nonionic organic chemicals on an organic carbon basis to freely-dissolved concentrations in interstitial water.

3. The distribution of sensitivities of benthic organisms to chemicals is similar to that of water column organisms; thus, the currently established water quality criteria (WQC) final chronic values (FCV) or secondary chronic values (SCV) can be used to define the acceptable effects concentration of a chemical freely-dissolved in interstitial water.

Because of their widespread release and persistent nature, metals such as cadmium, copper, lead, nickel, silver, and zinc are commonly elevated in aquatic sediments. These metals, in addition to nonionic organic chemicals, are of potential concern to aquatic environments. Thus, there have been various proposals for deriving sediment benchmarks for protecting benthic communities using measurement of total sediment metals followed by comparison with background metal concentrations, or in some cases, an effects-based endpoint (Sullivan et al., 1985; Persaud et al., 1989; Long and Morgan, 1990; Ingersoll et al., 1996; MacDonald et al., 1996). An important limitation to these types of approaches is that the causal linkage between the measured concentration of metals and the observed toxicity cannot be established, in part because of the procedures used to derive correlative values, and because values derived are based on total rather than bioavailable metal concentrations. That is, for any given total metal concentration, adverse toxicological effects may or may not occur, depending on the physicochemical characteristics of the sediment of concern (Tessier and Campbell, 1987; Luoma, 1989; Di Toro et al., 1990).

Many researchers have used elaborate sequential extraction procedures to identify sedimentary physicochemical fractions with which metals are associated in an attempt to understand the biological availability of metals in sediments (Tessier et al., 1979; Luoma and Bryan, 1981). Key binding phases for metals in sediments included iron and manganese oxides and organic carbon. Shortcomings with these approaches have limited their application largely to aerobic sediments instead of anaerobic sediments, where metals are often found in the greatest concentrations (see Section 2).

In developing ESBs for metals that causally link metals concentrations to biological effects and that apply across all sediments, it is essential that bioavailability be understood. Therefore, the EqP approach was selected as the technical basis for deriving ESBs for metals. Different studies have shown that although total (dry weight) metal concentrations in anaerobic sediments are not predictive of bioavailability, metal concentrations in interstitial water are correlated with observed biological effects (Swartz et al., 1985; Kemp and Swartz, 1986). However, as opposed to the situation for nonionic organic chemicals and organic carbon (see Di Toro et al., 1991), sediment partitioning phases controlling interstitial water concentrations of metals were not readily apparent. A key partitioning phase controlling cationic metal activity and metal-induced toxicity in the sediment–interstitial water system is acid volatile sulfide (AVS) (Di Toro et al., 1990, 1992). AVS binds, on a molar basis, a number of cationic metals of environmental concern (cadmium, copper, lead, nickel, silver, and zinc), forming insoluble sulfide complexes with minimal biological availability. (Hereafter in this document, the use of the term "metals" will apply only to these six metals.)

The data that support the EqP approach for deriving sediment benthmarks for nonionic organic chemicals were reviewed by Di Toro et al. (1991) and U.S. EPA (1997a; 2003a). The utility of the EqP approach for deriving sediment benchmarks for metals (U.S. EPA, 1994a) was reviewed and endorsed by EPA's Science Advisory Board (SAB) in 1994 and 1999 (U.S. EPA, 1995a, 1999). The data that support the EqP approach for deriving sediment benchmarks for metals presented in this document were taken largely from a series of papers published in the December 1996 issue of *Environmental Toxicology and Chemistry* by Ankley et al. (1996), Berry et al. (1996), DeWitt et al. (1996), Di Toro et al. (1996a,b), Hansen et al. (1996a,b), Leonard et al. (1996a), Liber et al. (1996), Mahony et al. (1996), Peterson et al. (1996), and Sibley et al. (1996). In addition, publications by Di Toro et al. (1990, 1992), Ankley et al. (1994), U.S. EPA (1995a), and Berry et al. (1999) were of particular importance in the preparation of this document.

The same three general principles observed in applying the EqP approach to nonionic organic chemicals listed above also apply with only minor adjustments to deriving ESBs for mixtures of the cationic metals—cadmium, copper, lead, nickel, silver, and zinc:

1. The concentrations of these six metals in sediments, normalized to the concentration of AVS and simultaneously extracted metals (SEM) (the metals extracted with AVS) in sediments and dissolved in interstitial waters, correlate with observed biological effects to sediment-dwelling organisms across a range of sediments (Di Toro et al., 1992).

2. Partitioning models can relate sediment concentrations for cationic divalent metals (and monovalent silver) on an AVS basis to the absence of freely-dissolved concentrations in interstitial water.

3. The distributions of sensitivities of benthic and water column organisms to organic chemicals and metals are similar (U.S. EPA, 2003a); thus, the currently established WQC FCVs can be used to define the acceptable effects concentration of the metals freely dissolved in interstitial water.

The EqP approach, therefore, assumes that (1) the partitioning of the metal between sediment AVS (or any other binding factors controlling bioavailability) and interstitial water approximates equilibrium; (2) organisms receive equivalent exposure from interstitial water–only exposure or from exposure to any other equilibrated sediment phase: either from interstitial water via respiration, sediment via ingestion, or sediment-integument exchange, or from a mixture of exposure routes; (3) for the cationic metals cadmium, copper, lead, nickel, zinc, and silver, partitioning of metal between the solid phase and interstitial water can be predicted based on the relative concentrations of AVS and SEM; (4) the WQC FCV concentration is an appropriate effects concentration for freely-dissolved metal in interstitial water; and (5) the toxicity of metals in interstitial water is no more than additive.

For the first time, the Agency is publishing ESBs that account for bioavailability in sediments and the potential for effects of a metal mixture in the aquatic environment, thus providing an ecologically relevant benchmark. Two equally applicable ESBs for metals, a solid phase and an interstitial water phase, are described. The solid-phase AVS ESBs is defined as the $\Sigma_i[\mathrm{SEM}_i] \leq [\mathrm{AVS}]$ (total molar concentration of simultaneously extracted metal is less than or equal to the total molar concentration of acid volatile sulfide). Note that cadmium, copper, lead, nickel, and zinc are divalent metals so that one mole of each metal can bind only with one mole of AVS. The molar concentrations of these metals are compared with AVS on a one-to-one basis. Silver, however, exists predominantly as a monovalent metal, so that silver monosulfide (Ag_2S) binds two moles of silver for each mole of AVS. Therefore, SEM_{Ag} by convention will be defined as the molar concentration of silver divided by two, [Ag]/2, which is compared with the molar AVS concentration. The interstitial water phase ESB is $\Sigma[M_{i,d}]/[\mathrm{FCV}_{i,d}] \leq 1$ (the sum of cadmium, copper, nickel, lead, and zinc of the concentration of each individual metal dissolved in the interstitial water divided by the metal-specific FCV based on dissolved metal is less than or equal to one; note that at present EPA does not have an FCV for silver). This latter value is termed an interstitial water benchmark unit (IWBU). A requirement of the IWBUapproach is that the toxicities of interstitial water metal concentrations be additive. The data presented in this document support the additivity of the toxicity of metal mixtures in water.

Importantly, both the solid-phase AVS ESB and interstitial water ESB are no-effect benchmarks; that is, they predict sediments that are acceptable for the protection of benthic organisms. These ESBs, when exceeded, do not unequivocally predict sediments that are unacceptable for the protection of benthic organisms. The solid-phase AVS benchmark avoids the methodological difficulties of interstitial water sampling that may lead to an overestimate of exposure and provides information on the potential for additional metal binding. Because the AVS benchmark does not include other metal-binding phases of sediments, the interstitial benchmark is also proposed. The use of both the AVS and interstitial water benchmarks will improve estimates of risks of sediment-associated metals. For example, the absence of significant concentrations of metal in interstitial water in toxic sediments having SEM≤AVS and in nontoxic sediments having SEM>AVS demonstrates that metals in these sediments are unavailable. The $(\Sigma\mathrm{SEM}-\mathrm{AVS})/f_{OC}$ correction, although not an ESB, can be used to refine the prediction of sediments where protection of benthic organisms is acceptable, uncertain, or unacceptable.

ESBs based on the EqP approach are developed using the latest available scientific data and are suitable for providing guidance to regulatory agencies because they are

- Numeric values
- Chemical-specific
- Applicable to most sediments
- Predictive of biological effects
- Protective of benthic organisms

It should be emphasized that these benchmarks are intended to protect benthic organisms from the direct effects of these six metals in sediments that are permanently inundated with water, intertidal, or inundated periodically for durations sufficient to permit development of benthic assemblages. They do not apply to occasionally inundated soils containing terrestrial organisms. The ESBs do not consider the antagonistic, additive or synergistic effects of other sediment contaminants in combination with metal mixtures or the potential for bioaccumulation and trophic transfer of metal mixtures to aquatic life, wildlife or humans. The ESBs presented in this document are the recommended concentrations of cadmium, copper, lead, nickel, silver, and zinc in sediment that will not adversely affect most benthic organisms. ESB values may be adjusted to account for future data or site-specific considerations (U.S. EPA, 2003b).

This document includes the theoretical basis and the supporting data relevant to the derivation of an ESBfor cadmium, copper, lead, nickel, silver, and zinc and their mixture. An understanding of the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" (Stephan et al., 1985); Response to Public Comment (U.S. EPA, 1985a); "Ambient Water Quality Criteria for Cadmium" (U.S. EPA, 1985b); "Ambient Water Quality Criteria for Copper" (U.S. EPA, 1985c); "Ambient Water Quality Criteria—Saltwater Copper Addendum" (U.S. EPA, 1995c); "Ambient Water Quality Criteria for Lead" (U.S. EPA, 1985d); "Ambient Water Quality Criteria for Nickel" (U.S. EPA, 1986); "Ambient Water Quality Criteria for Silver" (U.S. EPA, 1980); and "Ambient Water Quality Criteria for Zinc" (U.S. EPA, 1987) is necessary in order to understand the following text, tables, and calculations.

1.2 Applications of Sediment Benchmarks

ESBs are meant to be used with direct toxicity testing of sediments as a method of evaluation assuming the toxicity testing species is sensitive to the chemical of interest. They provide a chemical-by-chemical specification of what sediment concentrations are protective of benthic aquatic life. The EqP method should be applicable to nonionic organic chemicals with a K_{OW} above 3.0. Examples of other chemicals to which this methodology applies include endrin, dieldrin, and polycyclic aromatic hydrocarbon (PAH) mixtures.

For the toxic chemicals addressed by the ESB documents Tier 1 (U.S. EPA, 2003c, d, e, and this document) and Tier 2 (U.S. EPA, 2003f) values were developed to reflect the differing degrees of data availability and uncertainty. Tier 1 ESBs are more scientifically rigorous and data intensive than Tier 2 ESBs. The minimum requirements to derive a Tier 1 ESB include: (1) Each chemicalš organic carbon-water partition coefficient (K_{OC}) is derived from the octanol-water partition coefficient (K_{OW}) obtained using the SPARC (SPARC Performs Automated Reasoning in Chemistry) model (Karickhoff et al., 1991) and the K_{OW}-K_{OC} relationship from Di Toro et al. (1991). This K_{OC} has been demonstrated to predict the toxic sediment concentration from the toxic water concentration with less uncertainty than K_{OC} values derived using other methods. (2) The FCV is updated using the most recent toxicological information and is based on the National WQC Guidelines (Stephan et al., 1985). (3) EqP-confirmation tests are conducted to demonstrate the accuracy of the EqP prediction that the K_{OC} multiplied by the effect concentration from a water-only toxicity test predicts the effect concentration from sediment tests (Swartz, 1991; DeWitt et al., 1992). Using these specifications, Tier 1 ESBs have been derived for metal mixtures in this document, the nonionic organic insecticides endrin and dieldrin (U.S. EPA, 2003c, d) and PAH mixtures (U.S. EPA, 2003e). In comparison, the minimum requirements for a Tier 2 ESB (U.S. EPA, 2003f) are less rigorous: (1) The K_{ow} for the chemical that is used to derive the K_{OC} can be from slow-stir, generator column, shake flask, SPARC or other sources. (2) FCVs can be from published or draft WQC documents, the Great Lakes Initiative or developed from AQUIRE. Secondary chronic values (SCV) from Suter and Mabrey (1994) or other effects concentrations from water-only toxicity tests can be used. (3) EqP cconfirmation tests are recommended, but are not required for the development of Tier 2 ESBs. Because of these lesser requirements, there is greater uncertainty in the EqP prediction of the sediment effect concentration from the water-only effect concentration, and in the level of protection afforded by Tier 2 ESBs. Examples of Tier 2 ESBs for nonionic organic chemicals are found in U.S. EPA (2003f).

1.3 Overview

Section 1 provides a brief review of the EqP methodology as it applies to the individual metals cadmium, copper, lead, nickel, silver, and zinc and their mixture. Section 2 reviews published experimental results that describe the toxicity associated with the partitioning and bioavailability of these metals in interstitial water of freshwater and marine sediments. Section 3 reviews the results of acute and chronic toxicity tests conducted with spiked and field sediments that demonstrate that the partitioning and bioavailability of metals in sediments can be used to accurately predict the absence of toxicity of sediment-associated metals. Section 4 describes the AVS benchmark and interstitial water benchmark approaches for the derivation of the ESB for individual metals and mixtures of metals. Published WQC values for five of these six dissolved metals (the silver FCV is not available) are summarized for use in calculating IWBUs as required in the interstitial water ESB approach. The $ESB_{AVS:WQC}$ for metals is then compared with chemical monitoring data on environmental occurrence of SEM, AVS, and interstitial metals in sediments from Lake Michigan, the Virginian Province from EPA's Environmental Monitoring and Assessment Program (EMAP), and the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends monitoring program (NST). Section 5 describes recommended procedures for sampling, handling, and analysis of metals in sediments and interpretation of data from the sediment samples that is needed if the assessments of risks of sediment-associated metals are to be appropriately based on the EqP methodology. Section 6 concludes with the $ESB_{AVS:WQC}$ for a mixture of the metals: cadmium, copper, nickel, lead, silver, and zinc and discussion of their application and interpretation. The references cited in this document are listed in Section 7. Appendices A and B provide additional monitoring data. Appendix C reports on quality assurance for this document and Appendix D addresses chromium toxicity in sediments.

Section 2

Partitioning of Metals in Sediments

2.1 Metal Toxicity in Water-Only and in Interstitial Water of Sediment Exposures

The EqP approach for establishing sediment benchmarks (i.e., ESBs) requires that the chemicals be measured in phases that relate to chemical activity in sediment. The information provided in this section demonstrates that biological effects correlate to metal activity. Also, it demonstrates that biological response in sediment exposures is the same as in water-only exposures when sediment exposure is assessed on the basis of interstitial water concentrations. This is fundamental to satisfying the EqP approach for both metals and nonionic organic chemicals.

A direct method for establishing sediment benchmarks for metals would be to apply the WQC FCV to measured interstitial water concentrations. The validity of this approach depends both on the degree to which the interstitial water concentration represents free metal activity, and on whether free metal activity can be accurately measured in surface waters and water-only toxicity tests used to derive WQC, and in interstitial water of field sediments and sediments spiked with metals in the laboratory. For most metals, free metal activity cannot be directly measured at WQC concentrations. Therefore, present WQC are not based on free metal activity; rather, they are based on dissolved metals. However, many dissolved metals readily bind to dissolved (actually colloidal) organic carbon (DOC) forming complexes that do not appear to be bioavailable (Bergman and Dorward-King, 1997). Hence, sediment guidelines or benchmarks based on interstitial water concentrations of metals may be overly protective in cases where not all dissolved metal is bioavailable.

By implication, this difficulty extends to any complexing ligand that is present in sufficient quantity. Decay of sediment organic matter can cause substantial changes in interstitial water chemistry. In particular, bicarbonate increases because of sulfate reduction, which increases the importance of metal-carbonate complexes and further complicates the question of the bioavailable metal species (Stumm and Morgan, 1996).

Sampling sediment interstitial water for metals is not a routine procedure. The least invasive technique employs a diffusion sampler that has cavities covered with a filter membrane (Hesslein, 1976; Carignan, 1984; Carignan et al., 1985; Allen et al., 1993; Bufflap and Allen, 1995). The sampler is inserted into the sediment and the concentrations on either side of the membrane equilibrate. Because the sampler is removed after equilibration, the concentrations of metals inside the sampler should be equal to the concentrations of freely-dissolved metals in the interstitial water. The time required for equilibration, typically several days, depends on the size of the filter membrane and the geometry of the cavity.

An alternative technique for separating interstitial water is to obtain an undisturbed sediment sample as a whole sediment or core that can be sliced for vertical resolution, filter or centrifuge the sample, and then filter the resultant interstitial water twice. For anaerobic sediments, this must be done in a nitrogen atmosphere to prevent precipitation of iron hydroxide, which would scavenge the metals and yield artificially low dissolved concentrations of metals (Troup, 1974; Allen et al., 1993).

Although either technique is suitable for research investigations, they require more than the normally available sampling capabilities. If solid-phase chemical measurements were available from which interstitial water metal activity could be deduced, this would obviate the need for interstitial water sampling and analysis, circumvent the need to deal with complexing ligands, and provide fundamental insight into metal-binding phases in sediments needed to predict bioavailability. The recommended procedures for suitable sampling, handling, and analytical techniques for interstitial water and sediments are provided in Section 5 of this document.

2.1.1 *Toxicity Correlates to Metal Activity*

A substantial number of water-only exposures indicate that biological effects can be correlated to divalent metal activity $\{M^{2+}\}$ Although other forms of metal may also be bioavailable (e.g., MOH^{+}), DOC and certain other ligand-complexed fractions of the metal render it unavailable to organisms. Results from some of these exposures are summarized below.

Acute toxicity of various concentrations of cadmium to grass shrimp (*Palaemonetes pugio*) has been determined in water containing the complexing ligand nitrilotriacetic acid (NTA) or chloride (as salinity), each of which forms cadmium complexes (Sunda et al., 1978). The concentration response curves as a function of total cadmium are quite different at varying concentrations of NTA and chloride (Figure 2-1, A and B). However, if the organism response is evaluated with respect to measured Cd^{2+} activity, a single concentration–response relationship results (Figure 2-1, C and D). Comparable results have been reported by Anderson and Morel (1978) for the dinoflagellate *Gonyaulax tamarensis* exposed to copper-ethylene diamine tetra-acetic acid (EDTA) complexes (Figure 2-2, A and C). Likewise, Allen et al. (1980) observed that when the concentration of zinc is held constant and the concentration of the complexing ligand NTA is varied, growth (cells/mL) of *Microcystis aeruginosa* decreases as the addition of NTA is

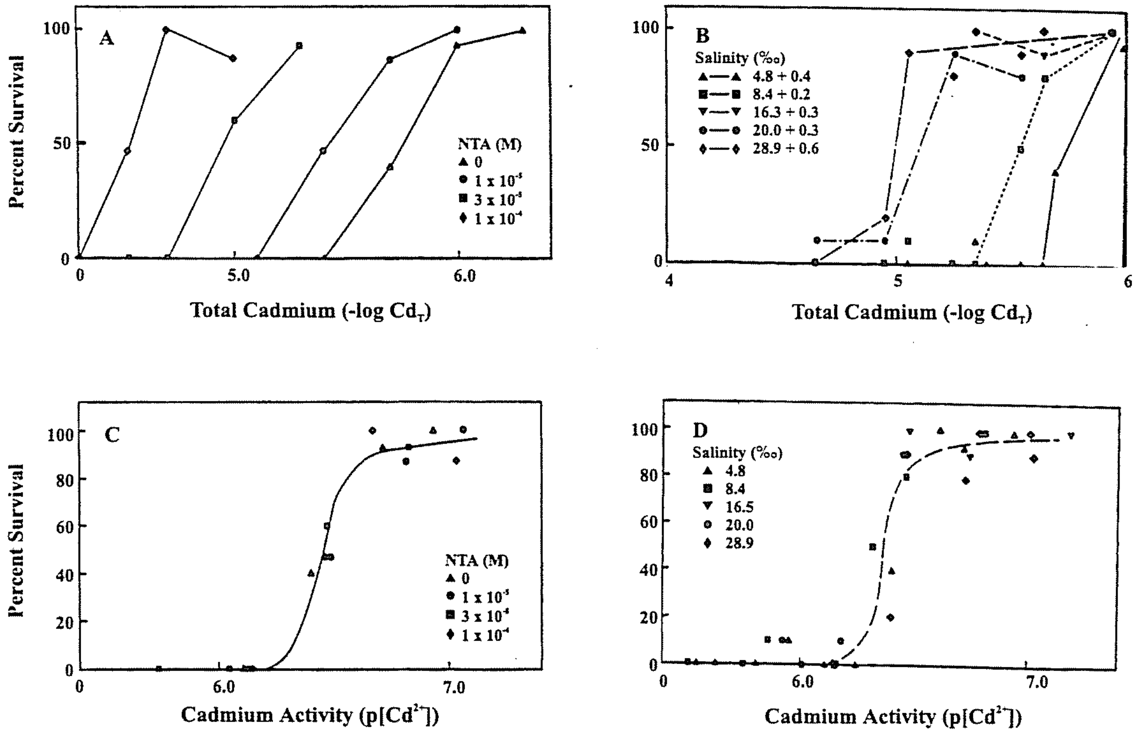

Figure 2-1. **Acute toxicity to grass shrimp (*Palaemonetes pugio*) of total cadmium (top) and cadmium activity (bottom) with different concentrations of the complexing ligands NTA (left) and chloride as salinity (right) (figures from Sunda et al., 1978).**

increased (Figure 2-2B). The authors correlated the effect to free zinc activity as shown in Figure 2-2D. A single concentration–response relationship is shown for the diatom, *Thalassiosira pseudonana*, and the unicellular alga, *Monochrysis lutheri*, exposed to copper and the complexing ligand Tris (Sunda and Guillard, 1976) as well as copper and DOC from natural river water (Sunda and Lewis, 1978) when exposure concentration is expressed as metal activity (Figure 2-3, A, B, C, and D, respectively).

Metal bioavailability, as measured by metal accumulation into tissues of organisms, has also

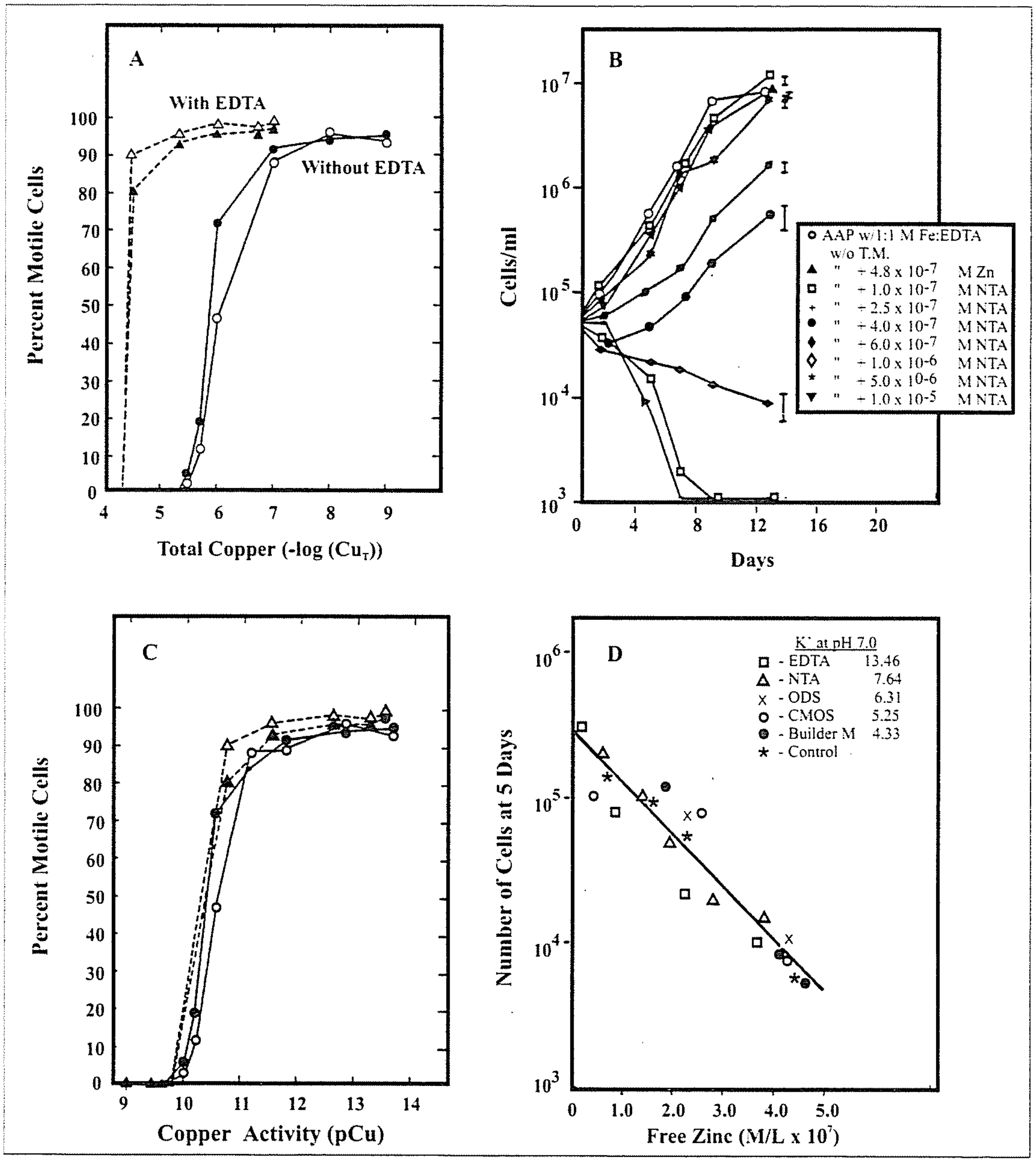

Figure 2-2. **Acute toxicity of total copper (A) and copper activity (C) to the dinoflagellate *Gonyaulax tamarensis* with and without the complexing ligand EDTA (figures from Anderson and Morel, 1978). Toxicity of zinc to *Microcystis aeruginosa* showing growth of cells/mL versus time with different levels of the complexing ligands EDTA and NTA (B) and number of cells at 5 days as a function of free zinc concentration (D) (figures from Allen et al., 1980).**

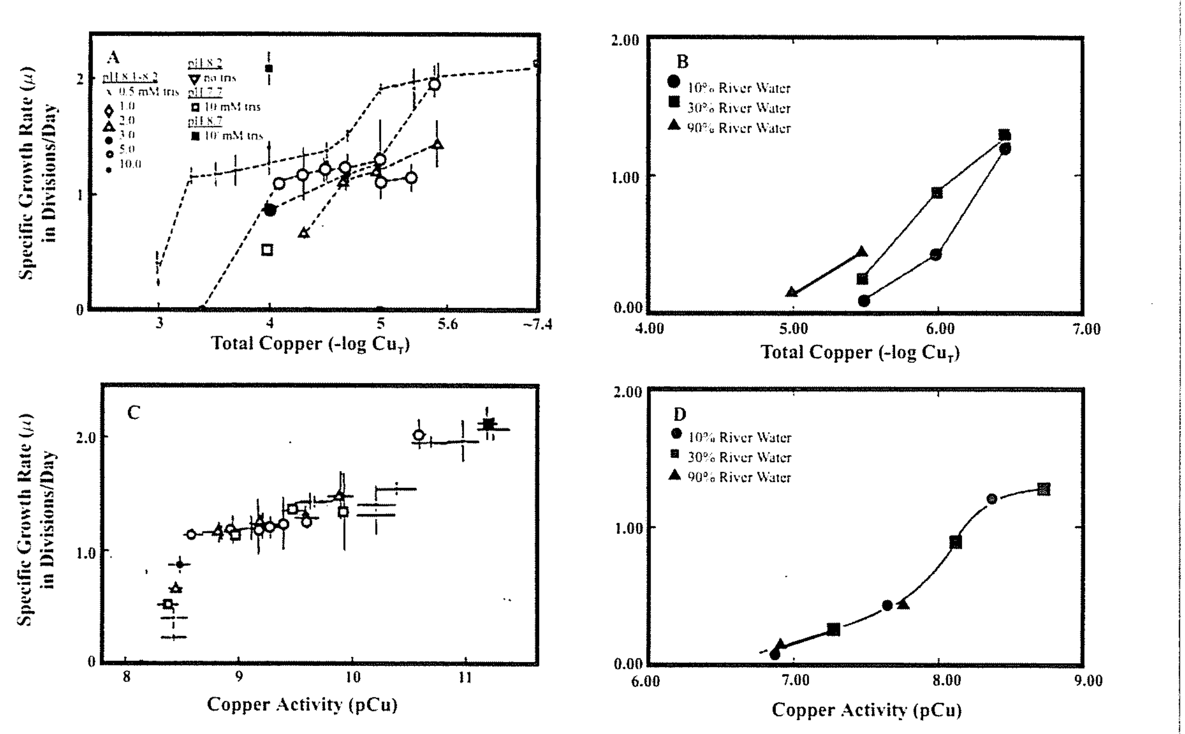

Figure 2-3. Specific growth rates of a diatom (*Thalassiosira pseudonana*) (left) and a unicellular algae (*Monochrysis lutheri*) (right) versus total copper (top) and copper activity (bottom) for a range of concentrations of the complexing ligands Tris (left; from Sunda and Guillard, 1976) and natural DOC in river water (right; from Sunda and Lewis, 1978).

been examined (Zamuda and Sunda, 1982). Uptake of copper by oysters is correlated not to total copper concentration (Figure 2-4A), but to copper activity (Figure 2-4B).

The implication to be drawn from these experiments is that the partitioning model required for establishing a sediment benchmark should predict dissolved metal activity in interstitial water, and that the benchmark based on dissolved metal would be conservative. The following subsection examines the utility of this idea.

2.1.2 *Toxicity Correlates to Interstitial Water Concentration*

This subsection presents early data that first indicated the equivalence of interstitial water concentrations and water-only exposures. Many more data of this sort are presented in Section 3. Swartz et al. (1985) tested the acute toxicity of cadmium to the marine amphipod *Rhepoxynius abronius* in sediment and water. An objective of the study was to determine the contributions of interstitial and particle-bound cadmium to toxicity. A comparison of the 4-day LC50 value of cadmium in interstitial water (1.42 mg/L) with the 4-day LC50 value of cadmium in water without sediment (1.61 mg/L) indicated no significant difference between the two (Figure 2-5). The LC50 represents the chemical concentration estimated to cause lethality to 50% of the test organisms within a specified time period.

Experiments were performed to determine the role of AVS in cadmium-spiked sediments using the amphipods *Ampelisca abdita* and *Rhepoxynius hudsoni* (Di Toro et al., 1990). Three sediments were used: a Long Island Sound sediment with high AVS, a Ninigret Pond sediment with low AVS concentration, and a 50/50 mixture of the two sediments Figure 2-6 presents a

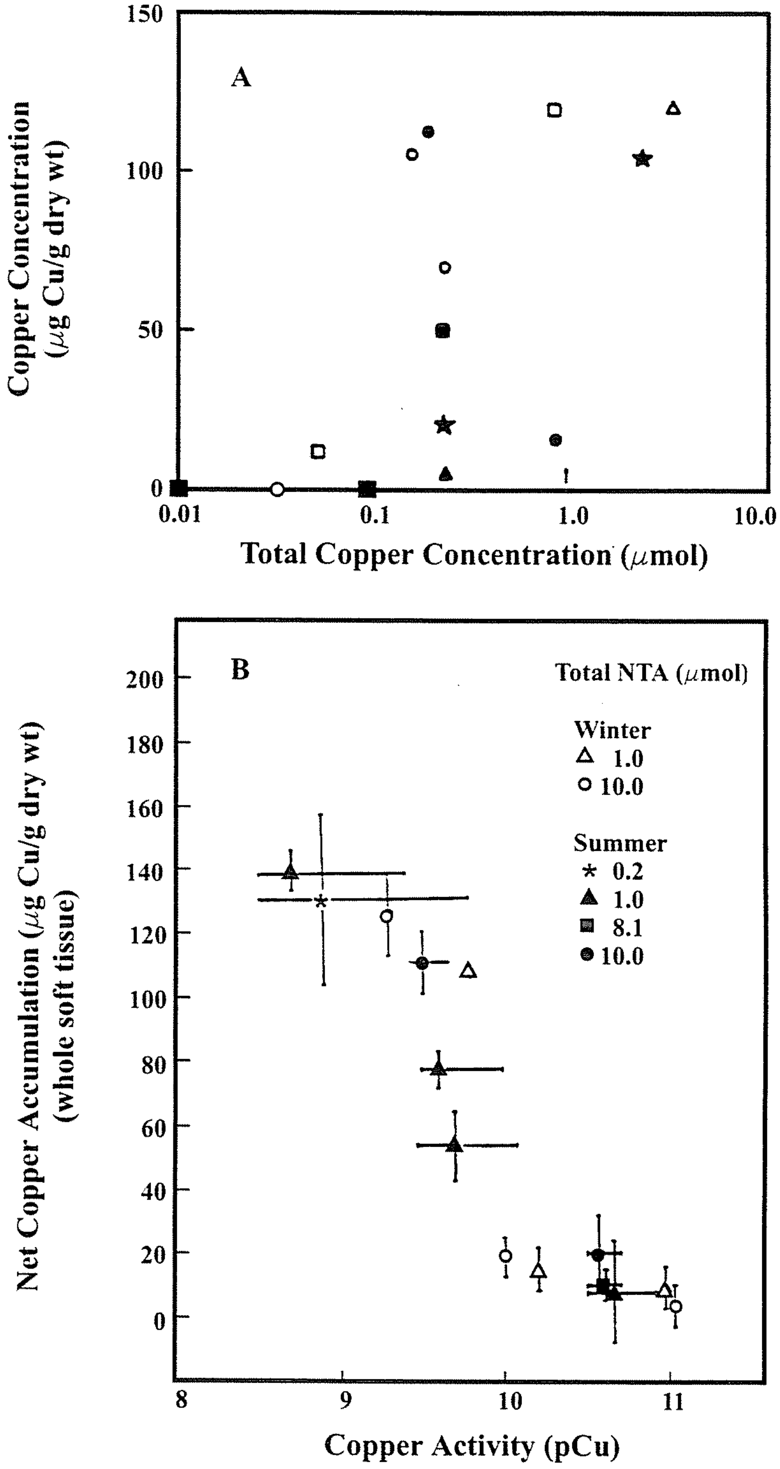

Figure 2-4. Copper accumulation in oysters (*Crassostrea virginica*) versus total copper (A) and copper activity (B) with different levels of the complexing ligand NTA (figures from Zamuda and Sunda, 1982).

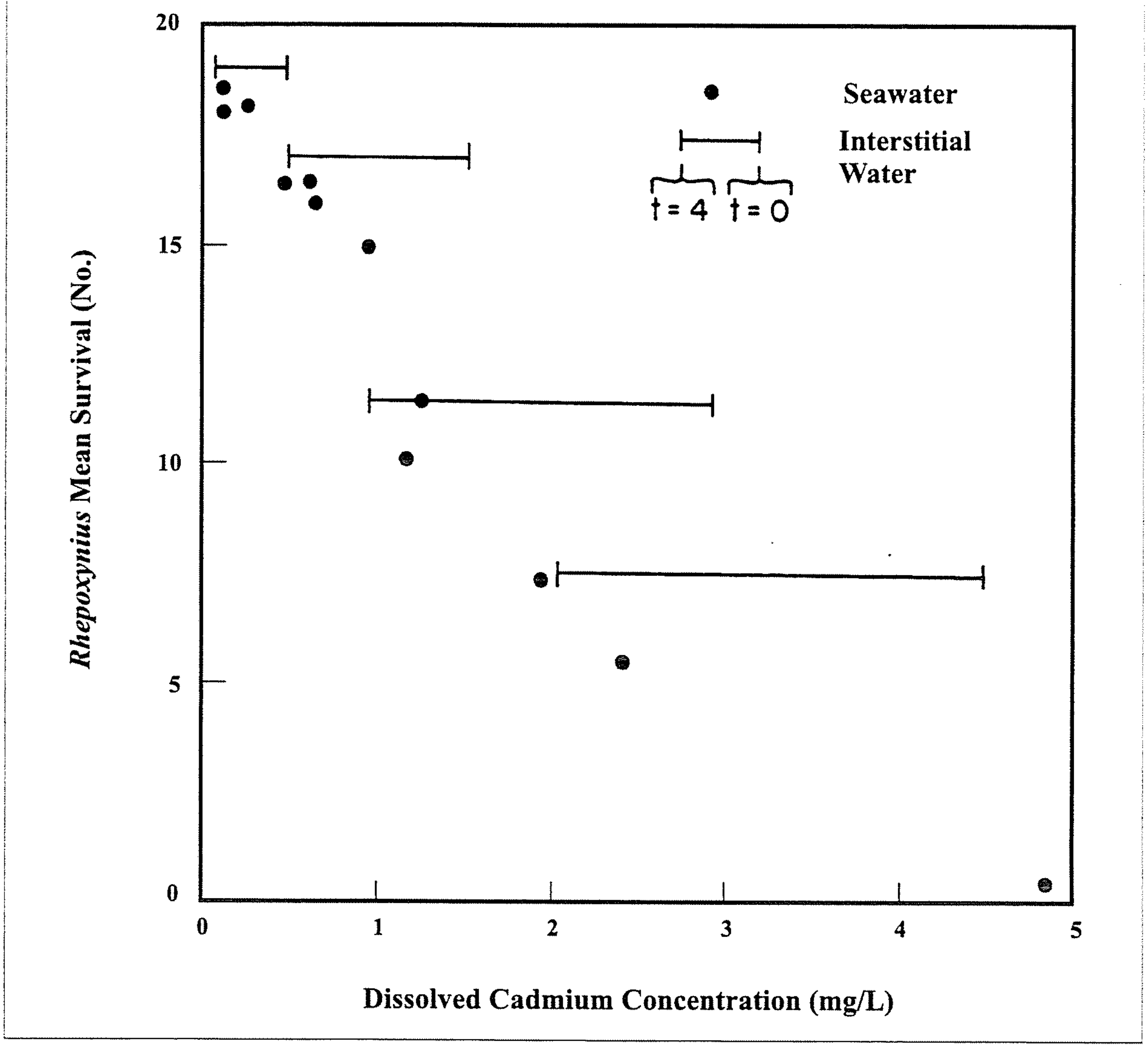

Figure 2-5. Mean survival of the amphipod *Rhepoxynius abronius* versus dissolved cadmium concentration for 4-day toxicity tests in seawater (symbols) and 0- and 4-day tests (bars) in interstitial water (figure from Swartz et al., 1985).

comparison of the observed mortality in three sediments with the interstitial water cadmium activity measured with a specific ion electrode. Four-day water-only and 10-day sediment toxicity tests were performed. The water-only response data for *A. abdita* and *R. hudsoni* are included for comparison although these data represent a shorter duration exposure. These experiments also demonstrate the equivalence of organism response to metal concentrations in interstitial water and in water-only exposures.

An elegant experimental design was employed by Kemp and Swartz (1986) to examine the relative acute toxicity of particle-bound and dissolved interstitial cadmium. They circulated water of the same cadmium concentration through different sediments. This resulted in different bulk sediment concentrations, but the same interstitial water concentrations. They found no statistically significant difference in organism response for the different sediments. Because the interstitial water concentrations were the same in each treatment,

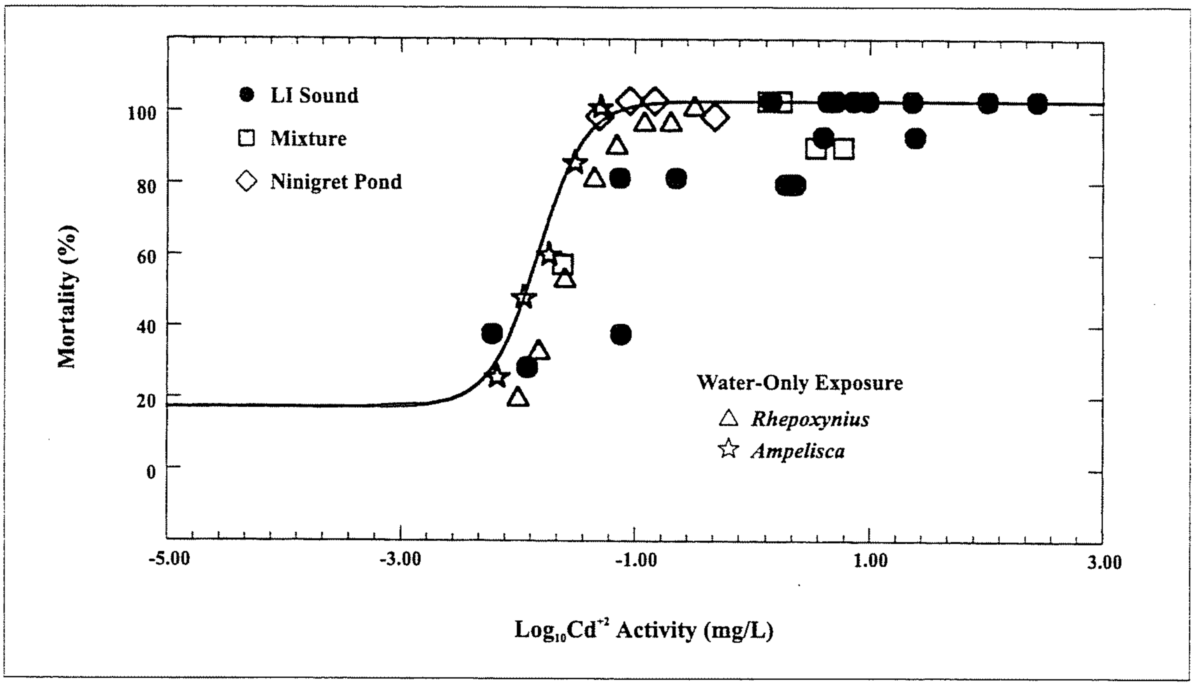

Figure 2-6. Mortality versus interstitial water cadmium activity for sediments from Long Island Sound, Ninigret Pond, and a mixture of these two sediments. Water-only exposure data are from separate experiments with both *Ampelisca abdita* and *Rhepoxynius hudsoni*. The line is a joint fit to both water-only data sets (figure from Di Toro et al., 1990).

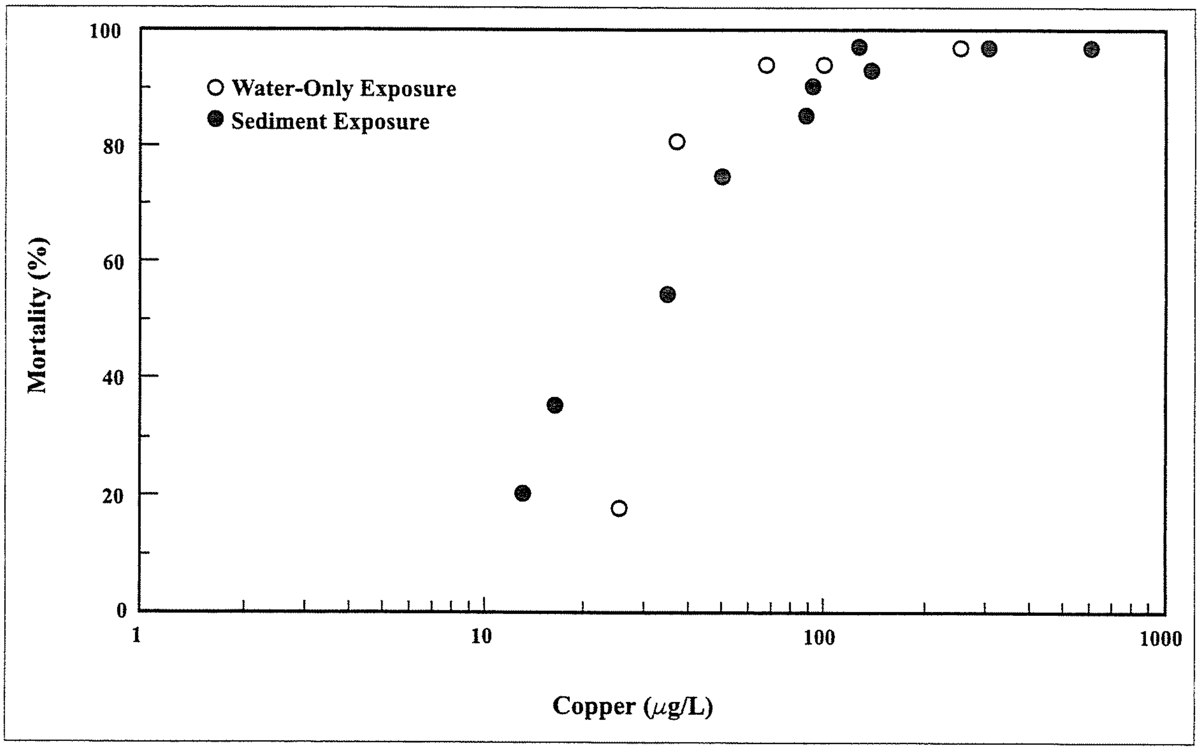

Figure 2-7. Toxicity of copper to *Hyalella azteca* versus copper concentrations in a water-only exposure (○) and interstitial water copper concentrations in sediment exposures (●) using Keweenaw Watershed sediments (figure from Ankley et al., 1993).

that is, the circulating water concentrations established the interstitial water concentrations, these experiments confirmed the hypothesis of equal response to concentrations in water-only and interstitial water.

A series of 10-day toxicity tests using the amphipod *Hyalella azteca* was performed to evaluate bioavailability of copper in sediments from two sites highly contaminated with this metal: Steilacoom Lake, WA, and Keweenaw Watershed, MI (Ankley et al., 1993). A water-only, 10-day copper toxicity test also was conducted with the same organism. The mortality resulting from the water-only test was strikingly similar to that from the Keweenaw sediment tests when related to interstitial water (Figure 2-7). The LC50 values show strong agreement for the water-only (31 μg/L) and the Keweenaw sediment test (28 μg/L) using the average of day 0 and day 10 interstitial water concentrations. Steilacoom Lake 10-day interstitial water concentrations were less than the 7 μg/L detection limit and were consistent with the observed lack of toxicity to *H. azteca.*

The data presented in this subsection, and the data in Section 3, demonstrate that in water-only exposures, metal activity and concentration can be used to predict toxicity. The results of the four experiments above demonstrate that mortality data from water-only exposures can be used to predict sediment toxicity using interstitial water concentrations. Therefore, the metal activity or dissolved concentration in interstitial water would be an important component of a partitioning model needed to establish sediment benchmarks. To complete the partitioning model, one would need to identify the solid metal-binding phase(s). The following subsection presents data that identifies solid-phase sulfides as the important metal-binding phase.

2.2 Solid-Phase Sulfide as the Important Binding Component

Modeling metal sorption to oxides in laboratory systems is well developed, and detailed models are available for cation and anion sorption (see Stumm [1987] and Dzombak and Morel [1990] for summaries). The models consider surface complexation reactions as well as electrical interactions by means of models of the double layer. Models for natural soil and sediment particles are less well developed. However, studies suggest that the models available for cation and anion sorption can be applied to soil systems (Allen et al., 1980; Barrow and Ellis, 1986a,b,c; Sposito et al., 1988). Because the ability to predict partition coefficients is required if interstitial water metal concentrations are to be inferred from the total concentration, some practical model is required. This subsection presents the state of the science in theoretical development of metal partitioning behavior in sediments.

2.2.1 *Metal Sorption Phases*

The initial difficulty selecting an applicable sorption model is that available models are complex and many of the parameter estimates may be specific to individual soils or sediments. However, the success of nonionic chemical sorption models based on organic carbon suggests that some model of intermediate complexity based on an identification of the dominant sorption phases may be more generally applicable.

A development in this direction has already been presented (Jenne et al., 1986; Di Toro et al., 1987). The basic idea was that instead of considering only one sorption phase, as is assumed for nonionic hydrophobic chemical sorption, multiple sorption phases must be considered. The conventional view of metal speciation in aerobic soils and sediments is that metals are associated with the exchangeable, carbonate and iron (Fe) and manganese (Mn) oxide forms, as well as organic matter, stable metal sulfides, and a residual phase. In oxic soils and freshwater sediments, sorption phases have been identified as particulate organic carbon (POC) and the oxides of Fe and Mn (Jenne, 1968, 1977; Oakley et al., 1980; Luoma and Bryan, 1981). These phases are important because they have a large sorptive capacity. Furthermore, they appear as coatings on the particles and occlude the other mineral components. It was thought that they provided the primary sites for sorption of metals. These ideas have been applied to metal speciation in sediments. However, they ignore the critical importance of metal sulfide interactions, which dominate speciation in the anaerobic layers of the sediment.

2.2.2 *Titration Experiments*

The importance of sulfide in the control of metal concentrations in the interstitial water of marine sediments is well documented (Boulegue et al., 1982; Emerson et al., 1983; Davies-Colley et al., 1985; Morse et al., 1987). Metal sulfides are very insoluble, and the equilibrium interstitial water metal concentrations in the presence of sulfides are small. If the interstitial water sulfide

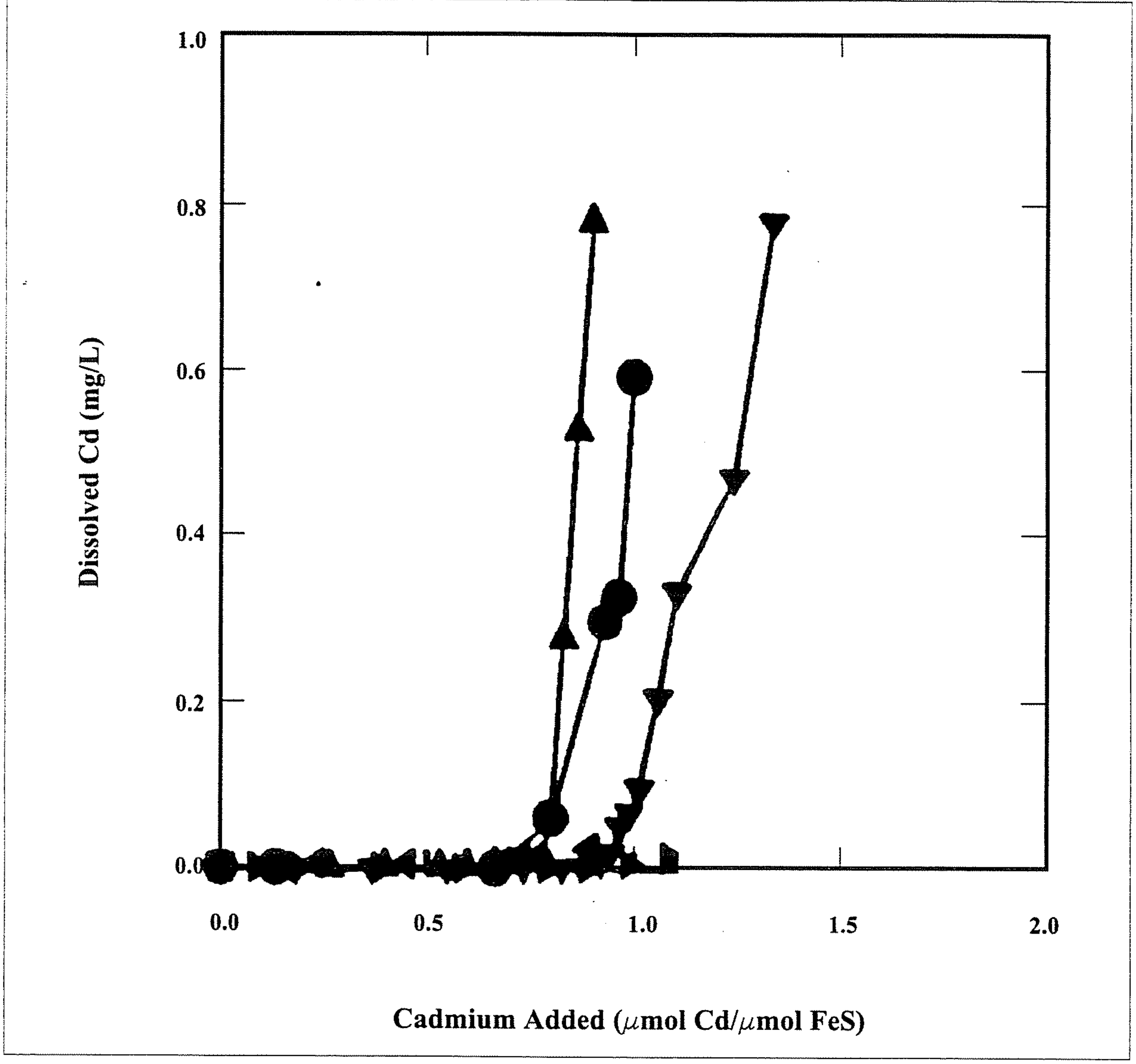

Figure 2-8. Cadmium titrations of amorphous FeS. The x-axis is the amount of cadmium added normalized by FeS initially present. The y-axis is total dissolved cadmium. The lines connecting the data points are an aid to visualizing the data. The different symbols represent replicate experiments (figure from Di Toro et al., 1990).

concentration, S^{2-}, in sediments is large, then the addition of metal, M^{2+}, to the sediment would precipitate metal sulfide (MS) following the reaction

$$M^{2+} + S^{2-} \rightleftharpoons MS(s) \qquad (2\text{-}1)$$

This appeared to be happening during a spiked cadmium sediment toxicity test (Di Toro et al., 1990) because a visible bright yellow cadmium sulfide precipitate formed as cadmium was added to the sediment. However, interstitial water sulfide activity, \$ ${}^{2-}$}measured with a sulfide electrode unexpectedly indicated that there was insufficient dissolved sulfide present in the unspiked sediment.

The lack of a significant quantity of dissolved sulfide in the interstitial water and the evident formation of solid-phase cadmium sulfide suggested the following possibility. The majority of the sulfide in sediments is in the form of solid-phase iron sulfides. Perhaps the source of the sulfide is from the solid-phase sulfide initially present. As cadmium is added to the sediment,

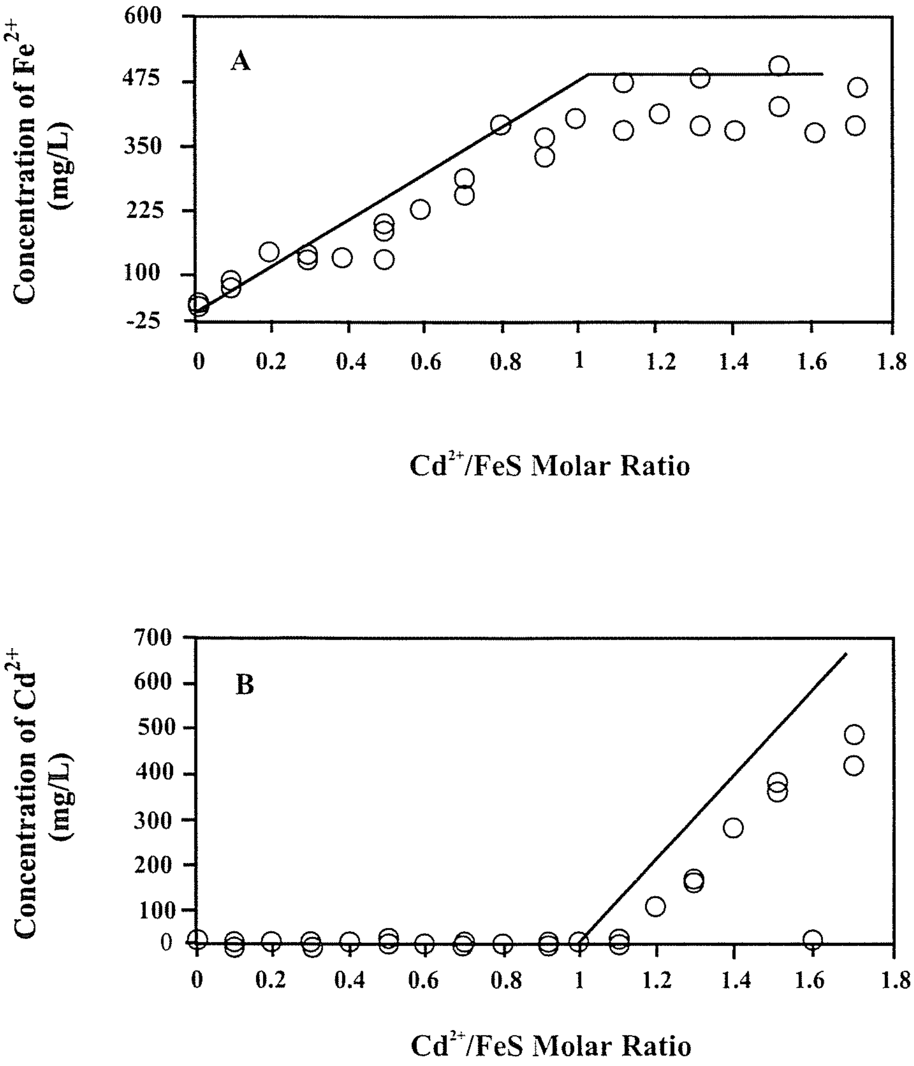

Figure 2-9. Concentrations of ionic iron (A) and cadmium (B) in the supernatant from titration of FeS by Cd^{2+} (Di Toro, unpublished data). The solid line represents the result expected from theory.

this causes the solid-phase iron sulfide to dissolve, releasing sulfide that is available for formation of cadmium sulfide. The reaction is

$$Cd^{2+} + FeS(s) \rightarrow CdS(s) + Fe^{2+} \qquad (2\text{-}2)$$

Cadmium titrations with amorphous FeS and with sediments were performed to examine this possibility.

2.2.2.1 *Amorphous FeS*

A direct test of the extent to which this reaction takes place was performed (Di Toro et al., 1990). A quantity of freshly precipitated iron sulfide was titrated by adding dissolved cadmium. The resulting aqueous cadmium activity, measured with the cadmium electrode, versus the ratio of cadmium added $[Cd_A]$ to the amount of FeS initially present $[FeS(s)]_i$ is shown in Figure 2-8. The plot of dissolved cadmium versus cadmium added illustrates the increase in dissolved cadmium that occurs near $[Cd_A]/[FeS(s)]_i = 1$. It is interesting to note that these displacement reactions among metal sulfides have been observed by other investigators (Phillips and Kraus, 1965). The reaction was also postulated by Pankow (1979) to explain an experimental result involving copper and synthetic FeS.

These experiments plainly demonstrate that solid-phase amorphous iron sulfide can be readily displaced by adding cadmium. As a consequence, the source of available sulfide must be taken into account when evaluating the relationship between solid-phase and aqueous-phase cadmium in sediments.

A direct confirmation that the removal of cadmium was through the displacement of iron sulfide is shown in Figure 2-9. The supernatant from a titration of FeS by Cd^{2+} was analyzed for both iron and cadmium. The solid lines are the theoretical expectations based on the stoichiometry of the reaction.

2.2.2.2 *Sediments*

A similar titration procedure has been used to evaluate the behavior of sediments taken from four different marine environments: sediments from Black Rock Harbor and the Hudson River, and the sediments from Long Island Sound and Ninigret Pond used in the toxicity tests (Di Toro et al., 1990). The binding capacity for cadmium is estimated by extrapolating a straight line fit to the dissolved cadmium data. The equation is

$$[\Sigma Cd(aq)] = \max \{m([Cd_A] - [Cd_B])\} \qquad (2\text{-}3)$$

where $[\Sigma Cd(aq)]$ is the total dissolved cadmium, $[Cd_A]$ is the cadmium added, $[Cd_B]$ is the bound cadmium, and m is the slope of the straight line. The different sediments exhibit quite different

Table 2-1. Cadmium binding capacity and AVS of sediments

Sediment	Initial AVS[a] (μmol/g)	Final AVS[b] (μmol/g)	Cd Binding Capacity[c] (μmol/g)
Black Rock Harbor	175 (41)	—	114(12)
Hudson River	12.6 (2.80)	—	8.58 (2.95)
LI Sound[d]	15.9 (3.30)	13.9 (6.43)	4.57 (2.52)
Mixture[d,e]	5.45 (—)	3.23 (1.18)	—
Ninigret Pond[d]	2.34 (0.73)	0.28 (0.12)	1.12 (0.42)

[a] Average (SD) AVS of repeated measurements of the stock.
[b] Average (SD) AVS after the sediment toxicity experiment.
[c] From Equation 2-3.
[d] From original cadmium experiment.
[e] 50/50 mixture of LI Sound and Ninigret Pond.

Source: Di Toro et al., 1990.

binding capacities for cadmium, listed in Table 2-1, ranging from approximately 1 μmol/g to more than 100 μmol/g. The question as to whether this binding capacity is explained by the solid-phase sulfide present in the samples is addressed in subsequent sections of this document.

2.2.3 *Correlation to Sediment AVS*

The majority of sulfide in sediments is in the form of iron monosulfides (mackinawite and greigite) and iron bisulfide (pyrite), of which the former is the most reactive. These sediment sulfides can be classified into three broad classes that reflect the techniques used for quantification (Berner, 1967; Goldhauber and Kaplan, 1974; Morse et al., 1987). The most labile fraction, AVS, is associated with the more soluble iron monosulfides. The more resistant sulfide mineral phase, iron pyrite, is not soluble in the cold acid extraction used to measure AVS. Neither is the third compartment, organic sulfide, which is associated with the organic matter in sediments (Landers et al., 1983).

The possibility that acid volatile sulfide is a direct measure of the solid-phase sulfide that reacts with cadmium is examined in Table 2-1, which lists the sediment-binding capacity for cadmium and the measured AVS for each sediment, and in Figure 2-10, which indicates the initial AVS concentration. The sediment cadmium-binding capacity appears to be somewhat less than the initial AVS for the sediments tested. However, a comparison between the initial AVS of the sediments and that remaining after the cadmium titration is completed suggests that some AVS is lost during the titration experiment (Table 2-1). In any case, the covariation of sediment-binding capacity and AVS is clear. This suggests that

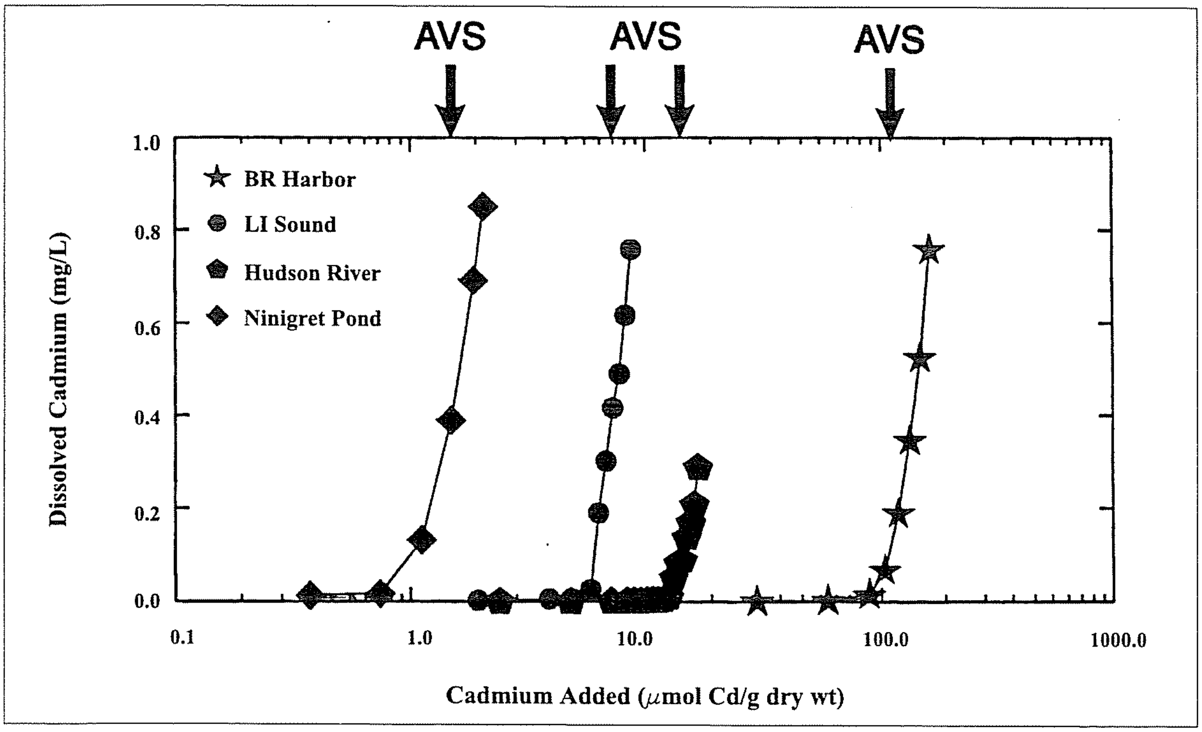

Figure 2-10. Cadmium titration of sediments from Black Rock Harbor, Long Island Sound, Hudson River, and Ninigret Pond. Cadmium added per unit dry weight of sediment versus dissolved cadmium. Arrows are the measured AVS concentrations for the four sediments (figure from Di Toro et al., 1990).

Table 2-2. Metal sulfide solubility products and ratios

Metal Sulfide	$\mathrm{Log}_{10}K_{sp,2}$[a]	$\mathrm{Log}_{10}K_{sp}$[b]	$\mathrm{Log}_{10}(K_{MS}/K_{FeS})$
FeS	-3.64	-22.39	—
NiS	-9.23	-27.98	-5.59
ZnS	-9.64	-28.39	-6.00
CdS	-14.10	-32.85	-10.46
PbS	-14.67	-33.42	-11.03
CuS	-22.19	-40.94	-18.55
Ag_2S	-36.14	-54.71	-32.32

[a] Solubility products, $K_{sp,2}$ for the reaction $M^{2+} + HS^- - MS(s) + H^+$ for FeS (mackinawite), NiS (millerite), and CdS (greenockite) from Emerson et al. (1983). Solubility products for ZnS (wurtzite), PbS (galena), CuS (covellite), and Ag_2S (acanthite) and $pK_2 = 18.57$ for the reaction $HS^- - H^+ + S^{2-}$ from Schoonen and Barnes (1988).
[b] K_{sp} for the reaction $M^{2+} + S^{2-} - MS(s)$ is computed from log $K_{sp,2}$ and pK_2.

measurement of AVS is the proper quantification of the solid-phase sulfides that can be dissolved by the addition of ionic cadmium. The chemical basis for this is examined below.

2.2.4 *Solubility Relationships and Displacement Reactions*

Iron monosulfide, FeS(s), is in equilibrium with aqueous-phase sulfide and iron via the reaction

$$\mathrm{FeS(s)} - \mathrm{Fe^{2+}} + \mathrm{S^{2-}} \qquad (2\text{-}4)$$

If cadmium is added to the aqueous phase, the result is

$$\mathrm{Cd^{2+}} + \mathrm{FeS(s)} - \mathrm{Cd^{2+}} + \mathrm{Fe^{2+}} + \mathrm{S^{2-}} \qquad (2\text{-}5)$$

As the cadmium concentration increases, $[Cd^{2+}][S^{2-}]$ will exceed the solubility product of cadmium sulfide and CdS(s) will start to form. Since the cadmium sulfide is more insoluble than iron monosulfide, FeS(s) should start to dissolve in response to the lowered sulfide concentration in the interstitial water. The overall reaction is

$$\mathrm{Cd^{2+}} + \mathrm{FeS(s)} - \mathrm{CdS(s)} + \mathrm{Fe^{2+}} \qquad (2\text{-}6)$$

The iron in FeS(s) is displaced by cadmium to form soluble iron and solid cadmium sulfide, CdS(s). The consequence of this replacement reaction can be seen using the analysis of the M(II)-Fe(II)-S(-II) system with both MS(s) and FeS(s) presented in Di Toro et al. (1992). M^{2+} represents any divalent metal that forms a sulfide that is more insoluble than FeS. If the added metal, $[M]_A$, is less than the AVS present in the sediment then the ratio of metal activity to total metal in the sediment–interstitial water system is less than the ratio of the MS to FeS solubility product constant

$$\{M^{2+}\}/[M]_A < K_{MS}/K_{FeS} \qquad (2\text{-}7)$$

This general result is independent of the details of the interstitial water chemistry. In particular, it is independent of the Fe^{2+} activity. Of course, the actual value of the ratio $\{M^{2+}\}/[M]_A$ depends on aqueous speciation, as indicated by Equation 2-6. However, the ratio is still less than the ratio of the sulfide solubility products.

This is an important finding because the data presented in Section 2.1.1 indicate that toxicity is related to metal activity, $\{M^{2+}\}$. This inequality guarantees that the metal activity, in contrast to the total dissolved metal concentration, is regulated by the iron sulfide–metal sulfide system.

The metal sulfide solubility products and the ratios are listed in Table 2-2. For example, the ratio of cadmium activity to total cadmium is less than $10^{-10.46}$. For nickel, the ratio is less than $10^{-5.59}$. By inference, this reduction in metal activity will occur for any other metal that forms a sulfide that is significantly more insoluble than iron monosulfide. The ratios for the other metals in Table 2-2 (Cu, Pb, Ag, and Zn) indicate that metal activity for these metals will be very small in the presence of excess AVS.

2.2.5 *Application to Mixtures of Metals*

A conjecture based on the sulfide solubility products for the metals listed in Table 2-2 is that the sum of the molar concentrations of metals should be compared with AVS. Because all these metals have lower sulfide solubility parameters than FeS, they would all exist as metal sulfides if their molar sum (and using [Ag]/2 because it is monovalent) is less than the AVS. For this case

$$\Sigma_i[M_T]_i < \text{AVS} \tag{2-8}$$

no metal toxicity would be expected, where $[M_T]_i$ is the total cold acid extractable i^{th} metal molar concentration in the sediment (divided by 2 for silver). On the other hand, if their molar sum is greater than the AVS concentration, then a portion of the metals with the largest sulfide solubility parameters would exist as free metal and potentially cause toxicity. For this case the following would be true

$$\Sigma_i[M_T]_i > \text{AVS} \tag{2-9}$$

These two equations are precisely the formulas that could be employed to determine the extent of metal toxicity in sediments assuming additive behavior and neglecting the effect of partitioning to other sediment phases. Whether the normalized sum is less than or greater than 1.0 discriminates between nontoxic and potentially toxic sediments. The additivity does not come from the nature of the mechanism that causes toxicity. Rather, it results from the equal ability of the metals to form metal sulfides with the same stoichiometric ratio of M and S (except silver).

The appropriate quantity of metals to use in the metals and AVS comparison is referred to as SEM, that is, the metal extracted with the cold acid used in the AVS procedure. This is the appropriate quantity to use because some metals form sulfides that are not labile in the AVS extraction (e.g., nickel, copper). If a more rigorous extraction were used to increase the fraction of metal extracted that did not also capture the additional sulfide extracted, then the sulfide associated with the additional metal release would not be quantified. This would result in an erroneously high metal value relative to AVS (Di Toro et al., 1992).

The above discussion is predicated on the assumption that all the metal sulfides behave similarly to cadmium sulfide. Furthermore, it has been assumed that only acid-soluble metals are reactive enough to affect the free metal activity. That is, the proper metal concentration to be used is the SEM. Both of these hypotheses were tested directly with benthic organisms using sediment toxicity tests. Results of these sediment-spiking experiments with cadmium, copper, lead, nickel, silver, zinc, and a mixture of these metals are presented in Section 3.

Section 3

Toxicity of Metals in Sediments

3.1 General Information

This section summarizes data from acute and chronic toxicity tests that demonstrate that absence of sediment toxicity caused by metals can be predicted by (a) the use of interstitial water concentrations of metals or (b) comparison of molar concentrations of AVS and SEM. Furthermore, they demonstrate that use of (ΣSEM-AVS)/f_{OC} reduces the variability associated with prediction of when sediments will be toxic. The ability to predict toxicity of metals in sediments, through a fundamental understanding of chemical bioavailability, is demonstrated using results of toxicity tests with benthic organisms in spiked or field sediments. A wide variety of individual benthic species having different habitat requirements have been tested in 10-day experiments in spiked and field sediments, including the following: an oligochaete (*Lumbriculus variegatus*), polychaetes (*Capitella capitata* and *Neanthes arenaceodentata*), amphipods (*A. abdita*, *R. hudsoni*, *Leptocheirus plumulosus*, and *Hyalella azteca*), a harpacticoid copepod (*Amphiascus tenuiremis*), a midge (*Chironomus tentans*), and a gastropod (*Helisoma* sp.). In addition, the approach was tested in life-cycle tests with *L. plumulosus* and *C. tentans*. Many other benthic species were tested in freshwater and saltwater benthic colonization studies.

3.1.1 *Terminology*

Early studies on use of AVS in prediction of biological effects (e.g., Di Toro et al., 1990) involved the ratio of SEM to AVS, expressed as SEM/AVS. The ratio appeared more useful in the early laboratory tests because it caused concentration-response data from spiking experiments with different sediments to fall on the same line (Di Toro et al., 1990, 1992; Casas and Crecelius, 1994; Pesch et al., 1995; Berry et al., 1996). Later studies, however, showed several advantages to the use of the difference, expressed as SEM-AVS (Hansen et al., 1996a). The two expressions—SEM/AVS ≤ 1 and SEM-AVS ≤ 0—are functionally equivalent. Both indicate an excess of AVS over SEM. The advantages to using SEM-AVS are that it does not get very large when AVS is very low (as the ratio does), and that it can be used to develop partitioning relationships that include other phases, such as total organic carbon (TOC) (see Section 3.4; see also the discussion in Section 3.2.5). For these reasons, the use of the SEM-AVS difference is the recommended method, and it will be used throughout the rest of this document except in the discussion of the historical development of AVS theory that follows. In the ensuing discussion, SEM/AVS ratios are presented because they were originally presented in this form.

3.2 Predicting Metal Toxicity: Short-Term Studies

3.2.1 *Spiked Sediments: Individual Experiments*

A key to understanding the bioavailability of sediment-associated contaminants was provided by Adams et al. (1985), who observed that the effects of kepone, a nonionic organic pesticide, were similar across sediments when toxicity was related to interstitial water concentrations. Swartz et al. (1985) and Kemp and Swartz (1986) first observed that metal concentrations in interstitial waters of different sediments were correlated with observed biological effects. However, as opposed to the situation for nonionic organic chemicals and organic carbon (see Di Toro et al., 1991), the sediment-partitioning phases that controlled interstitial water concentrations of metals and metal-induced sediment toxicity were initially not apparent.

Di Toro et al. (1990) first investigated the significance of sulfide partitioning in controlling metal bioavailability and metal-induced toxicity in marine sediments spiked with cadmium. In these experiments, the operational definition of Cornwell and Morse (1987) was used to identify that fraction of amorphous sulfide, or AVS, available to interact with cadmium in the sediments. Specifically, AVS was defined as the sulfide liberated from wet sediment when treated with cold 1N HCl acid. Di Toro et al. (1990) found that, when expressed on a dry weight basis, the toxicity of cadmium in sediments in 10-day tests with the amphipods *R. hudsoni* or *A. abdita* was sediment specific (Figure 3-1A; from Di Toro et al., 1990).

Toxicity increased with increasing cadmium concentration, but the concentration-response relationships were different for each sediment. Thus, it would not be possible to predict whether a particular sediment would be toxic or not. If the cadmium concentration is expressed on an interstitial water basis (Figure 3-1B), however, concentration response is not sediment specific. Similar results are observed when cadmium concentration is expressed as SEM/AVS (Figure 3-1C). Note that when the ratio of μmol Cd/μmol AVS was less than 1.0, the sediments were not toxic, and when the ratio was greater than 1.0, the sediments became increasingly toxic. Studies by Carlson et al. (1991) with cadmium-spiked freshwater sediments yielded similar results; when there was more AVS than total cadmium, significant toxicity was not observed in 10-day tests with an oligochaete (*L. variegatus*) or snail (*Helisoma* sp). Di Toro et al. (1992), in their studies with nickel-spiked sediments using *A. abdita* and field sediments contaminated with cadmium and nickel using the freshwater amphipod *H. azteca*, provided further support to the importance of AVS in controlling metal bioavailability in sediments. These studies suggested that it may be feasible to derive an ESB for mixtures of metals by direct comparison of molar AVS concentrations to the molar sum of the concentrations of cationic metals (specifically, cadmium, copper, lead, nickel, and zinc) extracted with the AVS (i.e., ΣSEM). They observed that expression of metals concentrations based on the sum of SEM concentrations is required because a significant amount of nickel sulfide is not completely soluble in the AVS extraction. Hence, AVS must be used as the measure of reactive sulfide and the sum of SEM as the measure of total reactive metal.

Casas and Crecelius (1994) further explored the relationship of SEM and AVS, interstitial water concentrations, and toxicity by conducting 10-day toxicity tests with the marine polychaete *C. capitata* exposed to sediments spiked with zinc, lead, and copper. As was true in earlier studies, elevated interstitial water metal concentrations were observed only when SEM concentrations exceeded those of AVS. Sediments were not toxic when SEM concentrations were less than AVS and when the concentrations in interstitial water were less than the water-only LC50 values. Green et al. (1993) reported results of another spiking experiment supporting this general EqP approach to deriving an ESB for metals. In their study, metal–sulfide partitioning was not directly quantified, but it was found that toxicity of cadmium-spiked marine sediments to the meiobenthic copepod *A. tenuiremis* was predictable based on interstitial water, but not sediment dry weight cadmium concentrations. Further spiking experiments by Pesch et al. (1995) demonstrated that 10-day survival of the marine polychaete *N. arenceodentata* was comparable to controls in cadmium- or nickel-spiked sediments with more AVS than SEM.

Berry et al. (1996) described experiments in which *A. abdita* were exposed for 10 days to two or three sediments spiked either singly, or in combination, with cadmium, copper, lead, nickel, and zinc. As in previous studies, significant toxicity to the amphipod did not occur when AVS concentrations exceeded those of SEM. They compared observed mortality with interstitial water metal concentrations expressed as interstitial water toxic units (IWTUs)

$$\mathrm{IWTU} = [\mathrm{M_d}]/\mathrm{LC50} \qquad (3\text{-}1)$$

where $[\mathrm{M_d}]$ is the dissolved metal concentration in the interstitial water, and the LC50 is the concentration of the metal causing 50% mortality of the test species in a water-only test. If interstitial water exposure in a sediment test is indeed equivalent to that in a water-only test, then 1.0 IWTU should result in 50% mortality of the test animals. Berry et al. (1996) reported that significant (>24%) mortality of the saltwater amphipod occurred in only 3.0% of sediments with less than 0.5 IWTU, whereas samples with greater than 0.5 IWTUs were toxic 94.4% of the time. Berry et al. (1996) also made an important observation relative to interstitial water metal chemistry in their mixed-metals test; chemical equilibrium calculations suggest that the relative affinity of metals for AVS should be silver> copper>lead>cadmium>zinc>nickel (Emerson et al., 1983; Di Toro et al., 1992); hence, the appearance of the metals in interstitial water as AVS is exhausted should occur in an inverse order. For example, zinc would replace nickel in a monosulfide complex and nickel would be liberated to the interstitial water, and so on. Berry et al. (1996) observed this trend in sediments spiked with cadmium, copper, nickel, and zinc (Figure 3-2). Furthermore, an increase in the concentration of a metal in a sediment with a low sulfide solubility product constant (K_{sp}) theoretically would displace a previously unavailable and nontoxic metal with a higher K_{sp}, making that metal available to bind to other sediment phases or enter interstitial water to become toxic. Berry et al. (1999) exposed the saltwater amphipod *A. abdita* to sediments spiked with silver. When AVS was detected in the sediments, they were not toxic and interstitial water contained no detectable silver. For sediments that contain no detectable AVS,

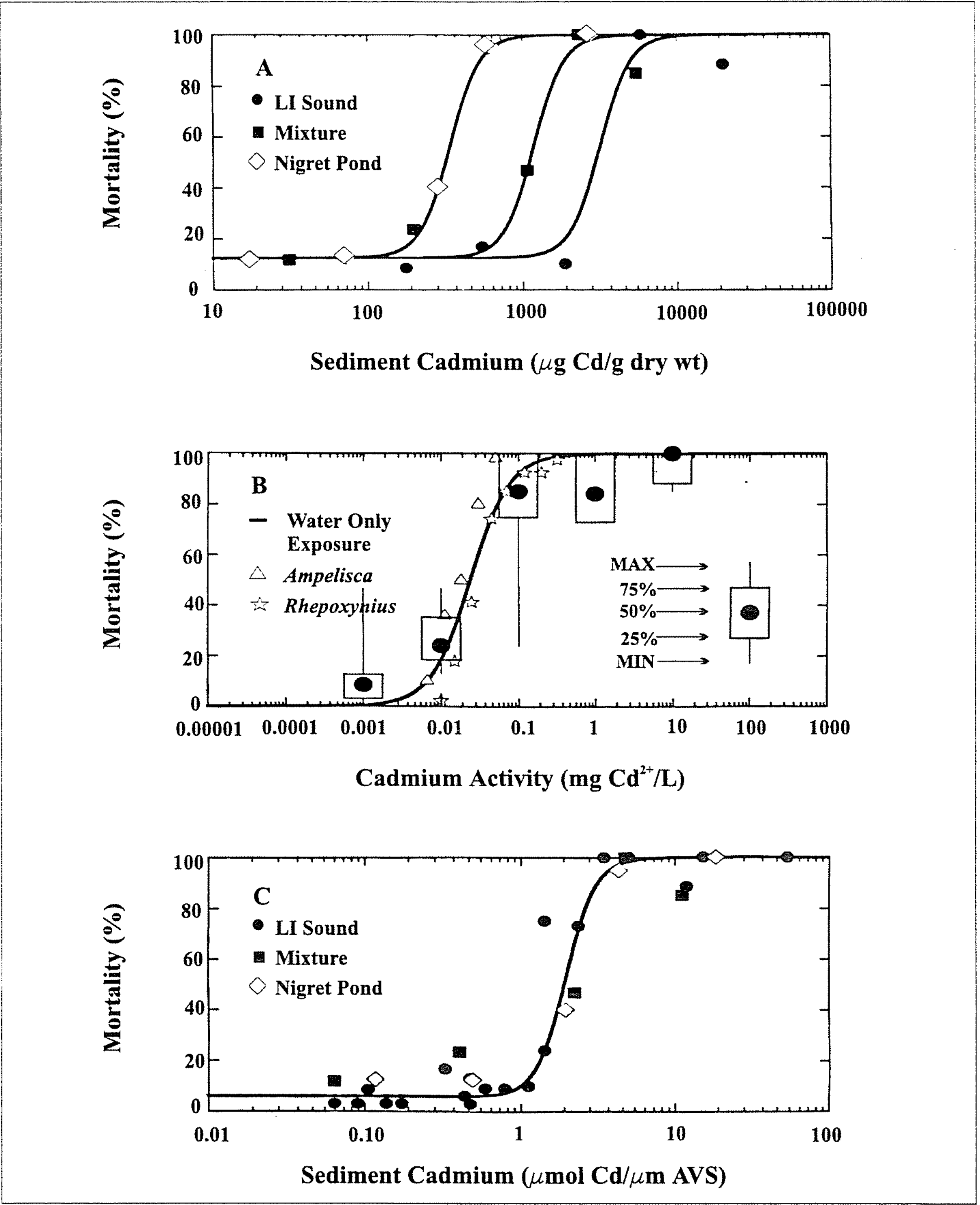

Figure 3-1. Percentage mortality of amphipods (*Ampelisca abdita* and *Rhepoxynius hudsoni*) exposed to sediments from Long Island Sound, Ninigret Pond, and a mixture of these two sediments as a function of the sum of the concentrations of metals in sediments expressed as: (A) dry weight, (B) interstitial water cadmium activity, and (C) the sediment cadmium/AVS ratio (figures from Di Toro et al., 1990).

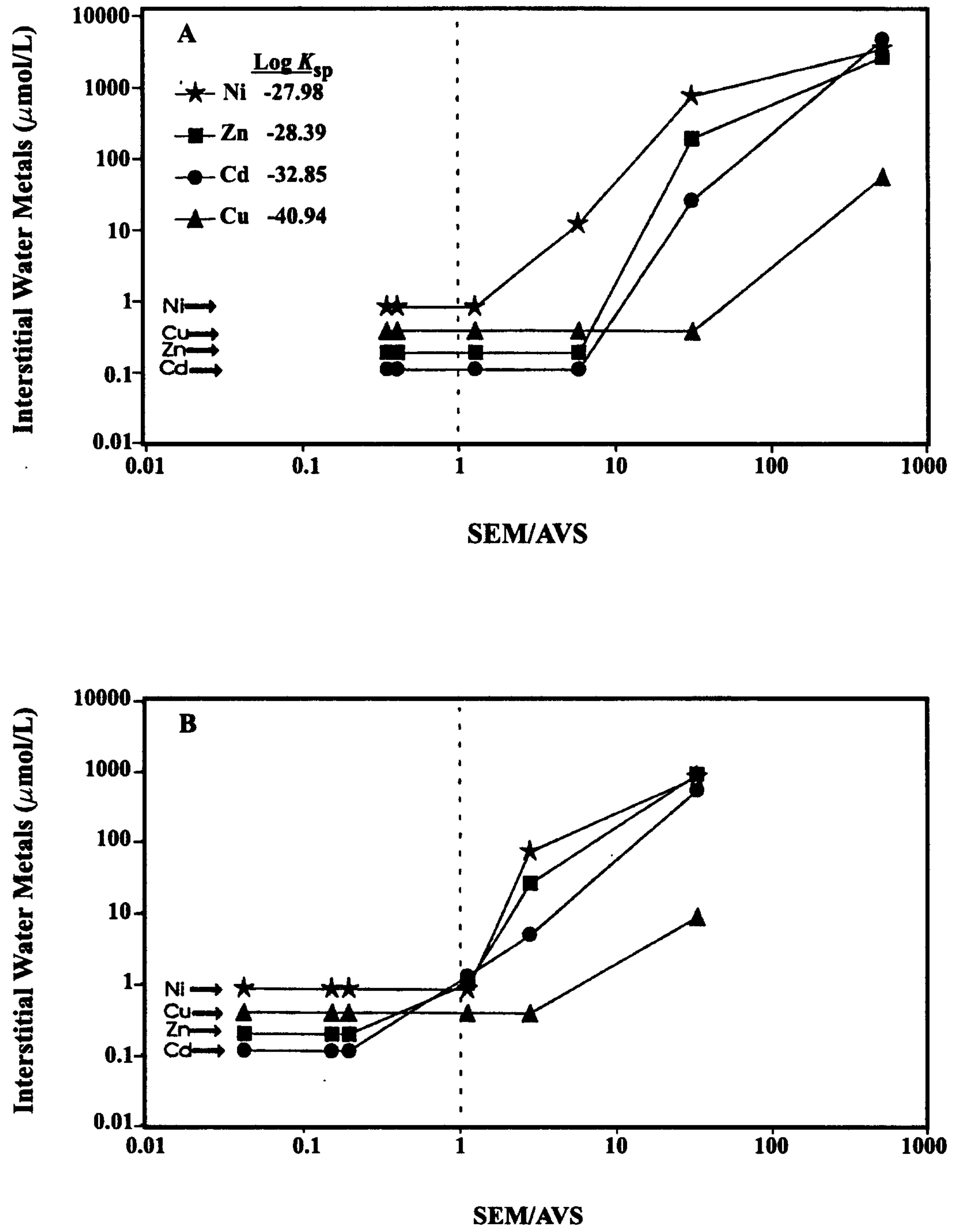

Figure 3-2. Concentrations of individual metals in interstitial water of sediments from Long Island Sound (A) and Ninigret Pond (B) in the mixed metals experiment as a function of SEM/AVS ratio. Concentrations below the interstitial water detection limits, indicated by arrows, are plotted at one-half the detection limit. K_{sp} is the sulfide solubility product constant (figures from Berry et al., 1996).

any SEM silver that is detected is dissolved interstitial silver, because silver sulfide and silver chloride precipitate are not extracted using the standard AVS procedure.

3.2.2 *Spiked Sediments: All Experimental Results Summarized*

This summary includes data from amphipods exposed in 10-day toxicity tests to saltwater sediments spiked with cadmium, copper, lead, nickel, silver, or zinc and their mixtures (Di Toro et al., 1990; Berry et al., 1996, 1999); polychaetes exposed to sediments spiked with cadmium, copper, lead, nickel, or zinc (Casas and Crecelius, 1994; Pesch et al., 1995); copepods exposed to sediments spiked with cadmium (Green et al., 1993; measured interstitial cadmium but not AVS); and freshwater tests using oligochaetes and snails exposed to sediments spiked with cadmium (Carlson et al., 1991). Seven species (freshwater and saltwater) and sediments from seven different locations were described. AVS concentrations ranged from 1.9 to 65.7 μmol/g dry weight, and TOC ranged from 0.15% to 10.6% in these sediments.

Overall, the results of these experiments demonstrate that predictions of the toxicity of sediments spiked with metals using the total metal concentration on a dry weight basis are not based on scientific theories of bioavailability and will have considerable error (Figures 3-3A and 3-4A). Sediments having ≤24% mortality are considered nontoxic as defined by Berry et al. (1996), which is indicated by the horizontal line in Figure 3-3. Furthermore, the concentration range where it is 90% certain that the sediment may be either toxic or nontoxic, shown as dashed lines in Figure 3-3, is almost two orders of magnitude for dry weight metals, a little over an order of magnitude for IWTUs, and only a half order of magnitude for SEM/AVS (see Section 3.4 for a description of the derivation of the uncertainty limits). The uncertain range for dry weight metals is approximately equal to the sum of the uncertainty range for SEM/AVS plus the range in the AVS concentrations of the spiked sediments in the database. If sediments with a lower AVS concentration had been tested, effects would have occurred at a lower dry weight concentration, and if sediments with lower or higher AVS concentrations had been tested, the uncertainty range would increase. Importantly, the uncertainty range for IWTUs or SEM/AVS would likely not be altered.

Even given the above, it is visually tempting to select a cutoff at a dry weight concentration of 1.0 μmol/g to indicate the separation of sediments that are toxic or nontoxic. This would be inappropriate because toxicity of metals in sediments when concentrations are expressed as dry weights have been shown to be sediment specific (Figure 3-1A). Also, had sediments with lower or higher AVS concentrations been tested, the cutoff would have been at lower or higher dry weight concentrations. However, to further demonstrate the risks of establishing a dry weight cutoff, the data from the 184 spiked sediments in Figure 3-3 were re-analyzed. A visually based cutoff of 1.0 μmol/g dry weight, and theoretically based cutoffs of 0.5 IWTU and 1.0 SEM/AVS were selected. Sediment concentrations were numerically ordered. Those with concentrations less than the cutoffs were divided into three groups containing approximately the same number of sediments (15, 22, or 25 sediments per group for dry weight metal concentrations, IWTUs, and SEM/AVS, respectively). Similarly, sediments containing greater concentrations were divided into six groups (21, 16, or 14 sediments per group for dry weight metal concentrations, IWTUs, and SEM/AVS, respectively). The percentages of nontoxic (≤24% mortality) and toxic (>24% mortality) sediments in each group are plotted in a stacked bar plot (Figure 3-4). Not surprisingly, because the distribution was visually selected, most sediments having less than 1.0 μmol/g dry weight metal were not toxic. The same was true for the toxicologically selected cutoffs of 0.5 IWTUs and SEM/AVS ratios of 1.0. The advantage of using IWTUs and SEM/AVS becomes more clear when the sediments above the cutoffs are considered. For dry weight metal concentrations, more of the sediments in the first four sediment groups (up to 26.8 μmol/g dry weight) were nontoxic than were toxic. It was only in the two sediment groups that contained the highest concentrations, >27.6 μmol/g dry weight, that toxic sediments predominated after the first two sediment groups. In contrast, toxic sediments predominated in only the first two sediment groups above the IWTU cutoff and after the first sediment group above the SEM/AVS ratio cutoff.

In some cases, the dry weight metal concentrations required to cause acute mortality in these experiments were very high relative to those often suspected to be of toxicological significance in field sediments (e.g., Figures 3-1A and 3-3A). This has sometimes been interpreted as a limitation of the use of SEM and AVS to predict metal-induced toxicity. However, the range of AVS in these sediments spiked with metals is similar to

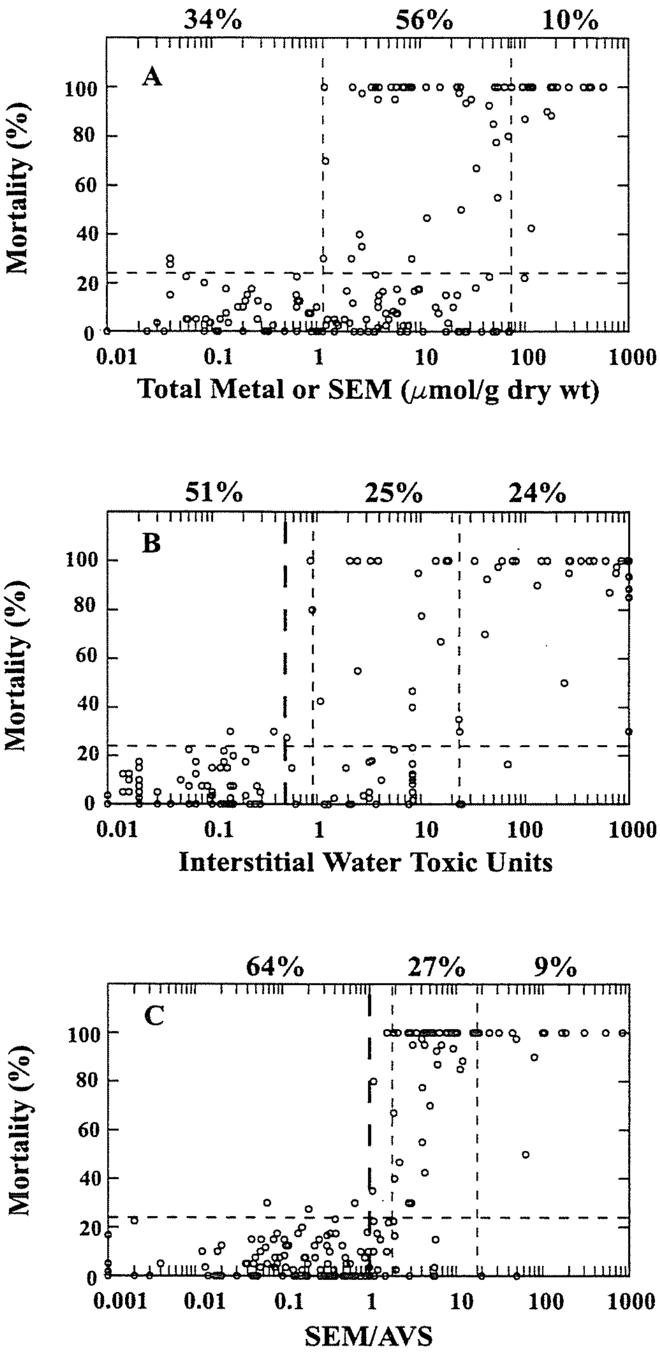

Figure 3-3. Percentage mortality of freshwater and saltwater benthic species in 10-day toxicity tests in sediments spiked with individual metals (Cd, Cu, Pb, Ni, Ag, or Zn) or a metal mixture (Cd, Cu, Ni, and Zn). Mortality is plotted as a function of: (A) the sum of the concentrations of the respective metal or metal mixture in μmol metal per gram dry weight of sediment; (B) IWTU; and (C) SEM/AVS ratio. Data below the detection limits are plotted at IWTU=0.01 and SEM/AVS=0.001. Heavy dashed lines are the theoretically based cutoffs of 0.5 IWTU and a SEM/AVS ratio of 1.0. Light vertical dashed lines are the 90% uncertainty bound limits derived as in Section 3.4. The percentage of the total number of sediments (n = 184) within the bounded limits is provided above each of the three panels for the purpose of comparison (silver data from Berry et al., 1999; all other data modified after Berry et al., 1996).

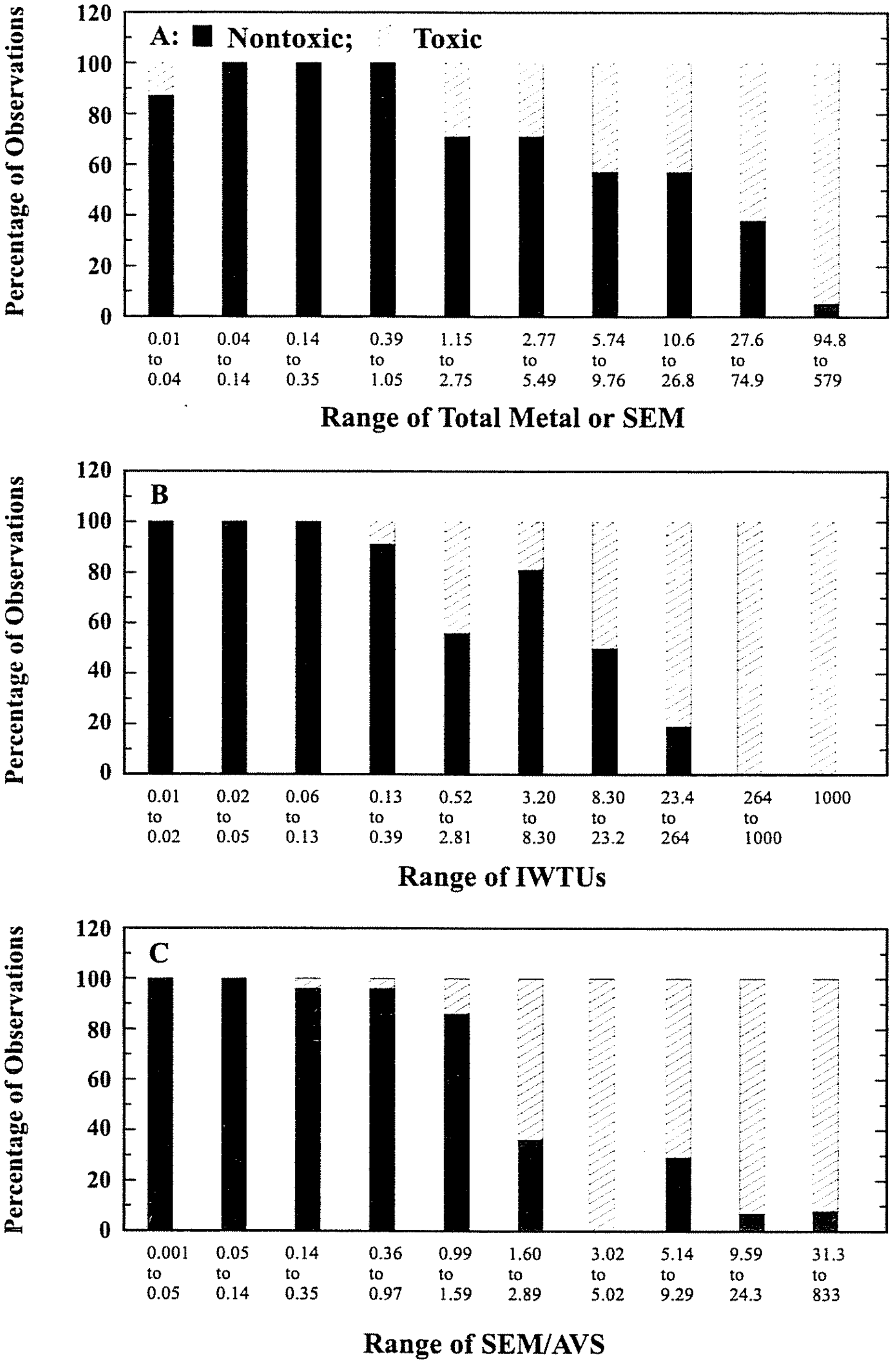

Figure 3-4. Percentage of the 184 spiked sediments from Figure 3-3 that were nontoxic or toxic over various intervals of (A) concentrations of metal based on sediment dry weight (μmol/g), (B) IWTU, and (C) SEM/AVS.

that of sediments commonly occurring in the field. The important point here is that even a sediment with only a moderate concentration of AVS has a considerable capacity for sequestering metals as a metal sulfide, a form that is not bioavailable (Di Toro et al., 1990).

In contrast, the combined data from all available freshwater and saltwater spiked-sediment experiments support the use of IWTUs to predict mortality of benthic species in spiked-sediment toxicity tests (Figure 3-3B). Mortality in these experiments was sediment independent when plotted against IWTUs. Sediments with IWTUs of <0.5 were generally not toxic. Of the 96 sediments with IWTUs <0.5, 96.9% were not toxic, whereas 76.4% of the 89 sediments with IWTUs ≥0.5 were toxic (Table 3-1). This close relationship between IWTUs and sediment toxicity in sediments spiked with metals was also observed in studies with field sediments contaminated with metals (see Section 3.2.3 below), as well as sediments spiked with nonionic organic chemicals (Adams et al., 1985; Swartz et al., 1990; Di Toro et al., 1991), and field sediments contaminated with nonionic organic chemicals (Hoke et al., 1994; Swartz et al., 1994).

Table 3-1. Toxicity of sediments from freshwater and saltwater lab-spiked sediment tests, field locations, and combined lab-spiked and field sediment tests as a function of the molar concentrations of SEM and AVS (SEM/AVS or the SEM-AVS), interstitial water toxic units (IWTUs), and both SEM/AVS or SEM-AVS and IWTUs

			Percent of Sediments	
Study Type/Parameter	Value	n	Nontoxic[a]	Toxic[b]
Laboratory Spike:				
SEM/AVS or SEM-AVS[c]	≤1.0 or ≤0.0	101	98.0	2.0
	>1.0 or >0.0	95	26.3	73.7
IWTU[d]	<0.5	96	96.9	3.1
	≥0.5	89	23.6	76.4
SEM/AVS or SEM-AVS[c]; IWTU[d]	≤1.0 or ≤0.0; <0.5	83	97.6	2.4
	>1.0 or >0.0; ≥0.5	78	14.1	85.9
Field:				
SEM/AVS or SEM-AVS[c]	≤1.0 or ≤0.0	57	98.2	1.8
	>1.0 or >0.0	79	59.5	40.5
IWTU[d]	<0.5	79	98.7	1.3
	≥0.5	53	45.3	54.7
SEM/AVS or SEM-AVS[c]; IWTU[d]	≤1.0 or ≤0.0; <0.5	49	100.0	0.0
	>1.0 or >0.0; ≥0.5	45	33.3	66.7
Lab-Spike and Field:				
SEM/AVS or SEM-AVS[c]	≤1.0 or ≤0.0	158	98.1	1.9
	>1.0 or >0.0	174	42.0	58.0
IWTU[d]	<0.5	175	97.7	2.3
	≥0.5	142	31.7	68.3
SEM/AVS or SEM-AVS[c]; IWTU[d]	≤1.0 or ≤0.0; <0.5	132	98.5	1.5
	>1.0 or >0.0; ≥0.5	123	21.1	78.9

[a] Nontoxic sediments ≤24% mortality.

[b] Toxic sediments >24% mortality.

[c] An SEM/AVS ratio of ≤1.0 or an SEM-AVS difference of ≤0.0 indicates an excess of sulfide and probable nontoxic sediments. An SEM/AVS ratio of >1.0 or an SEM-AVS difference of >0.0 indicates an excess of metal and potentially toxic sediments.

[d] An IWTU of <0.5 indicates a probable nontoxic interstitial water concentration of less than one-half of the water-only LC50 of the same duration. An IWTU of ≥0.5 indicates a possibly toxic interstitial water concentration of greater than one-half of the water-only LC50 of the same duration.

Source: Modified from Hansen et al., 1996a.

The interstitial water metal concentrations in spiked-sediment studies were most often below the limit of analytical detection in sediments with SEM/AVS ratios below 1.0 (Berry et al., 1996). Above an SEM/AVS ratio of 1.0, the interstitial metals concentrations increased up to five orders of magnitude with increasing SEM/AVS ratio. This increase of several orders of magnitude in interstitial water metals concentration with an increase of only a factor of two or three in sediment concentration is the reason why mortality is most often complete in these sediments, and why the chemistry of anaerobic sediments controls the toxicity of metals to organisms living in aerobic microhabitats. It also explains why toxicities of different metals in the same sediment to different species when expressed on the basis of sediment metals concentration are so similar. Interstitial water metals were often below or near detection limits when SEM/AVS ratios were only slightly above 1.0, indicating the presence of other metal-binding phases in sediments.

The combined data from all available freshwater and saltwater spiked-sediment experiments also support the use of SEM/AVS ratios to predict sediment toxicity to benthic species in spiked-sediment toxicity tests. All tests yield similar results when mortality is plotted against SEM/AVS ratios (Figure 3-3C). Mortality in these experiments was sediment independent when plotted on an SEM/AVS basis. With the combined data, 98.0% of the 101 metals-spiked sediments with SEM/AVS ratios ≤1.0 were not toxic, whereas 73.7% of the 95 sediments with SEM/AVS ratios >1.0 were toxic (Table 3-1).

The overall data show that when both SEM/AVS ratios and IWTUs are used, predictions of sediments that would be toxic were improved. Of the 83 sediments with SEM/AVS ratios ≤1.0 and IWTUs <0.5, 97.6% were not toxic, whereas 85.9% of the 78 sediments with SEM/AVS ratios >1.0 and IWTUs ≥0.5 were toxic (Table 3-1).

These results show that SEM/AVS and IWTUs are accurate predictors of the absence of mortality in sediment toxicity tests; however, predictions of sediments that might be toxic are less accurate. The fact that a significant number of sediments (26.3%) tested had SEM/AVS ratios of >1.0 but were not toxic indicates that other binding phases, such as organic carbon (Mahony et al., 1996), may also control bioavailability in anaerobic sediments.

Organism behavior may also explain why some sediments with SEM/AVS ratios of >1.0 were not toxic. Many of the sediments that had the highest SEM/AVS ratios in excess of 1.0 that produced little or no mortality were from experiments using the polychaete *N. arenaceodentata* (see Pesch et al., 1995). In these experiments, this polychaete did not burrow into some of the test sediments with the highest concentrations, thereby limiting its exposure to the elevated concentrations of metals in the interstitial water and sediments. This same phenomenon may also explain the low mortality of snails, *Heliosoma* sp., in freshwater sediments with high SEM/AVS ratios. These snails are epibenthic and crawl onto the sides of test beakers to avoid contaminated sediments (G.L. Phipps, U.S. EPA, Duluth, MN, personal communication). Increased mortality was always observed in sediments with SEM/AVS ratios >5.9 in tests with the other five species.

Similarly, a significant number of sediments (23.6%) with ≥0.5 IWTUs were not toxic. This is likely the result of interstitial water ligands, which reduces the bioavailability and toxicity of dissolved metals; sediment avoidance by polychaetes or snails; or methodological problems in contamination-free sampling of interstitial water. Ankley et al. (1991) suggested that a toxicity correction for the hardness of the interstitial water for freshwater sediments is needed to compare toxicity in interstitial water with that in water-only tests. Absence of a correction for hardness would affect the accuracy of predictions of metal-induced sediment toxicity using IWTUs. Furthermore, a significant improvement in the accuracy of metal-induced toxicity predictions using IWTUs might be achieved if DOC binding in the interstitial water is taken into account. Green et al. (1993) and Ankley et al. (1991) hypothesized that increased DOC in the interstitial water reduced the bioavailability of cadmium in sediment exposures, relative to the water-only exposures. Green et al. (1993) found that the LC50 value for cadmium in an interstitial water exposure without sediment was more than twice that in a water-only exposure, and that the LC50 value for cadmium in interstitial water associated with sediments was more than three times that in a water-only exposure.

3.2.3 *Field Sediments*

In addition to short-term laboratory experiments with spiked sediments, there have been several published studies of laboratory toxicity tests with metal-contaminated sediments from the field. Ankley et al. (1991) exposed *L. variegatus* and the amphipod *H. azteca* to 17 sediment samples along a gradient of cadmium and nickel contamination from a freshwater/

estuarine site in Foundry Cove, NY. In 10-day toxicity tests, *H. azteca* mortality was not significantly different from controls in all sediments where SEM (cadmium plus nickel) was less than AVS. Mortality was greater than controls only in sediments with more SEM than AVS. *L. variegatus* was far less sensitive to the sediments than *H. azteca*, which correlates with the differential sensitivity of the two species in water-only tests with cadmium and nickel.

In 10-day toxicity tests with the saltwater amphipod *A. abdita* in these same sediments, Di Toro et al. (1992) observed that metals concentrations ranging from 0.1 to 28 μmol SEM/g sediment were not toxic in some sediments, whereas metals concentrations ranging from 0.2 to 1,000 μmol SEM/g sediment were lethal in other sediments. These results indicate that the bioavailable fraction of metals in sediments varies from sediment to sediment. In contrast, the authors also observed a clearly discernible mortality-concentration relationship when mortality was related to the SEM/AVS molar ratio (i.e., there was no significant mortality where SEM/AVS ratios were <1.0, mortality increased in sediments having SEM/AVS ratios of 1.0 to 3.0, and there was 100% mortality in sediments with ratios >10). The sum of the IWTUs for cadmium and nickel ranged from 0.08 to 43.5. Sediments with ≤ 0.5 IWTUs were always nontoxic, those with >2.2 IWTUs were always toxic, and two of seven sediments with intermediate IWTUs (0.5 to 2.2) were toxic. Molar concentrations of cadmium and nickel in the interstitial water were similar. However, cadmium contributed over 95% to the sum of the toxic units because cadmium is 67 times more toxic to *A. abdita* than nickel. The latter illustrates the utility of interstitial water concentrations of individual metals in assigning the probable cause of mortality in benthic species (Hansen et al., 1996a).

In tests with the same sediments from Foundry Cove, Pesch et al. (1995) observed that 6 of the 17 sediments tested had SEM/AVS ratios <1.0 and IWTUs <0.5, and none of the 6 were toxic to the polychaete *N. arenaceodentata*. Interestingly, the other 11 sediments containing SEM/AVS ratios >1.0 were also not toxic. The results are not surprising given that in these particular tests only one sediment had >0.5 IWTUs, *N. arenaceodentata* is not sensitive to cadmium and nickel, and the polychaetes did not burrow into sediments containing toxic concentrations of these metals.

Ankley et al. (1993) examined the significance of AVS as a binding phase for copper in freshwater sediments from two copper-impacted sites. Based on interstitial water copper concentrations in the test sediments, the 10-day LC50 for *H. azteca* was 31 μg/L; this compared favorably with a measured LC50 of 28 μg/L in a 10-day water-only test. Sediments having SEM/AVS ratios <1.0 were not toxic. They also observed no toxicity in several sediments with markedly more SEM than AVS, suggesting that copper was not biologically available in these sediments. Absence of copper in interstitial water from these sediments corroborated this lack of bioavailability. This observation suggested the presence of binding phases in addition to AVS for copper in the test sediments. Two studies suggest that an important source of the extra binding capacity in these sediments was organic carbon (U.S. EPA, 1994a; Mahony et al., 1996).

Hansen et al. (1996a) investigated the biological availability of sediment-associated divalent metals to *A. abdita* and *H. azteca* in sediments from five saltwater locations and one freshwater location in the United States, Canada, and China using 10-day lethality tests. Sediment toxicity was not related to dry weight metals concentrations. In the locations where metals might be likely to cause toxicity, 49 sediments had less SEM than AVS and <0.5 IWTUs, and no toxicity was observed. In contrast, one-third of the 45 sediments with more SEM than AVS and >0.5 IWTUs were toxic (Table 3-1).

Hansen et al. (1996a) made an observation that is important to interpretation of toxicity of sediments from field locations, particularly those from industrial harbors. They observed that if sediments with SEM/AVS ratios <1.0 are toxic, even if metals concentrations on a dry weight basis are very high, the toxicity is not likely to be caused by metals. Furthermore, it is incorrect to use such data to reach the conclusion that the EqP approach is not valid. This is because when SEM/AVS ratios were <1.0, there was an almost complete absence of toxicity in both spiked sediments and field sediments where metals were the only known source of contamination and IWTUs for metals were <0.5. When metals concentrations expressed as the sum of the IWTUs are used in conjunction with SEM/AVS ratios, they together provide insight that can explain apparent anomalies between SEM/AVS ratios <1.0 and sediment toxicity in field sediments. Joint use of both SEM/AVS ratios and interstitial water concentrations is also a powerful tool for explaining absence of toxicity when SEM/AVS ratios are >1.0. Overall, when freshwater and saltwater field sediments were tested in the laboratory, 100% were not toxic when SEM/AVS was ≤ 1.0 and IWTUs were <0.5, and 66.7% were toxic when SEM/AVS was >1.0 and IWTUs were ≥0.5 (Table 3-1).

Therefore, because AVS can bind divalent metals in proportion to their molar concentrations, Hansen et al. (1996a) proposed the use of the difference between the molar concentrations of SEM and AVS (SEM-AVS) rather than SEM/AVS ratios used previously. The molar difference provides important insight into the extent of additional available binding capacity and the magnitude by which AVS binding has been exceeded (Figure 3-5). Further, absence of organism response when AVS binding is exceeded can indicate the potential magnitude of other important binding phases in controlling bioavailability. Figure 3-5 shows that for most nontoxic freshwater and saltwater field sediments, 1 to 100 μmol of additional metal would be required to exceed the sulfide-binding capacity (i.e., SEM-AVS = − 100 to − 1 μmol/g). In contrast, most toxic field sediments contained 1 to 1,000 μmol of metal beyond the binding capacity of sulfide alone. Data on nontoxic field sediments whose sulfide-binding capacity is exceeded (SEM-AVS is >1.0 μmol/g) indicate that other sediment phases, in addition to AVS, have significance in controlling metal bioavailability. In comparison to SEM/AVS ratios, use of SEM-AVS differences is particularly informative where AVS concentrations are low, such as those from Steilacoom Lake and the Keweenaw Watershed, where the SEM-AVS difference is numerically low and SEM/AVS ratios are high (Ankley et al., 1993). For these reasons, SEM-AVS is used instead of the SEM/AVS ratio almost exclusively for the remainder of this document.

3.2.4 *Field Sites and Spiked Sediments Combined*

Figure 3-6 and Table 3-1 summarize available data from freshwater and saltwater sediments spiked with individual metals or metal mixtures, freshwater field sites, and saltwater field sites on the utility of metals concentrations in sediments normalized by dry weight, IWTUs, and SEM-AVS. These data explain the

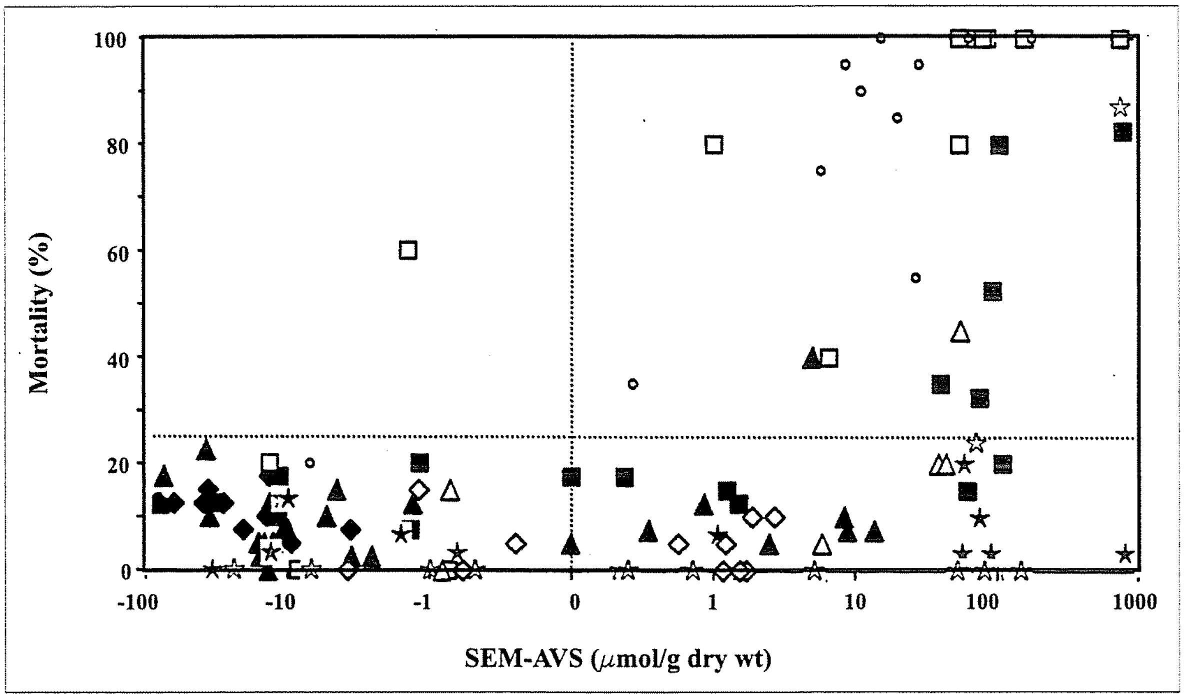

Figure 3-5. **Percentage mortality of amphipods, oligochaetes, and polychaetes exposed to sediments from four freshwater and three saltwater field locations as a function of the sum of the molar concentrations of SEM minus the molar concentration of AVS (SEM-AVS). Sediments having ≤24% mortality are considered nontoxic as defined by Berry et al. (1996), which is indicated by the horizontal dotted line in the figure. The vertical dotted line at SEM-AVS = 0.0 μmol/g dry wt indicates the boundary between sulfide-bound unavailable metal and potentially available metal. The different symbols represent field sediments from different locations (figure from Hansen et al., 1996a).**

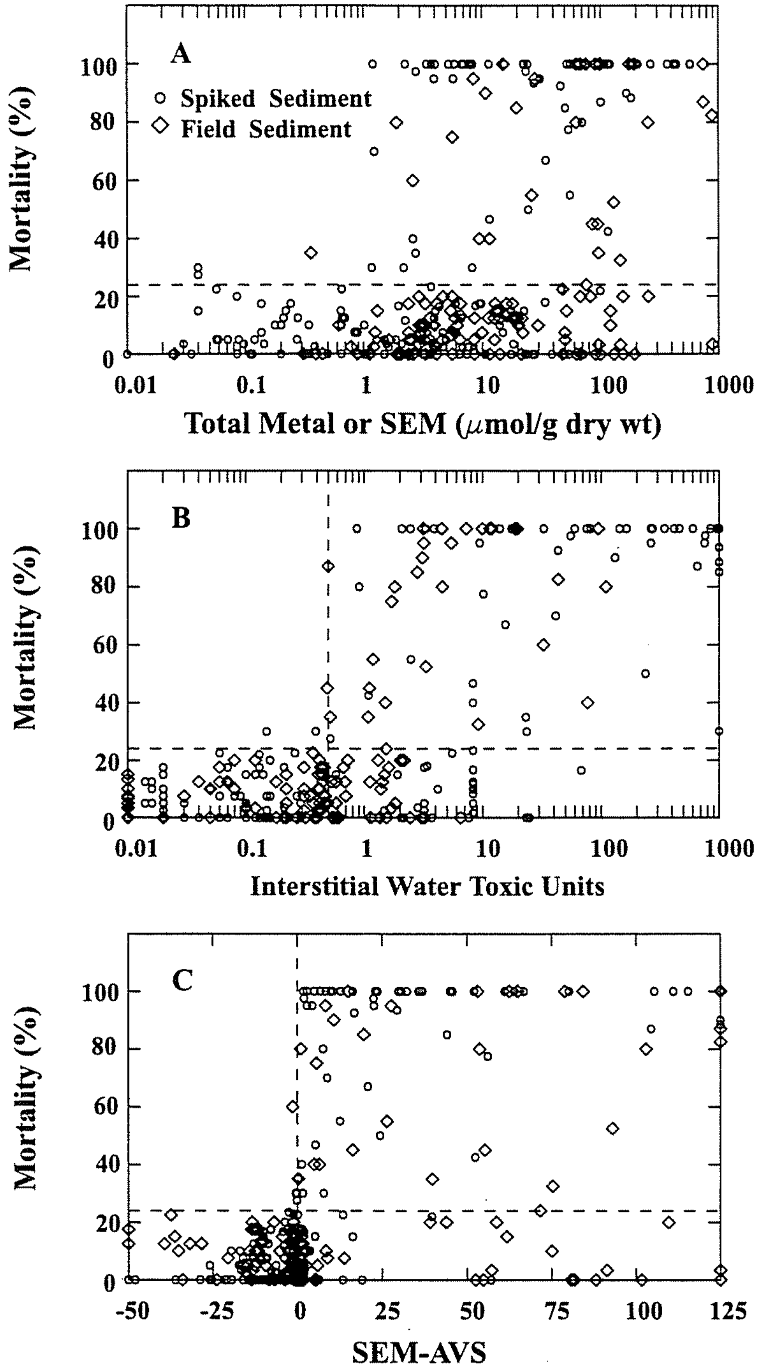

Figure 3-6. Percentage mortality of freshwater and saltwater benthic species in 10-day toxicity tests in spiked sediments and sediments from the field. Mortality is plotted as a function of: (A) the sum of the concentrations of the respective metal (Cd, Cu, Pb, Ni, Ag, or Zn) or metal mixture in μmol metal per gram dry weight of sediment; (B) IWTU; and (C) SEM-AVS difference. Data below the detection limits are plotted at IWTU = 0.01 and SEM-AVS = -50 μmol/g dry wt (silver data from Berry et al., 1999; all other data modified after Hansen et al., 1996a).

bioavailability and acute toxicity of metals in sediments (Hansen et al., 1996a; Berry et al., 1999). This analysis contains all available data from 10-day lethality tests where mortality, IWTUs, SEM, and AVS are known from experiments with sediments toxic only because of metals. The relationship between benthic organism mortality and total dry weight metals concentrations in spiked and field sediments is not useful to causally relate metal concentrations to organism response (Figures 3-4A and 3-6A). The overlap is almost four orders of magnitude in the bulk metals concentrations that cause no toxicity and those that are 100% lethal for these sediments where metals are the only source of toxicity (see discussion in Section 3.2.2).

Data in Figure 3-6B show that over all tests, the toxicity of sediments whose concentrations are normalized on an IWTU basis are typically consistent with the IWTU concept; that is, if IWTUs are ≤1.0, then sediments should be lethal to ≤50% of the organisms exposed, and significant mortality probably should be absent at <0.5 IWTUs. Of the spiked and field sediments evaluated that had IWTUs <0.5, 97.7% of 175 sediments were nontoxic (Table 3-1). For the 142 sediments having IWTUs ≥0.5, 68.3% were toxic. However, and as stated above, given the effect on toxicity or bioavailability of the presence of other binding phases (e.g., DOC) in interstitial water, water quality (hardness, salinity, etc.), and organism behavior, it is not surprising that many sediments having IWTUs ≥0.5 are not toxic.

Data in Figure 3-6C show that over all tests, organism response in sediments whose concentrations are normalized on an SEM-AVS basis is consistent with metal-sulfide binding on a mole to mole basis as first described by Di Toro et al. (1990), and later recommended for assessing the bioavailability of metals in sediments by Ankley et al. (1994). Saltwater and freshwater sediments either spiked with metals or from field locations with SEM-AVS differences ≤0.0 were uniformly nontoxic (98.1% of 158 sediments) (Table 3-1). The majority (58.0%) of 174 sediments having SEM-AVS >0.0 were toxic. It is not surprising that many sediments having SEM-AVS >0.0 are not toxic given the effect on toxicity or bioavailability of the presence of other sediment phases that also affect bioavailability (see Section 3-4; Di Toro et al., 1987, 2000; Mahony et al., 1996).

Over all tests, the data in Figure 3-6 indicate that use of both IWTUs and SEM-AVS together did not improve the accuracy of predictions of sediments that were nontoxic (98.5% of 132 sediments; Table 3-1). However, it is noteworthy that 78.9% of the 123 sediments with both SEM-AVS >0.0 and IWTUs ≥0.5 were toxic. Therefore, the approach of using SEM-AVS, IWTUs, and especially both indicators to identify sediments of concern is very useful.

The results of all available data demonstrate that using SEM, AVS, and interstitial water metals concentrations to predict the lack of toxicity of cadmium, copper, lead, nickel, silver, and zinc in sediments is certain. This is very useful, because the vast majority of sediments found in the environment in the United States have AVS concentrations that exceed the SEM concentration (SEM-AVS <0.0) (see Section 4.4). This may incorrectly suggest that there should be little concern about metals in sediments on a national basis, even though localized areas of biologically significant metal contamination do exist (Wolfe et al., 1994; Hansen et al., 1996a; Leonard et al., 1996a). It is potentially important that most of these data are from field sites where sediment samples were collected in the summer. At this time of year, the seasonal cycles of AVS produce the maximum metal-binding potentials (Boothman and Helmstetter, 1992; Leonard et al., 1993). Hence, sampling at seasons and conditions when AVS concentrations are at a minimum is a must in establishing the true overall level of concern about metals in the nation's sediments and in evaluations of specific sediments of local concern.

Predicting which sediments with SEM-AVS >0.0 will be toxic is presently less certain. Importantly, the correct classification rate seen in these experiments is high; that is, the accuracy of predicting which sediments were toxic was 58.0% using the SEM and AVS alone, 68.3% using IWTUs, and 78.9% using both indicators. An SEM-AVS >0.0, particularly at multiple adjacent sites, should trigger additional tiered assessments. These might include characterization of the spatial (both vertical and horizontal) and temporal distribution of chemical concentration (AVS and SEM) and toxicity, measurements of interstitial water metal, and toxicity identification evaluations (TIEs). In this context, the combined SEM-AVS and IWTU approach should be viewed as only one of the many sediment evaluation methodologies.

3.2.5 *Conclusions from Short-Term Studies*

Results from tests using sediments spiked with metals and sediments from the field in locations where toxicity is associated with metals demonstrate the value of explaining the biological availability of metals concentrations normalized by SEM-AVS and IWTUs instead of dry weight metal concentrations. Importantly, data from spiked-sediment tests strongly indicate that metals are not the cause of most of the toxicity observed in field sediments when both SEM-AVS is $\leq$0.0 and IWTUs are <0.5 (Table 3-1). Expressing concentrations of metals in sediments on an SEM-AVS basis provides important insight into the available additional binding capacity of sediments and the extent to which sulfide binding has been exceeded.

SEM-AVS and interstitial water concentrations of metals can aid in identifying the specific metal causing toxicity. For example, the metal(s) in excess of AVS can be identified by subtracting from the molar concentration of AVS the molar concentrations of specific metals in the SEM in order of their sulfide solubility product constants ($K_{sp,2}$) in the SEM. Alternatively, interstitial water concentrations of metals can be used to identify a specific metal causing sediment toxicity using the toxic unit concept, if appropriate water-only toxicity data for the tested species are available (Hansen et al., 1996a).

Predictions of sediments not likely to be toxic, based on use of SEM-AVS and IWTUs for all data from freshwater or saltwater field sediment and spiked-sediment tests, are extremely accurate (98.5%) using both parameters. Predictions of sediments likely to be toxic are less accurate. Nevertheless, SEM-AVS is extremely useful in identifying sediments of potential concern. Data were summarized from amphipod tests using freshwater and saltwater laboratory metals-spiked sediments and field sediments where metals were a known problem by comparing the percentage of sediments that were toxic with the SEM-AVS concentration (tests with polychaetes and gastropods were excluded because these organisms avoid exposure) (Hansen, 1995). Seventy percent of the sediments in these amphipod studies with an SEM-AVS concentration of $\geq$0.76 μmol of excess SEM/g were toxic. The corresponding values for 80%, 90%, and 100% of the sediments being toxic were 2.7, 16, and 115 μmol of excess SEM/g, respectively.

Of course, SEM, AVS, and IWTUs can only predict toxicity or the lack of toxicity caused by *metals* in sediments. They cannot be used alone to predict toxicity of sediments contaminated with toxic concentrations of other contaminants. However, SEM and AVS have been used in sediment assessments to rule out metals as probable causative agents of toxicity (Wolfe et al., 1994). Also, the use of SEM and AVS to predict biological availability and toxicity of cadmium, copper, lead, nickel, silver, and zinc is applicable only to anaerobic sediments that contain AVS; binding factors other than AVS control bioavailability in aerobic sediments (Di Toro et al., 1987; Tessier et al., 1993). Measurement of interstitial water metal may be useful for evaluations of these and other metals in aerobic and anaerobic sediments (Ankley et al., 1994). Even with these caveats, the combined use of SEM, AVS, and interstitial measurements is preferable to all other currently available sediment evaluation procedures to causally assess the implications to benthic organisms of these six metals associated with sediments (see discussion in Section 5, Sampling and Analytical Chemistry, for further guidance).

3.3 Predicting Metal Toxicity: Long-Term Studies

Taken as a whole, the short-term laboratory experiments with metal-spiked and field-collected sediments present a strong argument for the ability to predict the absence of metal toxicity based on sediment SEM and AVS relationships and/or interstitial water metal concentrations. However, if this approach is to serve as a valid basis for ESB derivation, comparable predictive success must be demonstrated in long-term laboratory and field experiments where chronic effects could be manifested (Luoma and Carter, 1993; Meyer et al., 1994). This demonstration was the goal of experiments described by Hare et al. (1994), DeWitt et al. (1996), Hansen et al. (1996b), Liber et al. (1996), and Sibley et al. (1996). An important experimental modification to these long-term studies, as opposed to the short-term tests described in Section 3.2, was the collection of horizon-specific chemistry data. This is required because AVS concentrations often increase, and SEM-AVS differences decrease, with an increase in sediment depth (Howard and Evans, 1993; Leonard et al., 1996a); hence, chemistry performed on homogenized samples might not reflect the true exposure of benthic organisms dwelling in surficial sediments (Luoma and Carter, 1993; Hare et al., 1994; Peterson et al., 1996).

3.3.1 *Life-Cycle Toxicity Tests*

DeWitt et al. (1996) conducted an entire life-cycle toxicity test with the marine amphipod *L. plumulosus* exposed for 28 days to cadmium-spiked estuarine sediments (Table 3-2). The test measured effects on survival, growth, and reproduction of newborn amphipods relative to interstitial water and SEM/AVS

Table 3-2. Summary of the results of full life-cycle and colonization toxicity tests conducted in the laboratory and field using sediments spiked with individual metals and metal mixtures

			Measured SEM-AVS[a] (μmol/g)			
Toxicity Test	Metal(s)	Duration (days)	NOEC(s)[b]	OEC(s)[c]	Effect	Reference
Life Cycle:						
Leptocheirus plumulosus	Cadmium	28	-3.5, -2.0, 0.78, 2.0	8.9, 15.6	Mortality 100%	DeWitt et al., 1996
Chironomus tentans	Zinc	56	-2.6, -1.4, 6.4	21.9, 32.4	Larval mortality 85%-100% Weight, emergence, and reproduction reduced	Sibley et al., 1996
Colonization:						
Laboratory-saltwater	Cadmium	118	-13.4	8.0, 27.4	Fewer polychaetes, shifts in community composition, fewer species, bivalves absent, tunicates increased	Hansen et al., 1996b
Field-saltwater	Cadmium, copper, lead, nickel, zinc	120	-0.31, -0.06, 0.02	—	No effects observed	Boothman et al., 2001
Field-freshwater	Cadmium	~365	-0.07, 0.08, 0.34	2.2	Reduced *Chironomus salinarius* numbers Bioaccumulation	Hare et al., 1994
Field-freshwater	Zinc	368	-3.6, -3.5, -2.9, -2.0, 1.0[d]	—	No effects observed	Liber et al., 1996

[a] SEM-AVS differences are used instead of SEM/AVS ratios to standardize across the studies referenced. An SEM-AVS difference of ≤0.0 is the same as an SEM/AVS ratio of ≤1.0. An SEM-AVS difference of >0.0 is the same as an SEM/AVS ratio of >1.0.

[b] NOECs = no observed effect concentration(s): all concentrations where response was not significantly different from the control.

[c] OECs = observed effect concentration(s); all concentrations where response was significantly different from the control.

[d] Occasional minor reductions in oligochaetes (Naididae).

normalization. Seven treatments of Cd were tested: 0 (control), -3.5, -2.0, 0.78, 2.0, 8.9, and 15.6 $\mathrm{SEM_{Cd}}$-AVS differences (measured concentrations). Gradients in AVS concentration as a function of sediment depth were greatest in the control treatment, decreased as the $\mathrm{SEM_{Cd}}$ ratio increased, and became more pronounced over time. Depth gradients in $\mathrm{SEM_{Cd}}$-AVS differences were primarily caused by the spatial and temporal changes in AVS concentration, because $\mathrm{SEM_{Cd}}$ concentrations changed very little with time or depth. Thus in most treatments $\mathrm{SEM_{Cd}}$-AVS differences were smaller at the top of sediment cores than at the bottom. This is expected because the oxidation rate of iron sulfide in laboratory experiments is very rapid (100% in 60 to 90 minutes) but for cadmium sulfide it is slow (10% in 300 hours) (Mahony et al., 1993; Di Toro et al., 1996a). Interstitial cadmium concentrations increased in a dramatic stepwise fashion in treatments having a SEM-AVS difference of ≥8.9 μmol of excess SEM, but were below the 96-hour LC50 value for this amphipod in lesser treatments. There were no significant effects on survival, growth, or reproduction in sediments containing more AVS than cadmium (-3.5 and -2.0 μmol/g) and those with a slight excess of $\mathrm{SEM_{Cd}}$ (0.78 and 2.0 μmol/g), in spite of the fact that these samples contained from 183 to 1,370 μg cadmium/g sediment. All amphipods died in sediments having SEM-AVS differences ≥8.9 μmol excess SEM/g. These results are consistent with predictions of metal bioavailability from 10-day acute tests with metal-spiked sediments (i.e., that sediments with SEM_{Cd}-AVS differences ≤ 0.0 are not toxic, interstitial water metal concentrations are related to organism response, and sediments with SEM_{Cd}-AVS differences >0.0 may be toxic).

Sibley et al. (1996) reported similar results from a 56-day life-cycle test conducted with the freshwater midge *C. tentans* exposed to zinc-spiked sediments (Table 3-2). The test was initiated with newly hatched larvae and lasted one complete generation, during which survival, growth, emergence, and reproduction were monitored. In sediments where the molar difference between SEM and AVS (SEM-AVS) was <0.0 (dry weight zinc concentrations were as high as 270 mg/kg), concentrations of zinc in the sediment interstitial water were low and no adverse effects were observed for any of the biological endpoints measured. Conversely, when SEM-AVS was 21.9 and 32.4 μmol of excess SEM/g, interstitial water concentrations of zinc increased (being highest in surficial sediments), and reductions in survival, growth, emergence, and reproduction were observed. Over the course of the study, the absolute concentration of zinc in the interstitial water in these treatments decreased because of the increase in sediment AVS and loss of zinc from twice-daily renewals of the overlying water.

3.3.2 *Colonization Tests*

Hansen et al. (1996b) conducted a 118-day benthic colonization experiment in which sediments were spiked to achieve nominal cadmium/AVS molar ratios of 0.0 (control), 0.1, 0.8, and 3.0 and then held in the laboratory in a constant flow of unfiltered seawater (Table 3-2). Oxidation of AVS in the surficial 2.4 cm of the control treatment occurred within 2 to 4 weeks and resulted in sulfide profiles similar to those occurring in sediments in nearby Narragansett Bay, RI (Boothman and Helmstetter, 1992). In the nominal 0.1 cadmium/AVS treatment, measured SEM_{Cd} was always less than AVS (SEM-AVS = −13.4 μmol AVS/g in the surficial 2.0 cm), interstitial cadmium concentrations (<3 to10 μg/L) were less than those likely to cause biological effects, and no significant biological effects were detected. In the nominal 0.8 cadmium/AVS treatment (SEM-AVS = 8.0 μmol SEM/g), measured SEM_{Cd} commonly exceeded AVS in the surficial 2.4 cm of sediment, and interstitial cadmium concentrations (24 to 157 μg/L) were sufficient to be of toxicological significance to highly sensitive species. In this treatment, shifts in the presence or absence of organisms were observed over all taxa, and there were fewer macrobenthic polychaetes (*Mediomastus ambiseta, Streblospio benedicti,* and *Podarke obscura*) and meiofaunal nematodes. In the nominal 3.0 cadmium/AVS treatment (SEM-AVS of 27.4 μmol SEM/g), concentrations of SEM_{Cd} were always greater than AVS throughout the sediment column. Interstitial cadmium ranged from 28,000 to 174,000 μg/L. In addition to the effects observed in the nominal 0.8 cadmium/AVS treatment, the following effects were observed: (a) sediments were colonized by fewer macrobenthic and polychaete species and harpacticoids, (b) the sediments had lower densities of diatoms, and (c) bivalve molluscs were absent. Over all treatments, the observed biological responses were consistent with predicted possible adverse effects resulting from elevated SEM_{Cd}-AVS differences in surficial sediments and interstitial water cadmium concentrations.

Boothman et al. (2001) conducted a field colonization experiment in which sediments from Narragansett Bay, RI, were spiked with an equimolar mixture of cadmium, copper, lead, nickel, and zinc at nominal SEM/AVS ratios of 0.1, 0.8, and 3.0; placed in boxes; and replaced in Narragansett Bay (Table 3-2). The AVS concentrations decreased with time in surface sediments (0 to 3 cm) in all treatments where the nominal SEM/AVS ratio was <1.0 (SEM-AVS decreased from −0.31 to −0.06 μmol SEM/g in the surficial 2.0 cm) but did not change in subsurface (6 to 10 cm) sediments or in the entire sediment column where nominal SEM/AVS ratios exceeded 1.0 (SEM-AVS = 0.02 μmol AVS/g). SEM decreased with time only where SEM exceeded AVS. The concentration of metals in interstitial water was below detection limits when there was more AVS than SEM. When SEM exceeded AVS, significant concentrations of metals were present in interstitial water, and appeared in the order of their sulfide solubility product constants. Interstitial water concentrations in these sediments decreased with time, although they exceeded the WQC in interstitial water for 60 days for all metals, 85 days for cadmium and zinc, and 120 days for the entire experiment for zinc. Benthic faunal assemblages in the spiked-sediment treatments were not different from those of the control treatment. Lack of biological response was consistent with the vertical profiles of SEM and AVS. AVS was greater than SEM in all surface sediments, including the top 2 cm of the 3.0 nominal SEM/AVS treatment, because of oxidation of AVS and loss of SEM. The authors speculated that interstitial metal was likely absent in the surficial sediments in spite of data demonstrating the presence of significant measured concentrations.

Interstitial water in the 3.0 nominal SEM/AVS treatment was sampled from sediment depths where SEM was in excess, rather than in the surficial sediments. Important to the biological data are the surficial sediments, where settlement by saltwater benthic organisms first occurs. Also, there was a storm event that allowed a thin layer of clean sediment to be deposited on top of the spiked sediment (W.S. Boothman, U.S. EPA, Narragansett, RI, personal communication). These data demonstrate the importance of sampling sediments and interstitial water in sediment horizons where benthic organisms are active.

Hare et al. (1994) conducted an approximately 1-year field colonization experiment in which uncontaminated freshwater sediments were spiked with cadmium and replaced in the oligotrophic lake from which they originally had been collected (Table 3-2). Cadmium concentrations in interstitial waters were very low at cadmium-AVS molar differences <0.0, but increased markedly at differences >0.0. The authors reported reductions in the abundance of only the chironomid *Chironomus salinarius* in the 2.2 μmol excess SEM/g treatment. Cadmium was accumulated by organisms from sediments with surficial SEM concentrations that exceeded those of AVS. These sediments also contained elevated concentrations of cadmium in interstitial water.

Liber et al. (1996) performed a field colonization experiment using sediments having 4.46 μmol of sulfide from a freshwater mesotrophic pond (Table 3-2). Sediments were spiked with 0.8, 1.5, 3.0, 6.0, and 12.0 μmol of zinc, replaced in the field, and chemically and biologically sampled over 12 months. There was a pronounced increase in AVS concentrations with increasing zinc concentration; AVS was lowest in the surficial 0 to 2 cm of sediment with minor seasonal variations. With the exception of the highest spiking concentration (approximately 700 mg/kg, dry weight), AVS concentrations remained larger than those of SEM. Interstitial water zinc concentrations were rarely detected in any treatment, and were never at concentrations that might pose a hazard to benthic macroinvertebrates. The only observed difference in benthic community structure across the treatments was a slight decrease in the abundance of Naididae oligochaetes at the highest spiking concentration. The absence of any noteworthy biological response was consistent with the absence of interstitial water concentrations of biological concern. The lack of biological response was attributed to an increase in concentrations of iron and manganese sulfides produced during periods of diagenesis, which were replaced by the more stable zinc sulfide, which is less readily oxidized during winter months. In this experiment, and theoretically in nature, excesses of sediment metal might be overcome over time because of the diagenesis of organic material. In periods of minimal diagenesis, oxidation rates of metal sulfides, if sufficiently great, could release biologically significant concentrations of the metal into interstitial waters. The phenomenon should occur metal by metal in order of their sulfide solubility product constants.

3.3.3 *Conclusions from Chronic Studies*

Over all full life-cycle and colonization toxicity tests conducted in the laboratory and field using sediments spiked with individual metals and metal mixtures (Table 3-2), no sediments with an excess of AVS (SEM-AVS $\leq$ 0.0) were toxic (Figure 3-7). Conversely, all sediments where chronic effects were observed, and 7 of 19 sediments where no effects were observed, had an excess of SEM (SEM-AVS >0.0) (Table 3-2; Figure 3-7). Therefore, the results from all available acute and chronic toxicity tests support the use of SEM-AVS $\leq$ 0.0 as an ESB that can be used to predict sediments that are unlikely to be toxic.

3.4 Predicting Toxicity of Metals in Sediments

3.4.1 *General Information*

The SEM-AVS method for evaluating toxicity of metals in sediments (Di Toro et al., 1990, 1992) has proven to be successful at predicting the lack of metal toxicity in spiked and field-contaminated sediments (Berry et al., 1996; Hansen et al., 1996a). However, because SEM-AVS does not explicitly consider the other sediment phases that influence interstitial water–sediment partitioning, and in spite of its utility in identifying sediments of possible concern, it was never intended to be used to predict the occurrence of toxicity. The proposed sediment quality criteria for metals using SEM, AVS, and IWTUs in Ankley et al. (1996)—now referred to as ESBs or equilibrium partitioning sediment benchmarks—were constructed as "one-tailed" guidelines. They should be used to predict the lack of toxicity but not its presence. Thus the problem of predicting the onset of toxicity in metal-contaminated sediments remained unsolved.

This section introduces a modification of the SEM-AVS procedure in which the SEM-AVS difference is

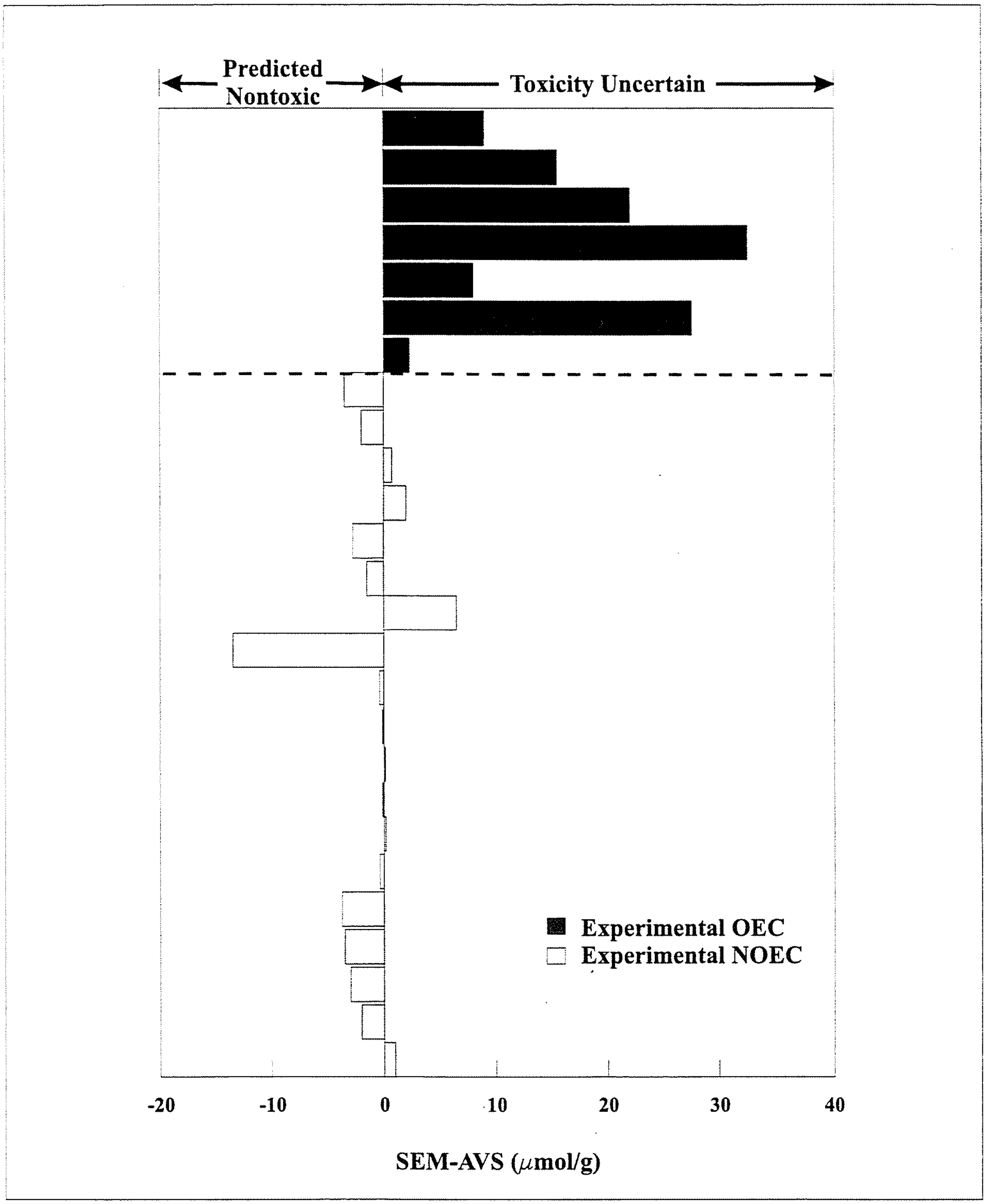

Figure 3-7. Comparison of the chronic toxicity of sediments spiked with individual metals or metal mixtures to predicted toxicity based on SEM-AVS (data from Table 3-2). Horizontal dashed line separates experimental observed effect concentrations (solid columns) from no observed effect concentrations (shaded columns). Values at SEM-AVS $\leq 0.0\ \mu mol/g_{OC}$ are predicted to be nontoxic. Values at SEM-AVS $>0.0\ \mu mol/g_{OC}$ are indicative of sediments that are likely to be toxic or toxicity is uncertain.

normalized by the fraction of organic carbon, f_{OC}, in a sediment. This section is largely taken from Di Toro et al. (2000). Their publication should be consulted for additional information about the utility of the f_{OC} procedure and comparison of this procedure with the sediment guidelines of Long et al. (1995a) and MacDonald et al. (1996). The $(\Sigma\text{SEM-AVS})/f_{OC}$ procedure significantly improves prediction of mortality by accounting for partitioning of metals to sediment organic carbon, as well as the effect of AVS. In addition, the approach used by Di Toro et al. (2000) to derive $(\Sigma\text{SEM-AVS})/f_{OC}$ uncertainty bounds for identifying sediments that are likely to be toxic, are of uncertain toxicity, or are nontoxic has applicability to SEM/AVS ratios, SEM-AVS differences, and IWTUs. Although not used as an ESB, the uncertainty bounds should be useful in prioritizing sediments of concern for further evaluations.

3.4.2 *EqP Theory for SEM, AVS, and Organic Carbon*

The EqP model provides for the development of causal sediment concentrations that predict toxicity or lack of toxicity in sediments (Di Toro et al., 1991). The sediment concentration C_S that corresponds to a measured LC50 in a water-only exposure of the test organism is

$$C_S^* = K_p\,\text{LC50} \tag{3-2}$$

where C_S^* is the sediment LC50 concentration (μg/kg dry wt), K_p (L/kg) is the partition coefficient between interstitial water and sediment solids, and LC50 is the concentration causing 50% mortality (μg/L). For application to metals that react with AVS to form insoluble metal sulfides, Equation 3-2 becomes

$$C_S^* = \text{AVS} + K_p\,\text{LC50} \tag{3-3}$$

where AVS is the sediment concentration of acid volatile sulfides. Equation 3-3 simply states that because AVS can bind the metal as highly insoluble sulfides, the concentration of metal in a sediment that will cause toxicity is at least as great as the AVS that is present. The sediment metal concentration that should be employed is the SEM concentration, because any metal that is bound so strongly that 1N of hydrochloric acid cannot dissolve it is not likely to be bioavailable (Di Toro et al., 1992). Of course, this argument is theoretical, which is why so much effort has been expended to demonstrate experimentally that this is actually the case (Di Toro et al., 1992; Hare et al., 1994; Berry et al., 1996; Hansen et al., 1996a; Sibley et al., 1996). Therefore, the relevant sediment metal concentration is SEM, and Equation 3-3 becomes

$$\text{SEM} = \text{AVS} + K_p\,\text{LC50} \tag{3-4}$$

The basis for the AVS method is to observe that if the second term in Equation 3-4 is neglected, then the critical concentration is SEM = AVS, and the criterion for toxicity or lack of toxicity is SEM-AVS ≤ 0.0 (μmol/g dry wt).

The failure of the difference to predict toxicity when there is an excess of SEM is due to neglect of the partitioning term K_pLC50. Note that ignoring the term does not affect the prediction of lack of toxicity in that it makes the condition conservative (i.e., smaller concentrations of SEM are at the boundary of toxicity and no toxicity).

The key to improving prediction of toxicity is to approximate the partitioning term rather than ignore it (Di Toro et al, *in prep.*). In sediments, the organic carbon fraction is an important partitioning phase, and partition coefficients for certain metals at certain pHs have been measured (Mahony et al., 1996). This suggests that the partition coefficient K_p in Equation 3-4 can be expressed using the organic carbon–water partition coefficient, K_{OC}, together with the fraction organic carbon in the sediment, f_{OC}

$$K_p = f_{OC}\,K_{OC} \tag{3-5}$$

Using this expression in Equation 3-4 yields

$$\text{SEM} = \text{AVS} + f_{OC}\,K_{OC}\,\text{LC50} \tag{3-6}$$

Moving the known terms to the left side of this equation yields

$$\frac{\text{SEM}-\text{AVS}}{f_{OC}} = K_{OC}\text{LC50} \tag{3-7}$$

If both K_{OC} and LC50 are known, then Equation 3-7 can be used to predict toxicity.

The method evaluated below uses $(\Sigma\text{SEM-AVS})/f_{OC}$ as the predictor of toxicity and evaluates the critical concentrations (the right side of Equation 3-7) based on observed SEM, AVS, f_{OC}, and toxicity data (Di Toro et al, *in prep.*). If multiple metals are present, it is necessary to use the total SEM

$$\Sigma\text{SEM} = \sum_{i=1}^{N} [\text{SEM}_i] \tag{3-8}$$

to account for all the metals present. Note that $(\Sigma\text{SEM-AVS})/f_{OC}$ is the organic carbon–normalized excess SEM for which we use the notation

$$(\Sigma\,\text{SEM} - \text{AVS})/f_{OC} = \left(\Sigma\frac{\text{SEM} - \text{AVS}}{f_{OC}}\right) \qquad (3\text{-}9)$$

3.4.3 *Data Sources*

Data from toxicity tests using both laboratory-spiked and field-collected sediments were compiled from the literature. Four sources of laboratory-spiked tests using marine sediments (Casas and Crecelius, 1994; Pesch et al., 1995; Berry et al., 1996, 1999) and one using freshwater sediments (Carlson et al., 1991) were included. Two sources for metal-contaminated field sediments were included (Hansen et al., 1996a; Kemble et al., 1994). The field data from the sediments where metals were not the probable cause of toxicity (Bear Creek and Jinzhou Bay) (Hansen et al., 1996a) were excluded. Data reported included total metals, SEM, AVS, f_{OC}, and 10- or 14-day mortality. In Hansen et al. (1996a), data were reported for five saltwater and four freshwater locations, but organic carbon concentrations were not available for freshwater field sediments from three locations. Organic carbon data for the Keweenaw Watershed were obtained separately (E.N. Leonard, U.S. EPA, Duluth, MN, personal communication).

Laboratory-spiked and field sediment data were grouped for analysis. Mortality data were compared against the SEM-AVS difference and the SEM-AVS difference divided by the f_{OC}. For each comparison, two uncertainty bounds were computed: a lower-bound concentration equivalent to a 95% chance that the mortality observed would be less than 24% (the percentage mortality considered to be toxic) (see Berry et al., 1996) and an upper-bound concentration equivalent to a 95% chance that the observed mortality would be greater than 24%. The lower-bound uncertainty limit was computed by evaluating the fraction of correct classification starting from the lowest x-axis value. When the fraction correct dropped to below 95%, the 95th percentile was interpolated. The same procedure was applied to obtain the upper-bound uncertainty limit. These uncertainty bounds are the concentration range where it is 90% certain that the sediment may be either toxic or not toxic.

3.4.4 *Acute Toxicity Uncertainty*

Mortality in the laboratory-spiked and field-contaminated sediment tests were both organism and metal independent when plotted against the SEM-AVS difference (Figure 3-8A). The horizontal dashed line indicating 24% mortality is shown for reference. The 90% lower and upper uncertainty bound limits for the SEM-AVS difference are from 1.7 and 120 μmol/g, a factor of 70. Thus, it appears that for both laboratory and spiked-sediment data, toxicity is likely when the SEM-AVS difference is >120, uncertain when the difference is from 1.7 to 120 μmol/g, and not likely when the difference is <1.7 μmol/g.

Although use of SEM-AVS differences to predict toxicity is not based on any theoretical foundation, use of SEM-AVS $\leq$0.0 to predict lack of toxicity is based on the equilibrium partitioning model (Di Toro et al., 1991) and the chemistry of metal–sulfide interactions. The stoichiometry of the uptake of divalent metals by AVS is such that 1 mol of AVS will stabilize 1 mol of SEM, except for silver, where the ratio is 2:1, hence the use of the difference of 0.0 μmol/g dry weight to predict lack of toxicity. In fact it is the very low solubility of the resulting metal sulfides that limits the interstitial water concentrations to below toxic levels regardless of the details of the sediment chemistry (e.g., pH, iron concentration) as has been demonstrated in this document and detailed in the Appendix in Di Toro et al. (1992).

The $(\Sigma\text{SEM-AVS})/f_{OC}$ approach provides an equivalent theoretical basis that is needed to derive an appropriately normalized sediment concentration that predicts occurrence of toxicity that is causally linked to bioavailable metal. When percent mortality is plotted against the organic carbon–normalized excess SEM $(\Sigma\text{SEM-AVS})/f_{OC}$) for the same data as contained in Figure 3-8A, toxicity is likely when the $(\Sigma\text{SEM-AVS})/f_{OC}$ is >3,000 μmol/g_{OC}, uncertain when the concentration is between 130 and 3,000 μmol/g_{OC}, and not likely when the concentration is <130 μmol/g_{OC} (Figure 3-8B). Thus, the width of the uncertainty bound is a factor of 70 for SEM-AVS differences and 23 for $(\Sigma\text{SEM-AVS})/f_{OC}$.

If the $(\Sigma\text{SEM-AVS})/f_{OC}$ approach improves predictions of sediment toxicity caused by metals, the uncertainty bounds should narrow and the percentages of sediments where toxicity predictions are uncertain should decrease. If the uncertainty bound analysis is not conducted, and SEM-AVS>0.0 is used as proposed in Sections 3.2 and 3.3, predictions of sediment toxicity

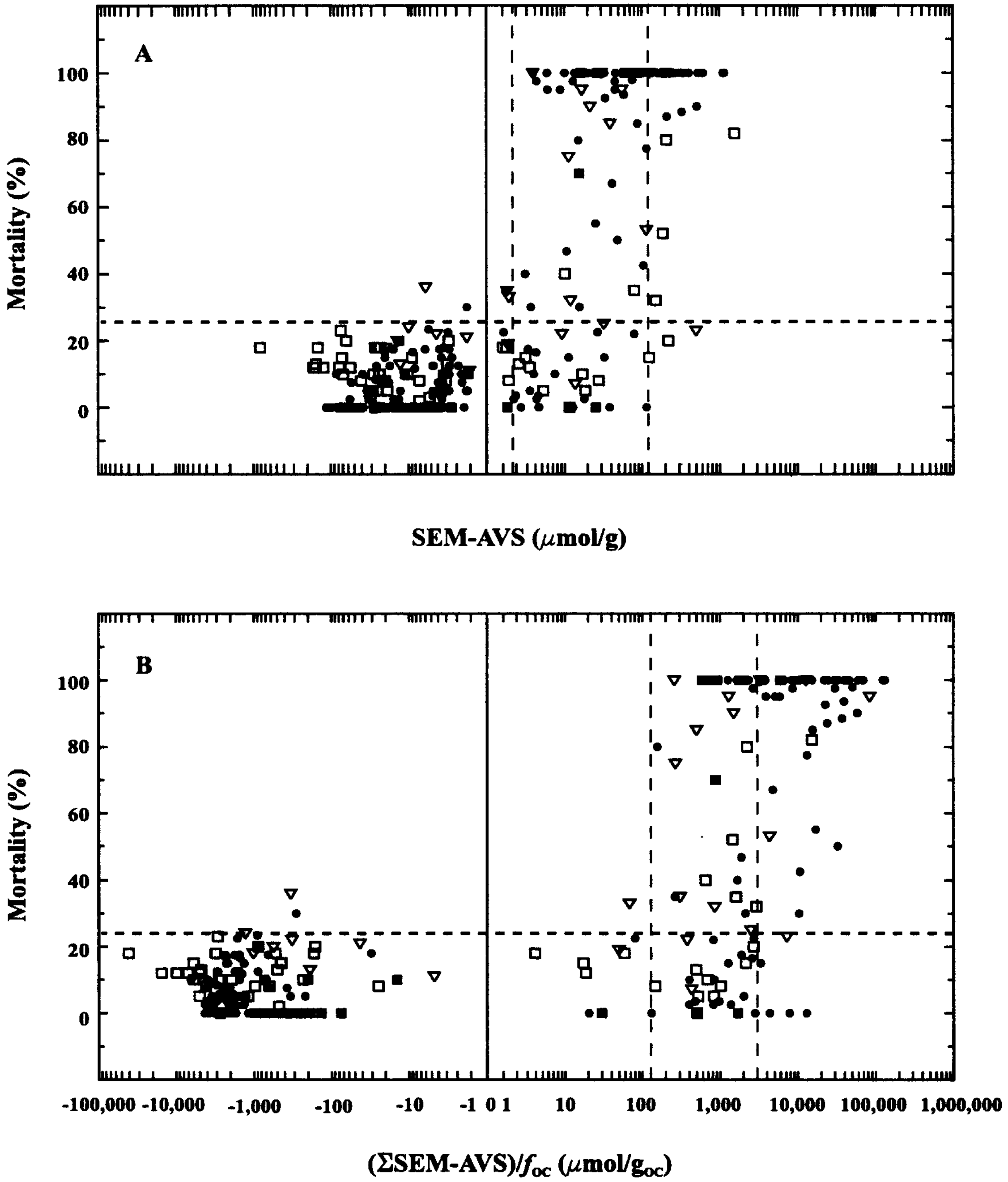

Figure 3-8. Percent mortality versus SEM-AVS (A) and (ΣSEM-AVS)/f_{oc} (B) for saltwater field data without Bear Creek and Jinzhou Bay (□), freshwater field data (▽), freshwater spiked data (▪), and saltwater spiked data (●); silver data excluded. Vertical dashed lines are the 90% uncertainty bound limits (figure from Di Toro et al., 2000).

for the 267 spiked sediments are classified as uncertain for 47.2% of the sediments. Using the uncertainty bounds on SEM-AVS of 1.7 to 120 μmol/g as described in this section results in reduction in the percentage of sediments where toxicity predictions are uncertain, to 34.1%. Use of (ΣSEM-AVS)/f_{OC} with uncertainty bounds of 130 to 3,000 μmol/g_{OC} results in further reduction in the percentage of sediments where toxicity predictions are uncertain, to 25.5%. Therefore, use of the uncertainty limits of the (ΣSEM-AVS)/f_{OC} approach classifies 33.7% more sediments as toxic or nontoxic than using the uncertainty limits of SEM-AVS, and 85% more than use of SEM-AVS without uncertainty limits. This improvement highlights the advantages of using (ΣSEM-AVS)/f_{OC} in assessing toxicity of metal-contaminated sediments.

Use of (ΣSEM-AVS)/f_{OC} uncertainty limits applies to all the metals regardless of their identity. Figure 3-9 presents the spiked-sediment data categorized by identity of the metal. The field-contaminated data cannot be included because the identity of the metal causing toxicity cannot be unambiguously determined. There is no apparent difference for any of the metals in the region of overlapping survival and mortality data between 130 and 3,000 μmol/g_{OC}.

It is interesting to note that organic carbon normalization appears not to work for silver. The spiked-sediment test data are presented in Figure 3-10A (Berry et al., 1999). Note that there is almost a complete overlap of mortality and no mortality data. This suggests that organic carbon is not a useful normalization for silver partitioning in sediments. Perhaps this is not surprising because the role of sulfur groups is so prominent in the complexation chemistry of silver (Bell and Kramer, 1999).

To not depend on the identity of the metal is an advantage in analyzing naturally contaminated sediments in that it is difficult to decide which metal is potentially causing the toxicity. Of course it can be done using the sequence of solubilities of the metal sulfides or interstitial metal concentrations (Di Toro et al., 1992; Ankley et al., 1996). The metal-independent method can be tested using the results of an experiment with an equimolar mixture of cadmium, copper, nickel, and zinc (see Figure 3-10B). The area of uncertainty falls within the carbon-normalized excess SEM boundaries above.

3.4.5 *Chronic Toxicity Uncertainty*

The results of chronic toxicity tests with metals-spiked sediments can also be compared to (ΣSEM-AVS)/f_{OC} (Figure 3-11; Table 3-3). Note that Figure 3-11 indicates a category for "predicted toxic." Significant chronic effects were observed in only 1 of the 19 sediments, where the uncertainty analysis of acute toxicity tests indicated that effects were not expected at (ΣSEM-AVS)/f_{OC} <130 μmol/g_{OC}. The concentration in the sediment where chronic effects were observed but not expected, i.e., (ΣSEM-AVS)/f_{OC} = 28 μmol excess SEM/g_{OC}. The previous analysis of the results of chronic toxicity tests using SEM-AVS indicated that concentrations of SEM exceeded AVS in 7 of 19 nontoxic sediments. Sediment concentrations based on (ΣSEM-AVS)/f_{OC} placed these sediments in the uncertain toxicity category. Importantly, use of (ΣSEM-AVS)/f_{OC} to classify sediments resulted in six of these same seven sediments being correctly classified as probably nontoxic. Chronic effects were observed in six of the seven sediments where predictions of effects are uncertain (130 to 3,000 μmol/g_{OC}). This suggests that chronic toxicity tests with sensitive benthic species will be a necessary part of the evaluations of sediments predicted to have uncertain effects.

3.4.6 *Summary*

The uncertainty bounds on SEM-AVS differences and organic carbon–normalized excess SEM ((ΣSEM-AVS)/f_{OC}) can be used to identify sediments that are likely to be toxic, are of uncertain toxicity, or are nontoxic. Use of (ΣSEM-AVS)/f_{OC} as a correction factor for excess SEM is attractive because it is based on the theoretical foundation of equilibrium partitioning. Likewise, it reduces the uncertainty of the prediction of toxicity over that of SEM-AVS differences.

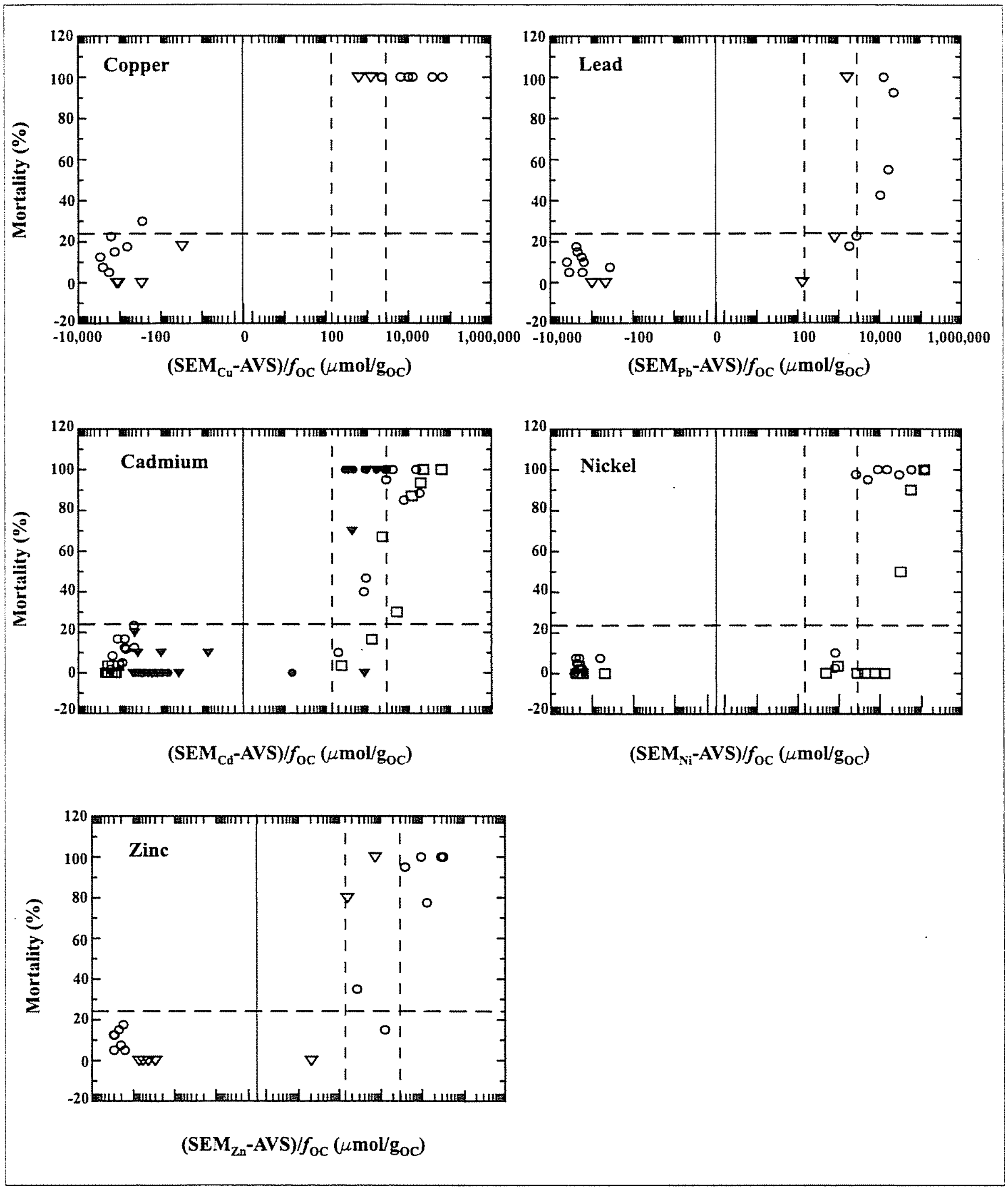

Figure 3-9. Percent mortality versus (SEM$_{\text{Metal}}$-AVS)/f_{OC} for each metal in spiked sediment tests using *Ampelisca* (○), *Capitella* (▽), *Neanthes* (□), *Lumbriculus* (●), and *Helisoma* (▼). Vertical dashed lines are the 90% uncertainty bound limits (figure from Di Toro et al., 2000).

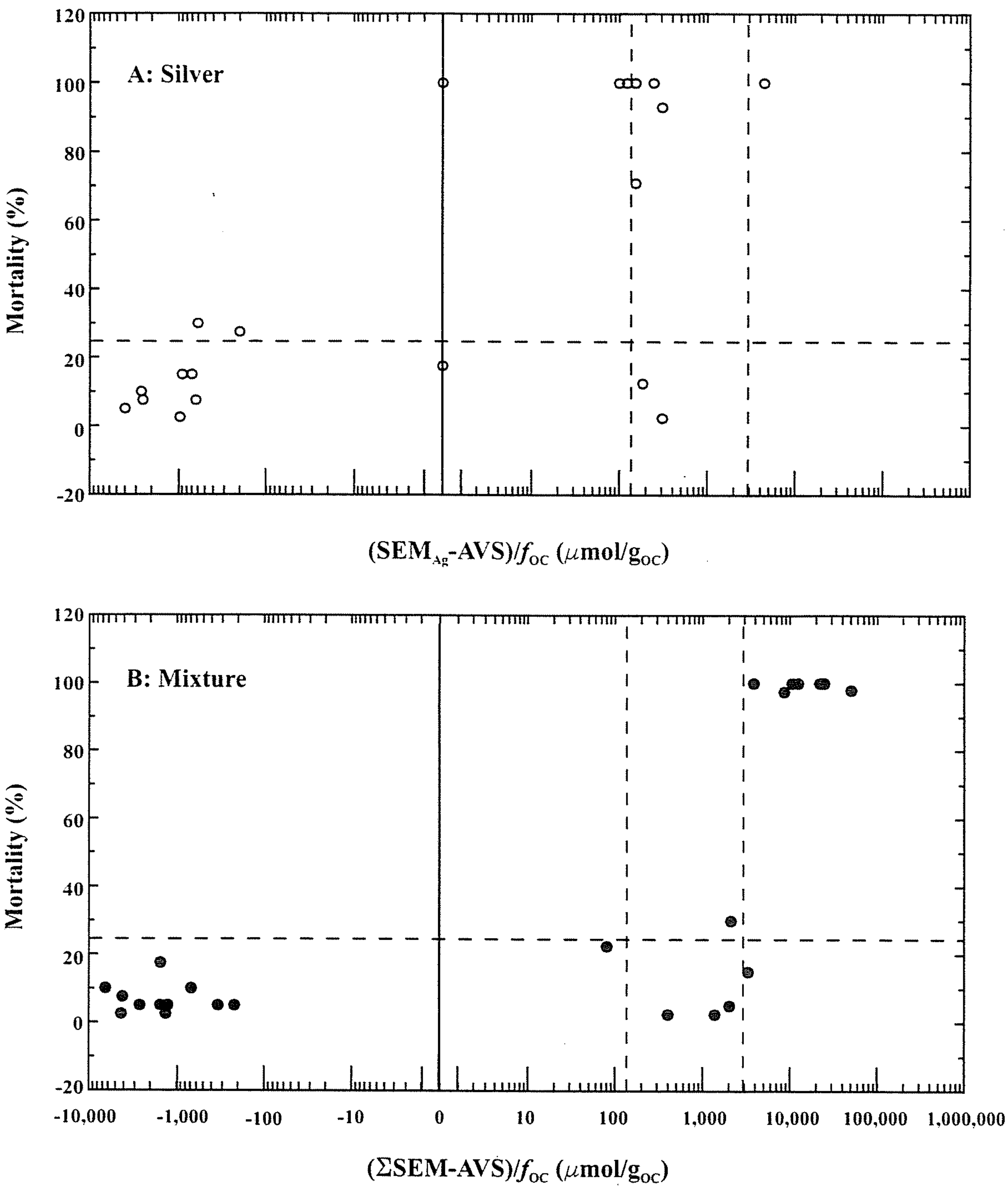

Figure 3-10. Percent mortality versus $(SEM_{Ag}\text{-}AVS)/f_{OC}$ for silver (A) and $(\Sigma SEM\text{-}AVS)/f_{OC}$ for a mixture experiment using Cd, Cu, Ni, and Zn (B; see Berry et al., 1996). Vertical dashed lines are the 90% uncertainty bound limits determined from Figure 3-8B (figures from Di Toro et al., 2000).

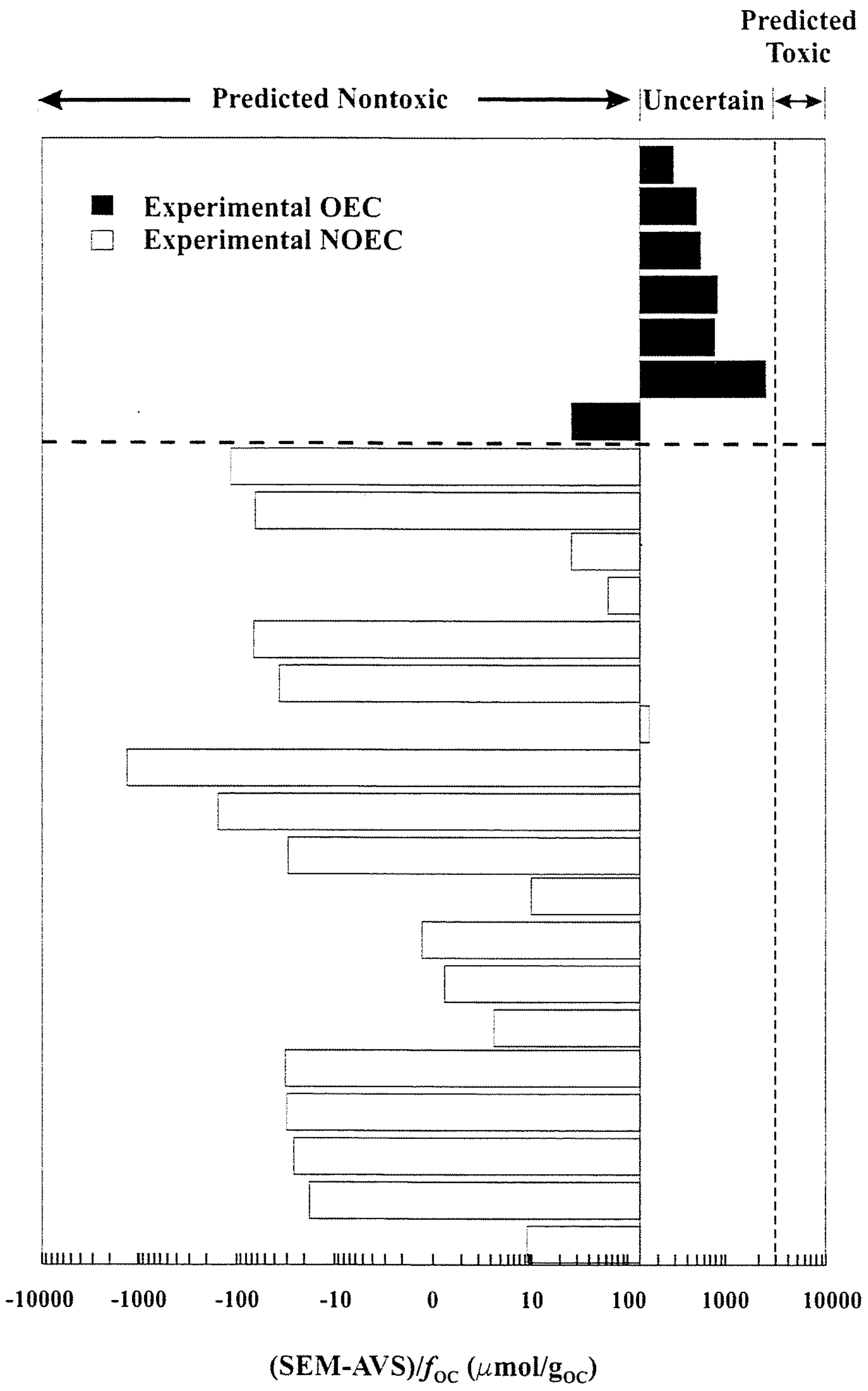

Figure 3-11. Comparison of the chronic toxicity of sediments spiked with individual metals or metal mixtures to predicted toxicity based on (SEM-AVS)/f_{OC} (data from Table 3-3). Horizontal dashed line separates experimental observed effect concentrations (solid columns) from no observed effect concentrations (shaded columns). Values at (SEM-AVS)/f_{OC} $\leq$ 130 μmol/g_{OC} are predicted to be nontoxic. Values between 130 and 3,000 μmol/g_{OC} lie where the prediction of toxicity is uncertain, and values greater than 3,000 μmol/g_{OC} are predicted to be toxic.

Table 3-3. Test-specific data for chronic toxicity of freshwater and saltwater organisms compared to $(\Sigma SEM\text{-}AVS)/f_{OC}$

			$(\Sigma SEM\text{-}AVS)/f_{OC}$[a] ($\mu mol/g_{OC}$)		
Toxicity Test	Metal(s)	f_{OC} (g_{OC}/g)	NOEC(s)[b]	OEC(s)[c]	Reference
Life Cycle:					
Leptocheirus plumulosus	Cadmium	0.030	-117, -66.7, 26, 63.3	**297, 520**	DeWitt et al., 1996
Chironomus tentans	Zinc	0.038	-68, -36.8, **168**	**576, 847**	Sibley et al., 1996
Colonization:					
Laboratory-saltwater	Cadmium	0.010	-1340	**800, 2740**	Hansen et al., 1996b
Field-saltwater	Cadmium, copper, lead, nickel, zinc	0.002	-155, -30, 10	—	Boothman et al., 2001
Field-freshwater	Cadmium	0.079	-0.92, 1.08, 4.30	*28*	Hare et al., 1994
Field-freshwater	Zinc	0.111	-32.7, -31.8, -26.4, -18.2, 9.1	—	Liber et al., 1996

[a] $(\Sigma SEM\text{-}AVS)/f_{OC}$ concentrations in bold type are those between 130 and 3,000 $\mu mol/g_{OC}$ for which the expectation of effects is uncertain. Italics indicates concentrations where effects were observed but not expected.

[b] NOECs = no observed effect concentration(s): all concentrations where response was not significantly different from the control.

[c] OECs = observed effect concentration(s): all concentrations where response was significantly different from the control.

Section 4

Derivation of Metal Mixtures ESB$_{AVS:WQC}$s

4.1 General Information

Section 4 of this document presents the technical basis for establishing the ESB for cadmium, copper, lead, nickel, silver, and zinc. The basis of the overall approach is the use of EqP theory linked to the concept of maintaining metal activity for the sediment interstitial water system below concentrations that cause adverse effects. Extensive toxicological concentration-response data from short-term and chronic laboratory and field experiments, with both marine and freshwater sediments and a variety of species, indicate that it is possible to reliably predict absence of metal toxicity based on EqP theory and derive ESBs for metals in sediments using either of two approaches referred to as ESB$_{AVS:WQC}$s . The ESB$_{AVS:WQC}$s for the six metals that collectively predicts absence of their toxicity in sediments can be derived by (a) comparing the sum of their molar concentrations, measured as SEM, with the molar concentration of AVS in sediments (solid-phase AVS benchmark); or (b) summing the measured interstitial water concentrations of the metals divided by their respective WQC FCVs (interstitial water benchmark). Lack of exceedence of the ESB$_{AVS:WQC}$ based on either of these two procedures indicates that metal toxicity should not occur.

At present, the technical basis for implementing these two approaches is supportable. The approaches have been presented to and reviewed by the SAB (U.S. EPA, 1994a, 1995a, 1999).

Additional research required to fully implement other approaches for deriving an ESB$_{AVS:WQC}$ for these metals and to derive an ESB for other metals such as mercury, arsenic, and chromium includes the development of uncertainty estimates; part of this would include their application to a variety of field settings and sediment types. Finally, the ESB approaches are intended to protect benthic organisms from direct toxicity associated with exposure to metal-contaminated sediments. The ESBs do not consider the antagonistic, additive or synergistic effects of other sediment contaminants in combination with metal mixtures or the potential for bioaccumulation and trophic transfer of metal mixtures to aquatic life, wildlife or humans. They are not designed to protect aquatic systems from metal release associated with, for example, sediment suspension, or the transport of metals into aquatic food webs. In particular, studies are needed to understand the toxicological significance of the biomagnification of metals that occurs when predators consume benthic organisms that have accumulated metals from sediments with more AVS than SEM (Ankley, 1996).

The following nomenclature is used in subsequent discussions of the ESB$_{AVS:WQC}$s derivation for metal mixtures. The ESB$_{AVS:WQC}$ for the metals, based on AVS, is expressed in molar units because of the molar stoichiometry of metal binding to AVS. Thus, solid-phase constituents (AVS, SEM) are in μmol/g dry weight. The interstitial water metal concentrations are expressed in μmol/L or μg/L, either as dissolved concentrations $[M_d]$ or activities $\{M^{2+}\}$ (Stumm and Morgan, 1981). The subscripted notation, M_d, is used to distinguish dissolved aqueous-phase molar concentrations from solid-phase molar concentrations with no subscript. For the combined concentration, $[SEM_T]$, the units are μmol of total metal per gram of dry weight sediment. Note also that when $[SEM_{Ag}]$ is summed and/or compared with AVS, one-half the molar silver concentration is applied.

One final point should be made with respect to nomenclature. The terms *nontoxic* and *having no effect* are used only with respect to the six metals considered in this document. Toxicity of field- collected sediments can be caused by other chemicals. Therefore, avoiding exceedences of the ESB$_{AVS:WQC}$ for metal mixtures does not mean that the sediments are nontoxic. It only ensures that the six metals being considered should not cause direct toxicity to benthic organisms. Moreover, as discussed in detail below, exceedence of the benchmarks for the six metals does not necessarily indicate that metals will cause toxicity. For these reasons,it is strongly recommended that the combined use of both AVS and interstitial water measurements; toxicity tests; TIEs; chemical monitoring in vertical, horizontal, and temporal scales; and other assessment methodologies as integral parts of any evaluation of the effects of sediment-associated contaminants (Ankley et al., 1994; Lee et al., 2000).

4.2 Sediment Benchmarks for Multiple Metals

It is neither sufficient nor appropriate to derive an ESB that considers each metal separately, because metals almost always occur as mixtures in field sediments and metal–sulfide binding is interactive.

4.2.1 *AVS Benchmarks*

Results of calculations using chemical equilibrium models indicate that metals act in a competitive manner when binding to AVS. That is, the six metals—silver, copper, lead, cadmium, zinc, and nickel— will bind to AVS and be converted to their respective sulfides in this sequence (i.e., in the order of increasing solubility). Therefore, they must be considered together. There cannot be a benchmark for just nickel, for example, because all the other metals may be present as metal sulfides, and therefore, to some extent, as AVS. If these other metals are not measured as a mixture, then the ΣSEM will be misleadingly small, and it might appear that Σ[SEM]<[AVS] when in fact this would not be true if all the metals are considered together. It should be noted that this document currently restricts this discussion to the six metals listed above; however, in situations where other sulfide-forming metals (e.g., mercury) are present at high concentrations, they also must be considered.

The equilibrium model used to derive the $\text{ESB}_{\text{AVS:WQC}}$ for a mixture of the metals is presented below (see Ankley et al., 1996, for details). If the molar sum of SEM for the six metals is less than or equal to the AVS, that is, if

$$\Sigma_i\,[\text{SEM}_i] \le [\text{AVS}] \tag{4-1}$$

where

$$\Sigma_i\,[\text{SEM}_i] = [\text{SEM}_{\text{Cd}}] + [\text{SEM}_{\text{Cu}}] + [\text{SEM}_{\text{Pb}}] + [\text{SEM}_{\text{Ni}}] + [\text{SEM}_{\text{Zn}}] + 1/2[\text{SEM}_{\text{Ag}}]$$

then the concentrations of the mixtures of metals in the sediment are acceptable for protection of benthic organisms from acute or chronic metal toxicity.

4.2.2 *Interstitial Water Benchmarks*

The application of the interstitial water benchmark to multiple metals is complicated, not by the chemical interactions of the metals in the sediment-interstitial water system (as in the case with the AVS benchmark), but rather because of possible toxic interactions. Even if the individual concentrations do not exceed the water quality final chronic value (FCV) of each metal

Table 4-1. Water quality criteria (WQC) final chronic value (FCV) based on the dissolved concentration of metal[a]

Metal	Saltwater FCV (μg/L)	Freshwater FCV (μg/L)[b]
Cadmium	9.3	$\text{CF}^{c}\,[e^{(0.7852[\ln(\text{hardness})]-3.490}]$
Copper[d]	3.1	$0.960[e^{(0.8545[\ln(\text{hardness})]-1.465)}]$
Lead	8.1	$0.791[e^{(1.273[\ln(\text{hardness})]-4.705)}]$
Nickel	8.2	$0.997[e^{(0.8460[\ln(\text{hardness})]+1.1645)}]$
Silver	NA[c]	NA[c]
Zinc	81	$0.986[e^{(0.8473[\ln(\text{hardness})]+0.7614)}]$

[a] These WQC FCV values are for use in the interstitial water benchmarks approach for deriving $\text{ESBs}_{\text{AVS:WQC}}$ based on the dissolved metal concentrations in interstitial water (U.S. EPA, 1995b).

[b] For example, the freshwater FCV at a hardness of 50, 100, and 200 mg CaCO_3/L are 0.62, 1.0, and 1.7 μg cadmium/L; 6.3, 10, and 20 μg copper/L; 1.0, 2.5, and 6.1 μg lead/L; 87, 160, and 280 μg nickel/L; and 58, 100, and 190 μg zinc/L.

[c] CF = conversion factor to calculate the dissolved FCV for cadmium from the total FCV for cadmium: CF=1.101672–[(ln hardness)(0.041838)].

[d] The saltwater FCV for copper is from U.S. EPA (1995c).

[c] The silver criteria are currently under revision to reflect water quality factors that influence the criteria such as hardness, DOC, chloride, and pH, among other factors.

presented in Table 4-1, the metals could exert additive effects that might result in toxicity (Biesinger et al., 1986; Spehar and Fiandt, 1986; Enserink et al., 1991; Kraak et al., 1994). Therefore, in order to address this potential additivity, the interstitial water metal concentrations are converted to interstitial water benchmark units (IWBUs). This conversion is done by dividing the individual metal interstitial water concentrations by their respective WQC FCV and summing these values for all the metals. IWBUs are conceptually similar to toxic units; however, the term IWBU was adopted because it is derived using the FCV, which is intended to be a "no effect" concentration (i.e., toxicity would not usually be expected at 1.0 IWBUs).

For freshwater sediments, the FCVs are hardness dependent for all of the divalent metals under consideration, and thus, need to be adjusted to the hardness of the interstitial water of the sediment being considered. Because there are no FCVs for silver in freshwater or saltwater, this approach is not applicable to sediments containing significant concentrations of silver (i.e., ΣSEM>AVS). Because silver has the smallest solubility product (see Table 2-2) and the greatest affinity for AVS, it would be the last metal to be released from the AVS or the first metal to bind with AVS. Therefore, it is unlikely that silver would occur in the interstitial water of any sediment with measurable AVS (Berry et al., 1996).

For the ith metal with a total dissolved concentration, $[M_{i,d}]$, the IWBU is

$$\Sigma_i \frac{[M_{i,d}]}{FCV_{i,d}} \leq 1.0 \qquad (4\text{-}2)$$

where

$$\Sigma_i \frac{[M_{i,d}]}{[FCV_{i,d}]} = \frac{[M_{Cd,d}]}{[FCV_{Cd,d}]} + \frac{[M_{Cu,d}]}{[FCV_{Cu,d}]} + \frac{[M_{Pb,d}]}{[FCV_{Pb,d}]} + \frac{[M_{Ni,d}]}{[FCV_{Ni,d}]} + \frac{[M_{Zn,d}]}{[FCV_{Zn,d}]}$$

4.2.3 *Summary*

In summary, the sediment benchmarks for these six metals are not exceeded, and benthic organisms are sufficiently protected, if the sediment meets either one of the following benchmarks.

$$\Sigma_i[SEM_i] \leq [AVS] \qquad (4\text{-}1)$$

or

$$\Sigma_i \frac{[M_{i,d}]}{FCV_{i,d}} \leq 1.0 \qquad (4\text{-}2)$$

If the AVS or interstitial water $ESB_{AVS:WQC}$s are exceeded, there is reason to believe that the sediment *might* be unacceptably contaminated by these metals. Further evaluation and testing would, therefore, be necessary to assess actual toxicity and its causal relationship to the metals of concern. If data on the sediment-specific SEM, AVS, and organic carbon concentrations are available, the uncertainty bounds for $(\Sigma SEM\text{-}AVS)/f_{OC}$ described in Section 3.4 could be used to further classify sediments as those in which metals are not likely to cause toxicity, metal toxicity predictions are uncertain, or metal toxicity is likely. For sediments in which toxicity is likely or uncertain, acute and chronic tests with species that are sensitive to the metals suspected to be of concern, acute and chronic sediment TIEs, in situ community assessments, and seasonal and spatial characterizations of the SEM, AVS, and interstitial water concentrations would be appropriate (Ankley et al., 1994).

4.3 Example Calculation of $ESB_{AVS:WQC}$s for Metals and EqP-Based Interpretation

To assist users of these $ESB_{AVS:WQC}$s for mixtures of metals, example calculations for deriving solid-phase and interstitial water $ESB_{AVS:WQC}$s are provided in Table 4-2. For each of the three sediments, the calculations began with measured concentrations (in bold) of AVS (μg/g), SEM_i (μg/g), and interstitial water metal (μg/L). All other values were calculated. The specific concentrations in each of the these sediments were selected to provide examples of how the chemical measurements are used with the $ESB_{AVS:WQC}$ to determine the acceptability of a specific sediment and how the risks of sediment-associated metals can be evaluated within the technical framework of the EqP approach. Sediments are arranged in the table in decreasing order of their sulfide solubility product constants (see Section 2.2.5).

Sediment A contains relatively high concentrations of metals in the SEM, between 14.2 and 16.5 μg/g for copper, lead, and zinc. However, because there is sufficient AVS (0.96 μmol/g) in the sediment, the solid-phase $ESB_{AVS:WQC}$ is −0.343 (μmol/g), and there is no

Table 4-2. Example calculations of $\text{ESB}_{\text{AVS:WQC}}$s for metal mixtures: three sediments.

	Sediment Concentration			Interstitial Water Concentration				$\text{ESB}_{\text{AVS:WQC}}$	
Sediment	Analyte	µg/g^{a}	µmol/g	Metal ($M_{i,d}$)	µg/L	FCV^{b}	IWBU	SEM-AVS (µmol/g)	IW
A	AVS	**30.8**	0.96	—	—	—	—		
	SEM_{Ni}	**2.85**	0.048	Nickel	**ND^{c} (<0.8)**	8.2	<0.10		
	SEM_{Zn}	**16.5**	0.25	Zinc	**ND^{c} (<5.0)**	81	<0.06		
	SEM_{Cd}	**0.05**	0.001	Cadmium	**ND^{c} (<0.2)**	9.3	<0.02		
	SEM_{Pb}	**14.2**	0.068	Lead	**ND^{c} (<0.7)**	8.1	<0.09		
	SEM_{Cu}	**16.0**	0.25	Copper	**ND^{c} (<0.6)**	3.1	<0.19		
	SEM_{Ag}	—	—	Silver	—	—	—		
ΣSEM = 0.617 µmol/g; SEM-AVS = -0.343 µmol/g							ΣIWBU <0.46	-0.34	<0.46
B	AVS	**1310**	40.8	—	—	—	—		
	SEM_{Ni}	**34.0**	0.58	Nickel	**4.8**	160	0.03		
	SEM_{Zn}	**2630**	40.2	Zinc	**43.2**	100	0.43		
	SEM_{Cd}	**82.9**	0.74	Cadmium	**ND^{c} (<0.01)**	1.0	<0.01		
	SEM_{Pb}	**282**	1.36	Lead	**ND^{c} (<0.10)**	2.5	<0.04		
	SEM_{Cu}	**227**	3.58	Copper	**ND^{c} (<0.05)**	11	<0.005		
	SEM_{Ag}	**ND^{c}**	NDc	Silver	**ND^{c} (<0.01)**	—	—		
ΣSEM = 46.5 µmol/g; SEM-AVS = 5.71 µmol/g							ΣIWBU ~0.46	5.71	~0.46
C	AVS	**146**	4.57	—	—	—	—		
	SEM_{Ni}	**269**	4.58	Nickel	**26.3**	87	0.30		
	SEM_{Zn}	**12.4**	0.19	Zinc	**4.3**	58	0.07		
	SEM_{Cd}	**573**	5.12	Cadmium	**24.9**	0.62	40.1		
	SEM_{Pb}	**66.2**	0.32	Lead	**ND^{c} (<0.10)**	1.0	<0.10		
	SEM_{Cu}	**4.44**	0.07	Copper	**ND^{c} (<0.05)**	6.3	<0.008		
	SEM_{Ag}	**ND^{c}**	NDc	Silver	**ND^{c} (<0.01)**	—	—		
ΣSEM = 10.28 µmol/g; SEM-AVS = 5.71 µmol/g							ΣIWBU ~40.47	5.71	~40.5

[a] Molecular weights: sulfur, 32.06; nickel, 58.7; zinc, 65.4; cadmium, 112; lead, 207; copper, 63.5; silver, 108.
[b] Saltwater sediment: sediment A. Freshwater sediments: sediment B, interstitial hardness 100 mg/L; sediment C, 50 mg/L.
[c] ND = not detected.

metal detected in the interstitial water. This sediment is acceptable for protection of benthic organisms from direct toxicity of the metals in the sediment. Silver was not measured in this sediment. However, because AVS is present, any silver in the sediment is not of toxicological concern and none should occur in interstitial water. One final consideration is the need for detection limits for metals in the sediment that are significantly below their respective WQC FCVs. For this sediment there were no detectable metals in the interstitial water and ΣIWBU was <0.46.

Sediment B is from a Superfund site heavily contaminated with all of the metals (ΣSEM = 46.5

μmol/g), but most severely with zinc (2,630 μg/g). There is an excess of SEM in this sediment (SEM-AVS = 5.71 μmol/g). Importantly for sediment B, the interstitial concentrations of the metals were all less than the WQC FCVs and the ΣIWBU was <1.0 (~ 0.46). Therefore, this sediment is acceptable for protection of benthic organisms from direct toxicity of this mixture of metals in the sediment. It should be noted that, if interstitial metal concentrations had not been quantified, the sediment would have exceeded the $ESB_{AVS:WQC}$ and additional testing would be advisable. A possible explanation for the absence of significant metals in the interstitial water of this sediment is its higher organic carbon concentration (f_{OC} = 0.05). The (ΣSEM-AVS)/f_{OC} of 114 μmol excess SEM/g_{OC} for this sediment is, therefore, predicted to be nontoxic because it is <130 μmol excess SEM/g_{OC} (see Section 3.4.4).

Sediment C is heavily contaminated with approximately equimolar concentrations of cadmium and nickel. It exceeds the $ESB_{AVS:WQC}$ for metals for both solid and interstitial water phases. The ΣSEM (10.28 μmol/g) exceeds the AVS (4.57 μmol/g); therefore, SEM-AVS = 5.71 μmol excess SEM/g, a concentration identical to that of sediment B. Although lead and copper are found in the sediment, they are not found in detectable concentrations in the interstitial water. This is because they have the lowest sulfide solubility product constants and the sum of their SEM concentrations (0.39 μmol/g) is less than AVS. If the dry weight concentrations of metals had been analyzed, silver and additional copper and nickel might have been detected. Silver will not be detected in the SEM or interstitial water when AVS is present (see Section 3.2.1). Nickel, cadmium, and zinc occur in interstitial water because in the sequential summation of the SEM_i concentrations in order of increasing sulfide solubilities, the concentrations of these metals exceed the AVS. Therefore, these three metals are found in the SEM that is not a metal sulfide and in the interstitial water, and contribute to the ΣIWBU (~40.47) as well as to the overall exposure of benthic organisms. Because only cadmium concentrations exceed the WQC FCV, any effects observed in toxicity tests or in faunal analyses with this sediment should principally be a result of cadmium. This sediment is low in organic carbon concentration (TOC = 0.2%; f_{OC} = 0.002). The organic carbon–normalized concentration (ΣSEM-AVS/f_{OC}) of 2,855 μmol excess SEM/g_{OC} was within the uncertainty bounds of 130 to 3,000 μmol excess SEM/g_{OC}, suggesting that additional evaluations should be conducted (see Section 3.4.4).

4.4 $ESB_{AVS:WQC}$ for Metals vs. Environmental Monitoring Databases

This section compares the $ESB_{AVS:WQC}$ based on AVS or IWBUs with chemical monitoring data from freshwater and saltwater sediments in the United States. This comparison of AVS-SEM and interstitial water concentrations is used to indicate the frequency of sediments in the United States where metals toxicity is unlikely. When data were available in the monitoring programs, (ΣSEM-AVS)/f_{OC} is used to indicate sediments where toxicity is unlikely, likely, or uncertain. When toxicity or benthic organism community health data are available in conjunction with these concentrations it is possible to speculate as to potential causes of the observed effects. These data, however, cannot be used to validate the usefulness of the AVS approach because sediments that exceed the benchmarks are not always toxic, and because observed sediment toxicity may be the result of unknown substances.

4.4.1 *Data Analysis*

Three monitoring databases were identified that contain AVS, SEM, and f_{OC} information; one also had data on concentrations of metals in interstitial water. Toxicity tests were conducted on all sediments from these sources. The sources are the Environmental Monitoring and Assessment Program (EMAP) (Leonard et al., 1996a), the National Oceanographic and Atmospheric Administration National Status and Trends monitoring program (NOAA NST) (Wolfe et al., 1994; Long et al., 1995b, 1996), and the Regional Environmental Monitoring and Assessment Program (REMAP) (Adams et al., 1996).

4.4.1.1 *Freshwater Sediments*

The AVS and SEM concentrations in the 1994 EMAP database from the Great Lakes were analyzed by Leonard et al. (1996a). A total of 46 sediment grab samples and 9 core samples were collected in the summer from 42 locations in Lake Michigan. SEM, AVS, TOC, interstitial water metals (when sufficient volumes were present), and 10-day sediment toxicity to the midge *C. tentans* and the amphipod *H. azteca* were measured in the grab samples (the concentrations are listed in Appendix A).

The AVS concentrations versus SEM-AVS differences from Appendix A are plotted in Figure 4-1. Grab sediment samples containing AVS concentrations

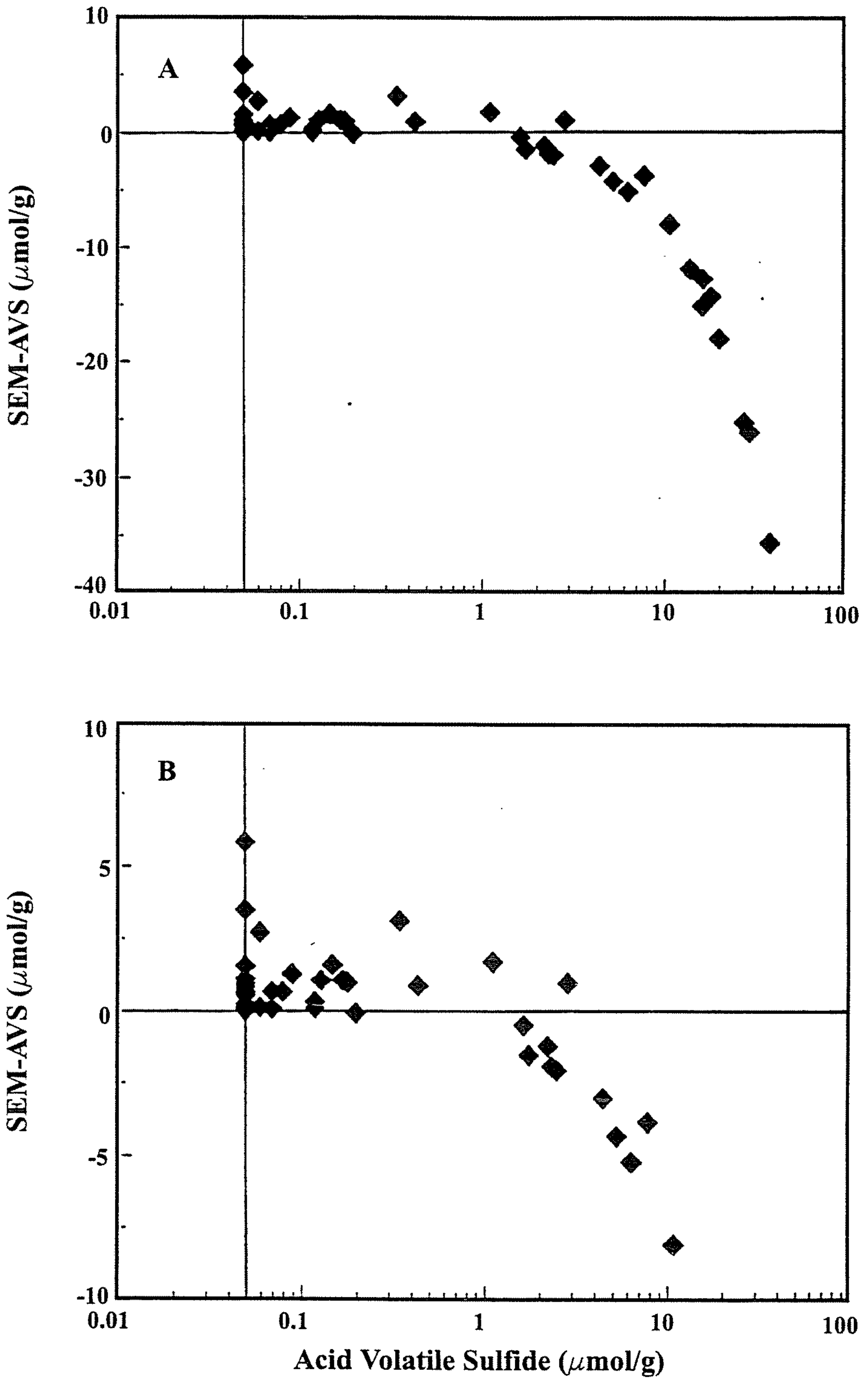

Figure 4-1. SEM-AVS values versus AVS concentrations in EMAP-Great Lakes sediments from Lake Michigan. Data are from surficial grab samples only. Plot (A) shows all values; plot (B) has the ordinate limited to SEM-AVS values between −10 and +10 μmol/g.

below the detection limit of 0.05 µmol/g AVS are plotted at that concentration. Forty-two of the 46 samples (91%) had SEM-AVS differences greater than 0.0. Thirty-six of these had less than 1.0 µmol of excess SEM/g sediment; and none had over 5.8 µmol excess SEM/g sediment. Sediments with SEM concentrations in excess of that for AVS have the potential to be toxic because of metals. However, the majority of sediments with an excess of SEM had low concentrations of both AVS and SEM. For 20 of these Lake Michigan sediments, interstitial water metals concentrations were measured. The sum of the IWBUs for cadmium, copper, lead, nickel, and zinc was always less than 0.4 (Leonard et al., 1996a). In 10-day toxicity tests using *C. tentans* and *H. azteca*, no toxicity was observed in 81% of the 21 sediments not exceeding the $\mathrm{ESB_{AVS:WQC}}$. Leonard et al. (1996a) concluded that when toxicity was observed it was not likely from metals, because of the low interstitial water metals concentrations. These data demonstrate the value of using both SEM-AVS and IWBUs to evaluate the risks of metals in sediments.

4.4.1.2 *Saltwater Sediments*

Saltwater data from a total of 398 sediment samples from 5 monitoring programs representing the eastern coast of the United States are included in Appendix B. The EMAP Virginian Province database (U.S. EPA, 1996) consists, in part, of 127 sediment samples collected from August to mid-September 1993 from randomly selected locations in tidal rivers and small and large estuaries from the Chesapeake Bay to Massachusetts (Strobel et al., 1995). The NOAA data are from Long Island Sound, Boston Harbor, and the Hudson River Estuary. Sediments were collected from 63 locations in the coastal bays and harbors of Long Island Sound in August 1991 (Wolfe et al., 1994). Sediment samples from 30 locations in Boston Harbor were collected in June and July 1993 (Long et al., 1996). Sediment samples from 38 locations in the Hudson River Estuary were collected from March to May 1991 (Long et al., 1995b). Sediment samples were collected in the REMAP program from 140 locations from the New York/New Jersey Harbor Estuary System (Adams et al., 1996). All of the above sediment grab samples were from approximately the top 2 cm of undisturbed sediment.

For saltwater sediments, the molar concentration of AVS typically exceeds that for SEM (SEM-AVS ≤0.0 µmol/g) for most of the samples across the entire range of AVS concentrations (Figure 4-2). A total of 68 of the 398 saltwater sediments (17%) had an excess of metal, and only 4 of the 68 (6%) had over 2 µmol excess SEM/g. As AVS levels increase, fewer and fewer sediments have SEM-AVS differences that are positive; none occurred when AVS was >8.1 µmol/g. Interstitial water metal was not measured in these saltwater sediments. Only 5 of the 68 sediments (7%) having excess of up to 0.9 µmol SEM/g were toxic in 10-day sediment toxicity tests with the amphipod *A. abdita*, whereas 79 of 330 sediments (24%) having an excess of AVS were toxic. Toxicity was not believed to be metals related in the 79 toxic sediments where AVS was in excess over SEM. Metals were unlikely the cause of toxicity in those sediments having an excess of SEM because there was only ≤0.9 µmol excess SEM/g. Finally, the absence of toxicity in sediments having an excess of SEM of up to 4.4 µmol/g indicates significant metal-binding potential over that of AVS in some sediments. Organic carbon concentrations from 0.05% to 15.2% (average 1.9%) provide for some of this additional metal binding.

Organic carbon, along with SEM and AVS, was measured in these 398 saltwater sediments. Therefore, the $(\Sigma\text{SEM-AVS})/f_{OC}$ concentrations of concern can be compared with the organic carbon–normalized concentrations of SEM-AVS differences (Figure 4-3). No sediments containing an AVS concentration in excess of 10 µmol/g had an excess of SEM; that is, all $(\Sigma\text{SEM-AVS})/f_{OC}$ values were negative. Excess of SEM relative to AVS became more common as sediment AVS decreased. None of the sediments contained greater than 130 µmol excess $\mathrm{SEM/g_{OC}}$, the lower uncertainty bound from Section 3.4. This indicates that metals concentrations in all of the sediments monitored in the summer by EPA EMAP and REMAP and by NOAA are below concentrations of concern for benthic organisms.

4.5 Bioaccumulation

The data appear to suggest that, for these sediments collected from freshwater and marine locations in the United States, direct toxicity caused by metals in sediments is expected to be extremely rare. Although this might be true, these data by themselves are inconclusive. Importantly, it would be inappropriate to use the data from the above studies to conclude that metals in sediments are *not* a problem. In all of the above studies, the sediments were conducted in the summer when the seasonal biogeochemical cycling of sulfur should produce the highest concentrations of iron monosulfide, which

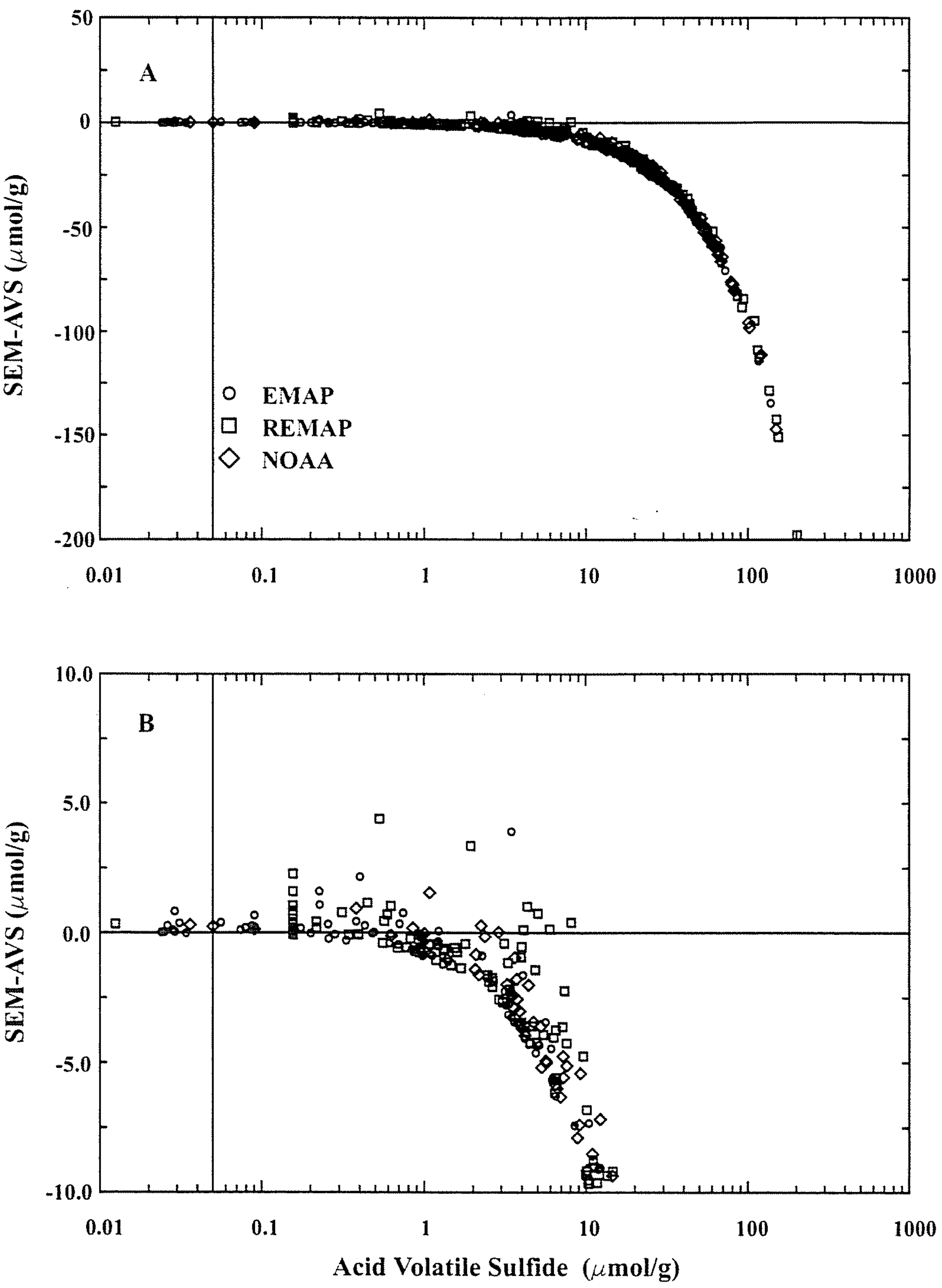

Figure 4-2. SEM-AVS values versus AVS concentrations in EMAP-Estuaries Virginian Province (U.S. EPA, 1996); REMAP-NY/NJ Harbor Estuary (Adams et al., 1996); NOAA NST-Long Island Sound (Wolfe et al., 1994); Boston Harbor (Long et al., 1996); and Hudson-Raritan Estuaries (Long et al., 1995b). Plot A shows all values; plot B has the ordinate limited to SEM-AVS values between -10 and +10 μmol/g (see data in Appendix B).

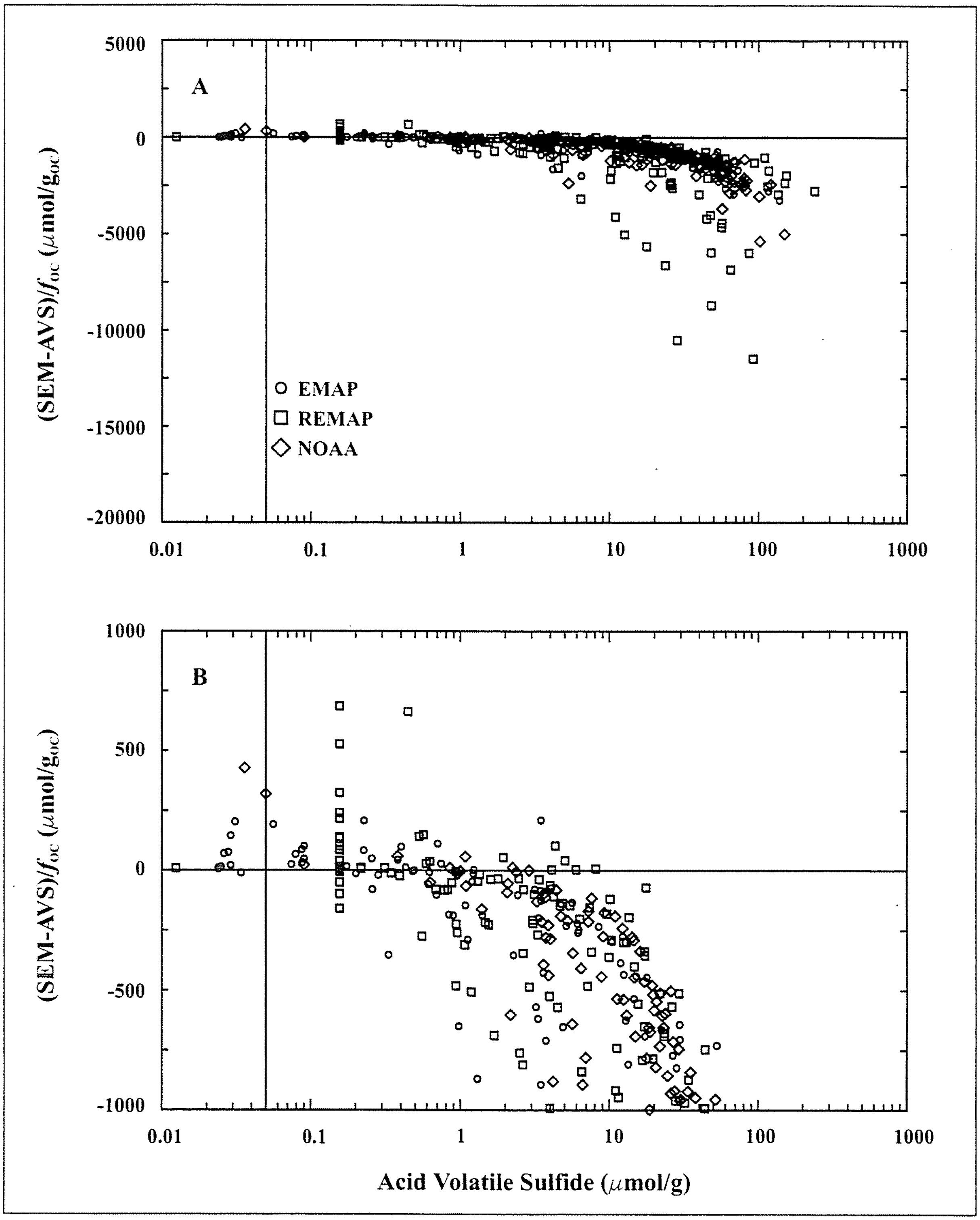

Figure 4-3. (ΣSEM-AVS)/f_{OC} versus AVS concentrations in EMAP-Estuaries Virginian Province (U.S. EPA, 1996); REMAP-NY/NJ Harbor Estuary (Adams et al., 1996); NOAA NST-Long Island Sound (Wolfe et al., 1994); Boston Harbor (Long et al., 1996); and Hudson-Raritan Estuaries (Long et al., 1995b). Plot A shows all values; plot B has the ordinate limited to (ΣSEM-AVS)/f_{OC} values between -10 and +10 μmol/g (see data in Appendix B).

might make direct metal-associated toxicity less likely than in the winter/spring months. Accurate assessment of the extent of the direct ecological risks of metals in sediments requires that sediment monitoring occur in the months of minimum AVS concentration; typically, but not always, in November to early May. These yet-to-be-conducted studies must monitor, at a minimum, SEM, AVS, f_{OC}, interstitial water metal, and toxicity.

Bioaccumulation of metals from sediments when SEM is less than AVS was not expected based on EqP theory. However, there is a significant database that demonstrates that metals concentrations in benthic organisms increase when metals concentrations in sediments on a dry weight basis increase (Ankley, 1996). This has caused considerable debate (Lee et al., 2000a,b) because it suggests that metal bioavailability may be related to dry weight metals concentrations, and if the increase in bioaccumulated metal is related to effects, then effects may be related to dry weight metals concentrations. Most importantly, these studies, and all other AVS-related testing, has overwhelming demonstrated that toxic effects of metals are absent in sediments when SEM is less than AVS, even when bioaccumulation is observed, and that toxicity is not related to dry weight metals concentrations. For example, careful evaluation of Lee et al. (2000b) results, demonstrates that in order to understand and predict metal toxicity AVS normalization is critical. Although Lee et al. (2000b) note the accumulation of metal by the test organisms, no adverse effects were reported. This suggests that the bioaccumulated metals may not be toxicologically available or of sufficient concentration in the organism to cause effects. In addition, these metals do not biomagnify to higher trophic levels in aquatic ecosystems (Suedel et al., 1994). Therefore, an $ESB_{AVS:WQC}$ based on the difference between the concentrations of SEM and AVS is appropriate for protecting benthic organisms from the direct effects of sediment-associated metals, and not for protecting against metal bioaccumulation.

Section 5

Sampling and Analytical Chemistry

5.1 General Information

This section provides guidance on procedures for sampling, handling, and analysis of metals in sediments, and on the interpretation of data from the sediment samples that are needed if the assessments of the risks of sediment-associated metals are to be appropriately based on the EqP methodology. The design of any assessment should match the goal of the specific assessment and how evaluation tools such as $ESB_{AVS:WQC}$s are to be applied.

Results of the short- and long-term laboratory and field experiments conducted to date using sediments spiked with individual metals and mixtures of metals represent convincing support for the conclusion that absence (but not necessarily presence) of metal toxicity can be reliably predicted based on metal–sulfide relationships or interstitial water metal concentrations. In contrast, much confusion exists on how to use this convincing evidence to interpret the significance of metals concentrations in sediments from the field. Using these observations as a basis for predicting metal bioavailability, or deriving an $ESB_{AVS:WQC}$, raises a number of conceptual and practical issues related to sampling, analytical measurements, and effects of additional binding phases. Many of these were addressed by Ankley et al. (1994). Those most salient to the proposed derivation of the $ESB_{AVS:WQC}$s are described below.

5.2 Sampling and Storage

Accurate prediction of exposure of benthic organisms to metals is critically dependent on sampling appropriate sediment horizons at appropriate times. This is because of the relatively high rates of AVS oxidation caused by natural processes in sediments and the requirement that oxidation must be avoided during sampling of sediments and interstitial water. In fact, the labile nature of iron monosulfides has led some to question the practical utility of using AVS as a basis for an EqP-derived ESB for metals (Luoma and Carter, 1993; Meyer et al., 1994). For example, there have been many observations of spatial (depth) variations in AVS concentrations, most of which indicate that surficial AVS concentrations are less than those in deeper sediments (Boothman and Helmstetter, 1992; Howard and Evans, 1993; Brumbaugh et al., 1994; Hare et al., 1994; Besser et al., 1996; Hansen et al., 1996b; Leonard et al., 1996a; Liber et al., 1996; Boothman et al., 2001). This is likely because of oxidation of AVS (principally FeS) at the sediment surface, a process enhanced by bioturbation (Peterson et al., 1996).

In addition to varying with depth, AVS can vary seasonally. For example, in systems where overlying water contains appreciable oxygen during cold-weather months, AVS tends to decrease, presumably because of a constant rate of oxidation of the AVS linked to a decrease in its generation by sulfate-reducing bacteria (Herlihy and Mills, 1985; Howard and Evans, 1993; Leonard et al., 1993). Because of potential temporal and spatial variability of AVS, it appears that the way to avoid possible underestimation of metal bioavailability is to sample the biologically "active" zone of sediments at times when AVS might be expected to be present at low concentrations. It is recommended that, at a minimum, AVS and SEM measurements be made using samples of the surficial (0 to 2.0 cm) sediments during the period from November to early May. Minimum AVS concentrations may not always occur during cool-weather seasons; for example, systems that become anaerobic during the winter can maintain relatively large sediment AVS concentrations (Liber et al., 1996). Therefore, AVS, SEM, and interstitial metal concentrations may need to be determined seasonally. Importantly, the biologically active zones of some benthic communities may be within only the surficial first few millimeters of the sediment, whereas other communities may be biologically active at depths up to a meter. In order to determine the potential for exposure to metals, sediment and interstitial water samples from multiple sediment horizons may be required.

The somewhat subjective aspects of these sampling recommendations have been of concern. Multiple sediment samples are necessary because of the dynamic nature of the metal-binding phases in sediments. Depending on the depth of bioturbation, the possible oxidation rates of specific metal sulfides, and the extent of possible metal concentrations, the horizontal and vertical resolution of the needed monitoring is likely to be site specific. Even if neither of the sediment benchmarks is violated in extensive monitoring programs, metals concentrations on a dry weight basis may be high and widely distributed. This may be a good reason to conduct monitoring studies to determine the extent of metal bioaccumulation in benthic food chains. Furthermore, if the ultimate fate of the sediments is unknown, risk assessments to evaluate future risks caused by dynamic processes may be desirable.

Research suggests that the transient nature of AVS may be overstated relative to predicting the fate of all metal-sulfide complexes in aquatic sediments. Observations from the Duluth EPA laboratory made in the early 1990s indicate that AVS concentrations in sediments contaminated by metals such as cadmium and zinc tended to be elevated over concentrations typically expected in freshwater systems (G.T. Ankley, U.S. EPA, Duluth, MN, personal communication). The probable underlying basis for these observations did not become apparent, however, until a recent series of spiking and metal-sulfide stability experiments. The field colonization study of Liber et al. (1996) demonstrated a strong positive correlation between the amount of zinc added to test sediments and the resultant concentration of AVS in the samples. In fact, the initial design of their study attempted to produce test sediments with as much as five times more SEM_{Zn} (nominal) than AVS; however, the highest measured SEM_{Zn}/AVS ratio achieved was only slightly larger than 1. Moreover, the expected surficial depletion and seasonal variations in AVS were unexpectedly low in the zinc-spiked sediments. These observations suggested that zinc sulfide, which composed the bulk of AVS in the spiked sediments, was more stable than the iron sulfide present in the control sediments. The apparent stability of other metal sulfides versus iron sulfide also has been noted in laboratory spiking experiments with freshwater and saltwater sediments (Leonard et al., 1995; DeWitt et al., 1996; Hansen et al., 1996b; Peterson et al., 1996; Sibley et al., 1996; Boothman et al., 2001).

In support of these observations, metal-sulfide oxidation experiments conducted by Di Toro et al. (1996b) have confirmed that cadmium and zinc form more stable sulfide solid phases than iron. If this is also true for sulfide complexes of copper, nickel, silver, and lead, the issue of seasonal/spatial variations in AVS becomes of less concern because most of the studies evaluating variations in AVS have focused on iron sulfide (i.e., uncontaminated sediments). Thus, further research concerning the differential stability of metal sulfides, from both temporal and spatial perspectives, is definitely warranted.

5.2.1 *Sediments*

At a minimum, sampling of the surficial 2.0 cm of sediment between November and early May is recommended. A sample depth of 2.0 cm is appropriate for monitoring. However, for instances such as dredging or in risk assessments where depths greater than 2 cm are important, sample depths should be planned based on particular study needs. Sediments can be sampled using dredges, grabs, or coring, but mixing of aerobic and anaerobic sediments must be avoided because the trace metal speciation in the sediments will be altered (see Bufflap and Allen, 1995, for detailed recommendations to limit sampling artifacts). Coring is generally less disruptive, facilitates sampling of sediment horizons, and limits potential metal contamination and oxidation if sealed PVC core liners are used.

Sediments not immediately analyzed for AVS and SEM must be placed in sealed airtight glass jars and refrigerated or frozen. Generally, enough sediment should be added to almost fill the jar. If sediments are stored this way, there will be little oxidation of AVS even after several weeks. Sampling of the stored sediment from the middle of the jar will further limit potential effects of oxidation on AVS. Sediments experiencing oxidation of AVS during storage will become less black or grey if oxidized. Because the rate of metal-sulfide oxidation is markedly less than that of iron sulfide, release of metal during storage is unlikely.

5.2.2 *Interstitial Water*

Several procedures are available to sample interstitial water in situ or ex situ. Carignan et al. (1985) compared metals concentrations in interstitial water obtained by ex situ centrifugation at 11,000 rpm followed by filtration (0.45 μm and 0.2 or 0.03 μm) and in situ diffusion samplers with 0.2 μm polysulfone membranes. For the metals of concern in this benchmark document, concentrations of nickel and cadmium were equivalent using both methods, and concentrations of copper and zinc were higher and more variable using centrifugation. They recommended using in situ dialysis for studying trace constituents in sediments because of its inherent simplicity and the avoidance of artifacts that can occur with the handling of sediments in the laboratory.

More recently, Bufflap and Allen (1995) reviewed four procedures for collection of interstitial water for trace metals analysis. These included ex situ squeezing, centrifugation, in situ dialysis, and suction filtration. These authors observed that each method has its own advantages and disadvantages. Importantly, interstitial water must be extracted by centrifugation or squeezing in an inert atmosphere until acidified, because oxidation will alter metal speciation. Artifacts may be caused by temperature changes in ex situ methods that may be overcome by maintaining temperatures similar to those in in situ methods. Contamination of interstitial water by fine particles is important in all methods, because differentiation of particulate and dissolved metal is a function of the pore size of the filter or diffusion sampler membrane. The use of 0.45 μm filtration, although an often accepted definition of "dissolved" metals, may result in differences from laboratory to laboratory. Use of suction filtration devices is limited to coarser sediments, and they do not offer depth resolution.

Use of diffusion samplers is hampered by the time required for equilibrium (7 to 14 days) and the need for diver placement and retrieval in deep waters. Acidification of interstitial water obtained by diffusion or from suction filtration must occur immediately to limit oxidation. Bufflap and Allen (1995) conclude that in situ techniques have less potential for producing sampling artifacts than ex situ procedures. They concluded that, of the in situ procedures, suction filtration has the best potential for producing artifact-free interstitial water samples directly from the environment. Of the ex situ procedures, they concluded that centrifugation under a nitrogen atmosphere followed immediately by filtration and acidification was the simplest technique likely to result in an unbiased estimate of metal concentrations in interstitial water. At present, it is recommended filtration of the surface water through 0.40 to 0.45 μm polycarbonate filters to better define that fraction of aqueous metal associated with toxicity (Prothro, 1993). This guidance applies to interstitial water. Thurman (1985) equates the organic carbon retained on a 0.45 μm glass-fiber filter to suspended organic carbon, so that this filtration procedure under nitrogen atmosphere followed immediately by acidification is acceptable for interstitial waters. However, in studies comparing collection and processing methods for trace metals, sorption to filter membranes or the filtering apparatus does occur (Schults et al., 1992). These authors later presented a method combining longer centrifugation times with a unique single-step interstitial water withdrawal procedure that has potential for minimizing metal losses by eliminating the need for filtration (Ozretich and Schults, 1998).

Use of dialysis samplers to obtain samples of interstitial water is recommended for comparison of measured concentrations of dissolved metals with WQC. This is primarily because diffusion samplers obtain interstitial water with the proper in situ geochemistry, thus limiting artifacts of ex situ sampling. Furthermore, in shallow waters, where contamination of sediments is most likely, placement of diffusion samplers is easily accomplished and extended equilibration times are not a problem. Second, use of centrifugation under nitrogen and 0.45 μm filtration using polycarbonate filters for obtaining interstitial water from sediments in deeper aquatic systems. Care must be taken to ensure that filters or the filter apparatus do not remove metal from or add metal to the interstitial water sample to be analyzed. Perhaps most importantly, the extremely large database comparing interstitial metals concentrations with organism responses from spiked- and field-sediment experiments in the laboratory has demonstrated that, where the IWTU concept predicted that metals concentrations in interstitial water should not be toxic, toxicity was not observed when either dialysis samplers or centrifugation were used (Berry et al., 1996; Hansen et al., 1996a). Therefore, it is likely that when either methodology is used to obtain interstitial water for comparison with WQC, if metals concentrations are below 1.0 IWBU, sediments should be acceptable for protection of benthic organisms. The exception is for some silver-spiked freshwater and saltwater sediments that were toxic in spite of the absence of interstitial silver. It is for this reason that IWBUs are not used as $\mathrm{ESB}_{\mathrm{AVS:WQC}}$s for silver (see Sections 4.2.1 and 4.2.2).

5.3 Analytical Measurements

An important aspect to deriving ESB values is that the methods necessary to implement the approach must be reasonably standardized or have been demonstrated to produce results comparable to those of standard methodologies. From the standpoint of the $\mathrm{ESB}_{\mathrm{AVS:WQC}}$s, a significant amount of research has gone into defining methodologies to obtain interstitial water and sediments (see Section 5.2 above), to extract SEM and AVS from sediments, and to quantify AVS, SEM, and the metals in interstitial water.

5.3.1 *Acid Volatile Sulfide*

The SEM/AVS extraction method suggested is that of Allen et al. (1993). In terms of AVS quantification, a number of techniques have been successfully utilized, including gravimetric (Di Toro et al., 1990; Leonard et al., 1993), colorimetric (Cornwell and Morse, 1987), gas chromatography– photoionization detection (Casas and Crecelius, 1994; Slotton and Reuter, 1995), and specific ion electrodes (Boothman and Helmstetter, 1992; Brouwer and Murphy, 1994; Brumbaugh et al., 1994; Leonard et al., 1996b). Allen et al. (1993) report a detection limit for 50% accuracy of 0.01 µmol/g for a 10 g sediment sample using the colorimetric method. Based on several studies, Boothman and Helmstetter (1992) report a detection limit of 1 µmol AVS, which translates to 0.1 µmol/g dry weight for a 10 g sediment sample using the ion specific electrode method.

5.3.2 *Simultaneously Extracted Metals*

SEMs are operationally defined as metals extracted from sediment into solution by the AVS extraction procedure. The dissolved metals in this solution are also operationally defined as the metal species that pass through filter material used to remove the residual sediment. Common convention defines "dissolved" as metal species <0.45 µm in size. SEM concentrations measured in sediments are not significantly different, however, using Whatman #1 filter paper alone (<11 µm nominal interstitial size) or in combination with a 0.45 µm filter (W. Boothman, U.S. EPA, Narragansett, RI, personal communication). SEM solutions generated by the AVS procedure can be analyzed for metals, commonly including cadmium, copper, lead, nickel, silver, and zinc, by routine atomic spectrochemical techniques appropriate for environmental waters (e.g., inductively coupled plasma atomic emission or graphite furnace atomic absorption spectrophotometry [GFAA]) (U.S. EPA, 1994b). Because of the need to determine metals at relatively low concentrations, additional consideration must be given to preclude contamination during collection, transport, and analysis (U.S. EPA, 1995d,e,f).

5.3.3 *Total Organic Carbon*

Several methods for measuring organic carbon exist and are reviewed by Nelson and Sommers (1996). U.S. EPA (2001) summarizes the minimum requirements of acceptable methods for quantifying total organic carbon in sediments.

5.3.4 *Interstitial Water Metal*

Interstitial water can be analyzed for the metals cadmium, copper, lead, nickel, silver, and zinc by routine atomic spectrochemical techniques appropriate for environmental waters (e.g., inductively coupled plasma atomic emission or GFAA) (U.S. EPA, 1994b). Because of the need to determine metals at concentrations at or below the threshold of biological effects (i.e., WQC concentrations), additional consideration must be given to preclude contamination during collection, transport and analysis (U.S. EPA, 1995d,e,f; also see guidance on clean chemistry techniques in U.S. EPA, 1994c). Generally, detection limits should be at ≤0.1 IWBU because the contributions of each of the metals must be summed.

Section 6

Sediment Benchmark Values: Application and Interpretation

The procedures described in this document indicate that, except possibly where a locally, commercially, or recreationally important species is very sensitive, benthic organisms should be acceptably protected in freshwater and saltwater sediments if at least one of the following two conditions are satisfied: the sum of the molar concentrations of SEM cadmium, copper, lead, nickel, silver, and zinc is less than or equal to the molar concentration of AVS (Section 6.1), or the sum of the dissolved interstitial water concentration of cadmium, copper, lead, nickel, and zinc divided by their respective WQC FCV is less than or equal to 1.0 (Section 6.2). The AVS benchmark is intended to apply to sediments having ≥0.1 μmol AVS/g. The two conditions for deriving $ESB_{AVS:WQC}$ are detailed in Section 4.2 and are repeated below.

Consistent with the recommendations of EPA's Science Advisory Board, publication of these documents does not imply the use of ESBs as stand-alone, pass-fail criteria for all applications; rather, exceedances of ESBs could trigger collection of additional assessment data.

As discussed in Section 3.4, a more accurate prediction of toxicity can be derived if the presence of organic carbon is considered along with AVS. For the multiple metals cadmium, copper, lead, nickel, silver and zinc, the following assumptions are useful in deriving a benchmark:

1) Any sediment in which $(SEM - AVS)/f_{OC} < 130$ μmols/g_{OC} should pose low risk of adverse biological effects due to cadmium, copper, lead, nickel and zinc.

2) Any sediment in which $130 \mu mols/g_{OC} < (SEM - AVS)/f_{OC} < 3000$ μmols/g_{OC} may have adverse biological effects due to cadmium, copper, lead, nickel or zinc.

3) In any sediment in which $(SEM - AVS)/f_{OC} > 3000$ μmols/g_{OC} adverse biological effects due to cadmium, copper, lead, nickel or zinc may be expected.

4) Any sediment with AVS > 0.0 will not cause adverse biological effects due to silver.

6.1 AVS ESB

$$\Sigma_i [SEM_i] \le [AVS]$$

where

$$\Sigma_i [SEM_i] = [SEM_{Cd}] + [SEM_{Cu}] + [SEM_{Pb}] + [SEM_{Ni}] + [SEM_{Zn}] + 1/2[SEM_{Ag}]$$

6.2 Interstitial Water ESB

$$\Sigma_i \frac{[M_{i,d}]}{FCV_{i,d}} \le 1.0$$

where

$$\Sigma_i \frac{[M_{i,d}]}{[FCV_{i,d}]} = \frac{[M_{Cd,d}]}{[FCV_{Cd,d}]} + \frac{[M_{Cu,d}]}{[FCV_{Cu,d}]} + \frac{[M_{Pb,d}]}{[FCV_{Pb,d}]} + \frac{[M_{Ni,d}]}{[FCV_{Ni,d}]} + \frac{[M_{Zn,d}]}{[FCV_{Zn,d}]}$$

It is repeated here that the interstitial water benchmark applies only to the five metals: cadmium, copper, lead, nickel, and zinc. Silver is not included in this benchmark because the FCV for silver is not available.

Arguably, the most important additional data needed for assessing contaminated sediments along with ESBs are the results of toxicity tests. Sediment toxicity tests provide an important complement to ESBs in interpreting overall risk from contaminated sediments. Toxicity tests have different strengths and weaknesses compared to chemical-specific guidelines, and the most powerful inferences can be drawn when both are used together (see U.S. EPA 2003c,d for further discussion of using toxicity testing with ESBs to assess contaminated sediments).

The ESB approaches are intended to protect benthic organisms from direct toxicity associated with exposure to metal-contaminated sediments. They are not designed to protect aquatic systems from metals release associated, for example, with sediment suspension, or the transport of metals into the food web from either sediment ingestion or ingestion of contaminated benthos. Furthermore, the ESBs do not consider the antagonistic, additive or synergistic effects of other sediment contaminants in combination with metal mixtures or the potential for bioaccumulation and trophic transfer of metal mixtures to aquatic life, wildlife or humans.

Section 7

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Appendix A

Lake Michigan EMAP Sediment Monitoring Database

Concentrations of SEM, AVS, TOC, and IWBU for cadmium, copper, lead, nickel, and zinc in 46 surficial samples from Lake Michigan

					IWBU						% Survival	
Sample	TOC (%)	SEM (μmol/g)	AVS (μmol/g)	SEM-AVS (μmol/g)	Cadmium	Copper	Lead	Nickel	Zinc	Sum	*Hyalella azteca*	*Chironomus tentans*
1	0.18	0.53	0.03[a]	0.51	—[b]	—	—	—	—	—	92.5	40
2	4.63	3.46	0.35	3.11	0.029	0.003[d]	0.00004	0.005	0.003	0.040	90	90
3	3.36	2.78	0.06	2.72	0.018	0.308	0.002	0.003	0.029	0.360	92.5	90
4	4.89	3.55	0.05	3.50	0.018	0.266	0.0004	0.003	0.006	0.293	100	97.5
5	0.92	0.14	0.03[a]	0.12	0.0002[c]	0.034	0.0008	0.006	0.032	0.073	0	90
6	4.37	2.82	1.13	1.69	0.024	0.049	0.0002	0.004	0.020	0.097	97.5	100
7	5.27	1.20	0.13	1.07	0.029	0.003[d]	0.0001[e]	0.006	0.020	0.058	92.5	100
8	0.08	0.17	0.03[a]	0.15	0.115	0.003[d]	0.001	0.006	0.055	0.180	95	87.5
9	4.27	1.47	4.49	-3.02	0.050	0.034	0.0008	0.004	0.026	0.115	95	100
10	2.11	0.25	0.03[a]	0.23	—	—	—	—	—	—	77.5	87.5
11	1.89	1.12	0.03[a]	1.10	—	—	—	—	—	—	97.5	100
12	0.41	0.74	0.07	0.67	0.0002[c]	0.070	0.002	0.0005[f]	0.001	0.074	—	—
13	2.87	1.17	0.18	0.99	—	—	—	—	—	—	97.5	97.5
14	3.68	1.56	0.03[a]	1.54	0.0002[c]	0.003	0.0004	0.006	0.015	0.025	96.5	92.5
15	0.28	1.32	0.44	0.88	0.0002[c]	0.119	0.0002	0.004	0.050	0.173	90	87.5
16	0.07	0.17	0.05	0.12	—	—	—	—	—	—	100	100
17	3.51	0.75	0.08	0.67	0.018	0.060	0.0008	0.008	0.058	0.145	100	100
18	0.40	0.97	0.03[a]	0.95	—	—	—	—	—	—	95	100
19	1.73	1.74	0.15	1.59	0.079	0.013	0.0008	0.010	0.020	0.123	97.5	97.5
20	0.69	0.70	0.03[a]	0.68	—	—	—	—	—	—	97.5	97.5
21	2.51	0.19	0.05	0.14	—[b]	—	—	—	—	—	75	92.5
22	1.17	0.59	0.03[a]	0.57	—	—	—	—	—	—	97.5	100
23	0.13	0.21	0.03[a]	0.19	—	—	—	—	—	—	57.5	65
24	1.03	0.62	0.03[a]	0.60	—	—	—	—	—	—	72.5	57.5
25	0.63	0.13	0.20	-0.07	—	—	—	—	—	—	95	90
26	0.30	0.15	0.03[a]	0.13	—	—	—	—	—	—	—	—
27	0.29	0.25	0.03[a]	0.23	—	—	—	—	—	—	35	35
28	0.21	0.12	0.03[a]	0.10	0.0002[c]	0.155	0.0001[e]	0.011	0.0003	0.167	75	72.5
29	0.11	0.20	0.06	0.14	0.0002[c]	0.003	0.0004	0.007	0.0003	0.011	80	82.5
30	0.05	0.04	0.03[a]	0.02	—	—	—	—	—	—	97.5	100
31	0.27	0.85	0.03[a]	0.83	—	—	—	—	—	—	97.5	97.5
32	4.95	1.17	1.66	-0.49	0.012	0.036	0.0004	0.002	0.020	0.070	97.5	95
33	0.54	0.44	0.12	0.32	—	—	—	—	—	—	100	100
34	6.75	1.37	0.09	1.28	0.018	0.041	0.0002	0.017	0.012	0.088	95	90
35	0.18	0.26	0.03[a]	0.24	—	—	—	—	—	—	95	100
36	0.15	0.06	0.05	0.01	—	—	—	—	—	—	95	92.5
37	0.56	0.17	0.05	0.12	—	—	—	—	—	—	—	—
38	0.10	0.22	0.12	0.10	—	—	—	—	—	—	60	55
39	0.06	0.06	0.03[a]	0.04	—	—	—	—	—	—	97.5	100
40	2.68	5.83	0.03[a]	5.81	0.003	0.119	0.001	0.0005[f]	0.020	0.144	90	95
41	0.16	0.16	0.07	0.09	—	—	—	—	—	—	62.5	65
42	1.80	0.56	0.03[a]	0.54	0.006	0.003[d]	0.0006	0.008	0.015	0.033	75	95
43	1.29	1.02	2.25	-1.23	0.0002[c]	0.028	0.002	0.0005[f]	0.044	0.075	100	55
44	0.05	0.06	0.03[a]	0.04	—	—	—	—	—	—	82.5	72.5
45	0.14	0.16	0.05	0.11	—	—	—	—	—	—	—	—
46	0.57	0.66	0.03[a]	0.64	—	—	—	—	—	—	70	67.5

[a] AVS Limit of Detection =0.03 μm S/g.

[b] Insufficient interstitial water volume for metals analysis.

[c] Cadmium LOD=0.01 μg/L (0.0002 IWBU).

[d] Copper LOD=0.2 μg/L (0.0003 IWBU).

[e] Lead LOD=0.1 μg/L (0.0001 IWBU).

[f] Nickel LOD=0.5 μg/L (0.0005 IWBU).

Source: Columns for Sample, TOC, SEM, AVS, SEM-AVS, and IWBU taken directly from Leonard et al. (1996a). Column for survival from personal communication with E.N. Leonard, U.S. EPA, Duluth, Minnesota.

Appendix B

Saltwater Sediment Monitoring Database

Concentrations of SEM, AVS, toxicity, and TOC for EMAP, NOAA NST, and REMAP databases

Study[a]	SEM (µmol/g)	AVS (µmol/g)	SEM-AVS (µmol/g)	Survival[b] %	Significance[c] %	TOC %
EMAP-VA	0.289	1.400	-1.111	100	0	0.60
EMAP-VA	1.500	0.742	0.758	98	0	2.68
EMAP-VA	0.066	0.029	0.037	99	0	0.17
EMAP-VA	0.134	0.028	0.106	103	0	0.14
EMAP-VA	0.266	3.740	-3.474	99	0	0.49
EMAP-VA	0.266	1.080	-0.814	102	0	0.56
EMAP-VA	1.292	1.230	0.062	107	0	1.80
EMAP-VA	0.347	0.087	0.260	102	0	0.30
EMAP-VA	0.750	0.948	-0.198	99	0	0.95
EMAP-VA	0.212	0.283	-0.071	108	0	0.37
EMAP-VA	0.497	0.490	0.007	103	0	1.00
EMAP-VA	0.624	13.400	-12.776	113	0	1.58
EMAP-VA	0.032	0.024	0.008	101	0	0.11
EMAP-VA	0.988	81.100	-80.112	101	0	3.36
EMAP-VA	0.604	3.340	-2.736	107	0	1.38
EMAP-VA	0.031	0.331	-0.300	98	0	0.09
EMAP-VA	1.597	72.400	-70.803	102	0	4.19
EMAP-VA	1.065	8.480	-7.415	93	0	3.17
EMAP-VA	0.189	6.460	-6.271	103	0	0.32
EMAP-VA	0.018	0.034	-0.016	99	0	0.15
EMAP-VA	0.079	0.976	-0.897	97	0	0.14
EMAP-VA	0.421	3.210	-2.789	111	0	0.49
EMAP-VA	0.798	68.000	-67.202	104	0	2.84
EMAP-VA	0.903	3.150	-2.247	99	0	2.85
EMAP-VA	1.202	67.700	-66.498	105	0	2.28
EMAP-VA	0.159	3.310	-3.151	104	0	0.51
EMAP-VA	0.246	4.870	-4.624	106	0	0.71
EMAP-VA	0.687	2.420	-1.733	93	0	1.70
EMAP-VA	0.699	0.430	0.269	91	0	2.05
EMAP-VA	1.663	116.000	-114.337	100	0	4.12
EMAP-VA	0.083	1.300	-1.217	99	0	0.14
EMAP-VA	0.740	0.976	-0.236	101	0	2.30
EMAP-VA	0.878	1.220	-0.342	98	0	2.84
EMAP-VA	0.044	0.025	0.019	106	0	0.15
EMAP-VA	0.910	3.430	-2.520	104	0	3.00
EMAP-VA	0.567	0.621	-0.054	104	0	0.76
EMAP-VA	0.734	25.000	-24.266	107	0	2.21
EMAP-VA	2.171	5.610	-3.439	102	0	2.57
EMAP-VA	3.423	138.000	-134.577	100	0	4.14
EMAP-VA	0.197	0.892	-0.695	107	0	0.37
EMAP-VA	0.162	3.590	-3.428	82	0	0.81
EMAP-VA	2.803	11.900	-9.097	101	0	2.36
EMAP-VA	0.472	12.500	-12.028	101	0	2.77
EMAP-VA	2.079	26.600	-24.521	94	0	3.18
EMAP-VA	0.445	0.056	0.389	106	0	0.20
EMAP-VA	2.228	15.100	-12.872	103	0	2.92
EMAP-VA	0.847	17.300	-16.453	99	0	2.38
EMAP-VA	1.402	52.700	-51.298	109	0	2.70
EMAP-VA	1.425	22.300	-20.875	88	0	3.14
EMAP-VA	0.263	0.079	0.184	84	0	0.27
EMAP-VA	2.936	29.600	-26.664	100	0	4.15
EMAP-VA	0.394	0.031	0.363	87	0	0.18
EMAP-VA	3.074	10.400	-7.326	104	0	2.47
EMAP-VA	2.555	0.402	2.153	96	0	2.18
EMAP-VA	0.452	0.480	-0.028	100	0	1.07
EMAP-VA	0.173	0.201	-0.028	98	0	0.22
EMAP-VA	0.578	0.257	0.321	101	0	0.65

Study[a]	SEM (μmol/g)	AVS (μmol/g)	SEM-AVS (μmol/g)	Survival[b] %	Significance[c] %	TOC %
EMAP-VA	0.209	3.460	-3.251	96	0	0.36
EMAP-VA	5.411	17.800	-12.389	100	0	2.78
EMAP-VA	1.298	0.228	1.070	100	0	0.51
EMAP-VA	1.039	0.705	0.334	102	0	0.30
EMAP-VA	0.960	12.900	-11.940	94	0	1.91
EMAP-VA	7.369	3.460	3.909	87	0	1.86
EMAP-VA	1.380	2.270	-0.890	97	0	0.25
EMAP-VA	4.259	54.600	-50.341	76	0	2.47
EMAP-VA	8.229	68.000	-59.771	43	0	4.98
EMAP-VA	3.535	61.800	-58.265	99	0	3.19
EMAP-VA	2.543	35.600	-33.057	33	0	2.50
EMAP-VA	2.124	35.600	-33.476	0	0	2.15
EMAP-VA	0.188	0.836	-0.648	108	0	0.35
EMAP-VA	0.229	0.692	-0.463	95	0	0.46
EMAP-VA	1.820	0.227	1.593	104	0	1.90
EMAP-VA	3.468	14.600	-11.132	102	0	2.08
EMAP-VA	1.622	6.080	-4.458	102	0	2.02
EMAP-VA	0.693	1.200	-0.507	99	0	1.11
EMAP-VA	0.294	0.026	0.268	95	0	0.38
EMAP-VA	0.178	0.074	0.104	81	0	0.42
EMAP-VA	0.223	0.087	0.136	104	0	0.43
EMAP-VA	0.239	1.120	-0.881	88	0	0.31
EMAP-VA	0.801	5.120	-4.319	92	0	1.88
EMAP-VA	0.751	0.090	0.661	102	0	0.66
EMAP-VA	0.299	0.090	0.209	104	0	0.43
EMAP-VA	0.341	0.174	0.167	105	0	0.99
EMAP-VA	0.205	0.611	-0.406	95	0	0.71
EMAP-VA	2.415	4.050	-1.635	100	0	2.25
EMAP-VA	0.632	28.200	-27.568	88	0	3.35
EMAP-VA	1.516	52.700	-51.184	85	0	7.01
EMAP-VA	3.249	12.300	-9.051	103	0	3.29
EMAP-VA	0.462	6.140	-5.678	108	0	2.19
EMAP-VA	0.043	0.024	0.019	100	0	0.18
EMAP-VA	0.050	0.025	0.025	102	0	0.17
EMAP-VA	1.177	3.460	-2.283	100	0	1.83
EMAP-VA	0.624	6.210	-5.586	104	0	2.25
EMAP-VA	0.799	29.700	-28.901	100	0	4.10
EMAP-VA	0.020	0.259	-0.239	96	0	0.30
EMAP-VA	0.088	4.150	-4.062	100	0	0.25
EMAP-VA	2.220	59.600	-57.380	74	0	2.18
EMAP-VA	0.813	0.381	0.432	93	0	0.98
EMAP-VA	0.851	0.029	0.822	87	0	0.57
NOAA- LI	0.701	3.600	-2.899	100	0	0.74
NOAA- LI	1.113	3.510	-2.397	96	0	1.12
NOAA- LI	0.601	6.440	-5.839	96	0	1.43
NOAA- LI	1.505	18.730	-17.225	93	0	2.56
NOAA- LI	0.701	5.630	-4.930	93	0	0.77
NOAA- LI	0.717	13.090	-12.373	93	0	2.05
NOAA- LI	2.163	65.310	-63.147	92	0	3.22
NOAA- LI	0.616	6.940	-6.324	92	0	0.81
NOAA- LI	2.368	19.990	-17.622	91	0	3.02
NOAA- LI	1.278	4.710	-3.432	91	0	1.81
NOAA- LI	2.253	59.590	-57.337	91	0	2.51
NOAA- LI	0.865	3.880	-3.015	91	0	1.32
NOAA- LI	0.950	16.520	-15.570	90	0	1.52
NOAA- LI	1.113	14.950	-13.837	89	0	2.00

Study[a]	SEM (μmol/g)	AVS (μmol/g)	SEM-AVS (μmol/g)	Survival[b] %	Significance[c] %	TOC %
NOAA- LI	1.026	0.850	0.176	88	0	1.63
NOAA- LI	1.446	12.480	-11.034	88	0	2.05
NOAA- LI	2.777	29.720	-26.943	87	0	2.81
NOAA- LI	0.211	0.090	0.121	87	0	0.54
NOAA- LI	2.665	78.900	-76.235	87	0	3.33
NOAA- LI	2.813	35.050	-32.237	86	0	3.83
NOAA- LI	1.235	2.080	-0.844	84	0	1.58
NOAA- LI	2.198	14.690	-12.492	84	0	2.80
NOAA- LI	3.624	21.800	-18.176	83	0	2.48
NOAA- LI	3.594	27.410	-23.816	82	0	2.59
NOAA- LI	1.342	37.970	-36.628	82	0	1.85
NOAA- LI	2.462	46.450	-43.988	82	0	3.18
NOAA- LI	0.964	1.000	-0.036	81	0	1.60
NOAA- LI	0.332	4.010	-3.678	81	0	1.29
NOAA- LI	2.311	79.890	-77.579	81	0	3.69
NOAA- LI	0.623	6.610	-5.987	80	0	0.67
NOAA- LI	0.896	16.370	-15.475	80	0	1.11
NOAA- LI	0.544	2.170	-1.626	79	1	0.27
NOAA- LI	0.641	2.060	-1.419	79	1	1.56
NOAA- LI	0.355	1.390	-1.035	79	1	0.64
NOAA- LI	0.222	4.180	-3.958	77	1	0.45
NOAA- LI	2.262	39.960	-37.698	77	1	2.67
NOAA- LI	1.307	0.380	0.927	76	1	1.56
NOAA- LI	1.963	51.820	-49.857	76	1	3.46
NOAA- LI	2.785	61.020	-58.235	76	1	3.81
NOAA- LI	4.333	16.080	-11.747	75	1	3.48
NOAA- LI	1.927	3.710	-1.783	75	1	1.60
NOAA- LI	0.004	24.580	-24.576	74	1	2.87
NOAA- LI	3.831	9.250	-5.419	73	1	3.08
NOAA- LI	0.808	0.960	-0.152	71	1	1.19
NOAA- LI	1.783	40.630	-38.847	70	1	2.50
NOAA- LI	2.622	61.840	-59.218	70	1	3.49
NOAA- LI	0.597	1.090	-0.493	69	1	0.76
NOAA- LI	1.181	3.730	-2.549	68	1	0.91
NOAA- LI	1.862	50.390	-48.528	67	1	2.81
NOAA- LI	2.726	62.760	-60.034	67	1	2.81
NOAA- LI	2.102	33.630	-31.528	64	1	3.42
NOAA- LI	2.471	7.220	-4.749	63	1	2.80
NOAA- LI	1.870	17.120	-15.250	61	1	3.29
NOAA- LI	1.607	17.810	-16.203	59	1	2.07
NOAA- LI	4.942	100.800	-95.858	54	1	3.15
NOAA- LI	2.705	83.010	-80.305	53	1	3.62
NOAA- LI	2.087	26.730	-24.643	47	1	3.45
NOAA- LI	1.514	30.880	-29.366	42	1	2.69
NOAA- LI	2.629	32.050	-29.421	39	1	2.68
NOAA- LI	3.194	35.390	-32.196	37	1	3.17
NOAA- LI	0.872	25.810	-24.938	34	1	1.83
NOAA- LI	1.080	11.300	-10.220	16	1	1.91
NOAA- LI	0.123	5.310	-5.187	10	1	0.22
NOAA- BO	2.914	2.893	0.021	8	1	3.05
NOAA- BO	2.218	2.369	-0.151	15	1	2.89
NOAA- BO	2.609	43.959	-41.350	26	1	3.74
NOAA- BO	3.650	101.984	-98.334	29	1	1.83
NOAA- BO	1.634	5.237	-3.603	36	1	1.72
NOAA- BO	1.267	3.256	-1.989	52	1	1.53
NOAA- BO	2.892	80.584	-77.692	83	0	6.98

Study[a]	SEM (μmol/g)	AVS (μmol/g)	SEM-AVS (μmol/g)	Survival[b] %	Significance[c] %	TOC %
NOAA- BO	2.511	2.241	0.270	86	0	2.12
NOAA- BO	0.661	13.490	-12.829	87	0	1.00
NOAA- BO	2.458	23.077	-20.619	87	0	3.15
NNOAA- BO	1.872	48.062	-46.190	89	0	3.25
NOAA- BO	0.959	53.288	-52.329	90	0	2.39
NOAA- BO	2.480	7.599	-5.119	90	0	4.45
NOAA- BO	0.784	22.486	-21.702	91	0	1.88
NOAA- BO	0.943	8.831	-7.888	91	0	1.78
NOAA- BO	1.683	42.399	-40.716	92	0	3.41
NOAA- BO	1.753	17.697	-15.944	94	0	1.41
NOAA- BO	2.447	10.958	-8.511	94	0	4.45
NOAA- BO	1.839	68.306	-66.467	95	0	2.54
NOAA- BO	1.296	56.838	-55.542	96	0	3.05
NOAA- BO	1.697	9.089	-7.392	97	0	2.68
NOAA- BO	1.390	43.801	-42.411	97	0	3.27
NOAA- BO	2.310	51.857	-49.547	97	0	3.35
NOAA- BO	0.399	3.899	-3.500	99	0	0.80
NOAA- BO	2.481	19.604	-17.123	99	0	3.31
NOAA- BO	1.736	148.969	-147.233	99	0	2.94
NOAA- BO	0.958	18.622	-17.664	99	0	1.77
NOAA- BO	9.192	120.622	-111.430	100	0	4.61
NOAA- BO	1.525	81.842	-80.317	102	0	2.96
NOAA- BO	0.678	5.679	-5.001	103	0	1.45
NOAA- HR	5.037	69.320	-64.283	0	1	5.02
NOAA- HR	4.202	21.980	-17.778	41	1	3.47
NOAA- HR	1.174	27.540	-26.366	11	1	1.88
NOAA- HR	1.855	14.170	-12.315	18	1	4.44
NOAA- HR	3.092	51.770	-48.678	101	0	3.86
NOAA- HR	2.997	79.710	-76.713	112	0	3.09
NOAA- HR	2.581	61.050	-58.469	119	0	2.86
NOAA- HR	2.869	28.080	-25.211	81	0	2.50
NOAA- HR	5.442	25.900	-20.458	95	0	2.20
NOAA- HR	2.618	1.080	1.538	109	0	2.67
NOAA- HR	5.061	12.240	-7.179	97	0	2.98
NOAA- HR	2.376	4.390	-2.014	108	0	2.49
NOAA- HR	6.998	63.450	-56.452	0	1	1.98
NOAA- HR	4.480	20.780	-16.300	20	1	2.98
NOAA- HR	4.662	23.720	-19.058	14	1	3.19
NOAA- HR	5.896	51.580	-45.684	2	1	4.78
NOAA- HR	3.103	59.780	-56.677	77	1	3.99
NOAA- HR	1.662	7.230	-5.568	19	1	2.61
NOAA- HR	3.512	25.840	-22.328	0	1	4.44
NOAA- HR	0.273	0.050	0.223	91	0	0.07
NOAA- HR	0.335	0.036	0.299	93	0	0.07
NOAA- HR	1.664	18.760	-17.096	69	1	0.69
NOAA- HR	2.674	3.630	-0.956	3	1	1.00
NOAA- HR	5.532	29.210	-23.678	96	0	3.18
NOAA- HR	4.029	18.440	-14.411	51	1	2.20
NOAA- HR	4.614	20.530	-15.916	91	0	1.94
NOAA- HR	3.379	30.120	-26.741	88	0	2.80
NOAA- HR	4.240	19.320	-15.080	101	0	3.15
NOAA- HR	4.303	22.570	-18.267	102	0	3.02
NOAA- HR	5.209	14.570	-9.361	101	0	3.21
NOAA- HR	4.801	35.370	-30.569	70	1	2.98
NOAA- HR	4.697	54.710	-50.013	38	1	3.47
NOAA- HR	2.600	56.730	-54.130	37	1	1.47

Study[a]	SEM (μmol/g)	AVS (μmol/g)	SEM-AVS (μmol/g)	Survival[b] %	Significance[c] %	TOC %
NOAA- HR	1.013	10.160	-9.147	29	1	0.77
NOAA- HR	1.527	15.130	-13.603	68	1	0.95
NOAA- HR	0.505	0.630	-0.125	105	0	0.25
NOAA- HR	3.341	43.920	-40.579	86	0	2.55
NOAA- HR	3.449	37.860	-34.411	76	1	3.63
NOAA- BA	0.270	0.950	-0.680	96	0	0.26
REMAP-BA	0.341	0.156	0.185	84	0	0.06
REMAP-BA	0.888	12.971	-12.083	92	0	4.05
REMAP-BA	0.722	4.948	-4.226	85	0	0.40
REMAP-BA	0.362	0.936	-0.574	98	0	0.26
REMAP-BA	2.138	3.295	-1.157	95	0	0.43
REMAP-BA	3.008	3.941	-0.933	95	0	0.18
REMAP-BA	0.151	0.555	-0.404	96	0	0.15
REMAP-BA	0.115	0.156	-0.041	99	0	0.08
REMAP-BA	0.543	0.156	0.387	94	0	0.07
REMAP-BA	0.103	0.156	-0.053	85	0	0.05
REMAP-BA	0.167	0.932	-0.765	97	0	0.16
REMAP-BA	0.073	0.156	-0.083	99	0	0.05
REMAP-BA	0.294	0.156	0.138	91	0	0.34
REMAP-BA	0.120	0.156	-0.036	84	0	0.83
REMAP-BA	0.109	0.156	-0.047	92	0	0.92
REMAP-BA	0.185	0.156	0.029	90	0	4.48
REMAP-BA	0.120	0.156	-0.036	88	0	0.83
REMAP-BA	0.347	0.156	0.191	89	0	1.26
REMAP-BA	0.120	0.156	-0.036	81	0	0.62
REMAP-BA	2.275	16.592	-14.317	69	1	1.81
REMAP-BA	0.344	0.012	0.332	91	0	3.85
REMAP-BA	0.258	0.343	-0.085	94	0	0.77
REMAP-BA	0.119	0.156	-0.037	84	0	2.23
REMAP-BA	0.258	0.156	0.102	91	0	0.88
REMAP-BA	0.494	0.156	0.338	86	0	2.10
REMAP-BA	0.109	0.156	-0.047	89	0	4.07
REMAP-BA	0.266	0.156	0.110	86	0	1.06
REMAP-JB	0.327	0.393	-0.066	93	0	0.29
REMAP-JB	0.230	6.400	-6.170	83	0	0.19
REMAP-JB	2.026	47.793	-45.767	51	1	0.77
REMAP-JB	14.550	389.857	-375.307	0	1	1.52
REMAP-JB	3.332	243.322	-239.990	37	1	0.83
REMAP-JB	3.763	201.687	-197.924	79	1	0.97
REMAP-JB	0.357	10.923	-10.566	95	0	0.26
REMAP-JB	0.524	3.974	-3.450	98	0	0.35
REMAP-JB	0.244	4.502	-4.258	84	0	0.27
REMAP-JB	1.247	48.130	-46.883	91	0	0.54
REMAP-JB	2.478	47.376	-44.898	36	1	1.12
REMAP-JB	1.744	0.156	1.588	69	1	1.14
REMAP-JB	0.131	1.184	-1.053	94	0	0.21
REMAP-JB	0.846	0.927	-0.081	73	1	1.58
REMAP-JB	4.399	116.954	-112.555	93	0	6.55
REMAP-JB	3.884	237.650	-233.766	89	0	8.45
REMAP-JB	0.673	21.769	-21.096	77	1	4.11
REMAP-JB	3.150	43.975	-40.825	91	0	5.47
REMAP-JB	0.270	4.491	-4.221	91	0	0.74
REMAP-JB	0.162	0.873	-0.711	98	0	1.40
REMAP-JB	2.880	153.755	-150.875	92	0	7.70
REMAP-JB	0.323	1.684	-1.361	93	0	0.20
REMAP-JB	0.413	3.056	-2.643	94	0	1.20

Study[a]	SEM (μmol/g)	AVS (μmol/g)	SEM-AVS (μmol/g)	Survival[b] %	Significance[c] %	TOC %
REMAP-JB	0.377	3.056	-2.679	92	0	1.30
REMAP-JB	0.099	0.686	-0.587	93	0	0.75
REMAP-JB	1.100	58.945	-57.845	96	0	3.86
REMAP-JB	0.209	1.466	-1.257	93	0	0.58
REMAP-JB	0.213	0.780	-0.567	95	0	0.69
REMAP-LS	0.954	1.542	-0.588	83	0	0.26
REMAP-LS	2.759	6.498	-3.739	96	0	0.45
REMAP-LS	0.711	10.240	-9.529	97	0	0.56
REMAP-LS	1.915	12.596	-10.681	97	0	0.21
REMAP-LS	2.186	17.605	-15.419	95	0	0.27
REMAP-LS	2.480	23.523	-21.043	99	0	0.32
REMAP-LS	0.606	2.501	-1.895	98	0	0.25
REMAP-LS	3.289	91.773	-88.484	95	0	0.77
REMAP-LS	3.241	56.100	-52.859	97	0	1.14
REMAP-LS	0.616	1.070	-0.454	95	0	0.15
REMAP-LS	1.506	26.201	-24.695	96	0	0.95
REMAP-LS	2.485	28.248	-25.763	96	0	0.25
REMAP-LS	1.894	25.394	-23.500	93	0	0.98
REMAP-LS	3.149	64.643	-61.494	93	0	0.90
REMAP-LS	0.632	1.310	-0.678	87	0	1.51
REMAP-LS	1.057	4.647	-3.590	90	0	2.44
REMAP-LS	0.638	0.218	0.420	92	0	3.52
REMAP-LS	1.087	0.312	0.775	90	0	7.36
REMAP-LS	3.711	17.184	-13.473	88	0	3.99
REMAP-LS	2.990	59.256	-56.266	80	0	5.24
REMAP-LS	8.894	60.816	-51.922	85	0	3.63
REMAP-LS	1.277	23.266	-21.989	92	0	3.18
REMAP-LS	3.925	42.727	-38.802	90	0	3.85
REMAP-LS	5.632	114.770	-109.138	86	0	4.29
REMAP-LS	6.809	135.354	-128.545	91	0	4.36
REMAP-LS	7.645	150.012	-142.367	92	0	6.04
REMAP-LS	4.012	43.663	-39.651	86	0	3.73
REMAP-LS	3.905	26.229	-22.324	89	0	3.93
REMAP-NB	0.942	6.531	-5.589	84	0	0.67
REMAP-NB	3.515	7.134	-3.619	87	0	0.75
REMAP-NB	2.216	11.243	-9.027	86	0	1.22
REMAP-NB	3.323	7.573	-4.250	85	0	1.25
REMAP-NB	3.391	4.820	-1.429	83	0	1.05
REMAP-NB	3.443	3.982	-0.539	95	0	0.88
REMAP-NB	2.466	20.273	-17.807	82	0	1.40
REMAP-NB	2.294	11.046	-8.752	84	0	0.95
REMAP-NB	5.768	5.028	0.740	75	1	1.77
REMAP-NB	1.013	11.079	-10.066	90	0	0.76
REMAP-NB	2.479	25.687	-23.208	83	0	0.99
REMAP-NB	0.554	2.634	-2.080	84	0	0.60
REMAP-NB	5.222	22.617	-17.395	83	0	1.48
REMAP-NB	5.116	7.352	-2.236	9	1	1.45
REMAP-NB	14.791	109.780	-94.989	8	1	9.15
REMAP-NB	4.917	0.530	4.387	89	0	3.10
REMAP-NB	0.398	0.218	0.180	94	0	2.42
REMAP-NB	4.855	9.606	-4.751	83	0	2.62
REMAP-NB	3.290	10.105	-6.815	60	1	5.70
REMAP-NB	5.822	51.460	-45.638	41	1	2.22
REMAP-NB	9.167	93.563	-84.396	25	1	6.48
REMAP-NB	6.214	42.415	-36.201	68	1	3.24
REMAP-NB	0.794	2.651	-1.857	93	0	2.36

Study[a]	SEM (μmol/g)	AVS (μmol/g)	SEM-AVS (μmol/g)	Survival[b] %	Significance[c] %	TOC %
REMAP-NB	4.985	43.663	-38.678	53	1	3.90
REMAP-NB	5.280	1.934	3.346	83	0	6.10
REMAP-NB	2.268	6.300	-4.032	16	1	1.99
REMAP-NB	6.678	17.559	-10.881	77	1	15.20
REMAP-NB	2.833	45.222	-42.389	54	1	2.02
REMAP-RB	0.333	22.315	-21.982	93	0	1.23
REMAP-RB	0.756	1.216	-0.460	92	0	0.33
REMAP-RB	0.582	0.821	-0.239	94	0	0.30
REMAP-RB	1.012	0.567	0.445	94	0	0.30
REMAP-RB	1.596	0.447	1.149	95	0	0.17
REMAP-RB	0.326	0.156	0.170	93	0	0.08
REMAP-RB	2.709	3.120	-0.411	70	1	0.42
REMAP-RB	5.485	14.666	-9.181	92	0	2.29
REMAP-RB	3.596	19.503	-15.907	62	1	0.88
REMAP-RB	5.329	4.321	1.008	91	0	0.97
REMAP-RB	0.337	2.901	-2.564	97	0	0.53
REMAP-RB	0.986	0.156	0.830	96	0	0.12
REMAP-RB	0.856	0.156	0.700	96	0	0.51
REMAP-RB	5.364	39.700	-34.336	91	0	1.17
REMAP-RB	1.706	23.515	-21.809	93	0	3.21
REMAP-RB	0.371	4.210	-3.839	91	0	3.54
REMAP-RB	0.193	0.156	0.037	92	0	2.52
REMAP-RB	0.869	19.617	-18.748	85	0	2.39
REMAP-RB	1.288	0.593	0.695	92	0	2.44
REMAP-RB	1.650	0.624	1.026	91	0	2.68
REMAP-RB	2.422	0.156	2.266	98	0	2.60
REMAP-RB	0.512	0.156	0.356	93	0	0.42
REMAP-RB	4.198	4.086	0.112	90	0	2.63
REMAP-RB	5.081	36.490	-31.409	89	0	2.08
REMAP-RB	6.095	5.957	0.138	4	1	3.03
REMAP-RB	8.471	8.078	0.393	91	0	5.30
REMAP-RB	3.370	17.247	-13.877	94	0	3.91
REMAP-RB	1.198	0.156	1.042	94	0	1.03
REMAP-UH	2.127	12.446	-10.319	83	0	3.43
REMAP-UH	1.360	1.790	-0.430	99	0	1.26
REMAP-UH	1.197	3.373	-2.176	92	0	5.85
REMAP-UH	1.975	17.136	-15.161	45	1	2.33
REMAP-UH	2.829	25.189	-22.360	84	0	0.91
REMAP-UH	2.830	56.401	-53.571	96	0	1.21
REMAP-UH	1.385	44.588	-43.203	88	0	1.03
REMAP-UH	1.519	11.549	-10.030	82	0	1.06
REMAP-UH	3.186	86.235	-83.049	93	0	1.39
REMAP-UH	2.086	11.713	-9.627	82	0	0.79
REMAP-UH	1.799	12.631	-10.832	37	1	1.06
REMAP-UH	0.930	10.093	-9.163	89	0	0.43
REMAP-UH	0.459	0.156	0.303	98	0	0.13
REMAP-UH	0.889	2.623	-1.734	95	0	0.21
REMAP-UH	0.833	2.464	-1.631	86	0	4.96
REMAP-UH	1.317	15.563	-14.246	88	0	2.56
REMAP-UH	2.480	32.123	-29.643	87	0	3.06
REMAP-UH	0.626	9.949	-9.323	97	0	2.58
REMAP-UH	1.500	5.427	-3.927	89	0	2.71
REMAP-UH	0.723	1.341	-0.618	89	0	3.89
REMAP-UH	4.158	13.504	-9.346	96	0	4.78
REMAP-UH	2.241	27.788	-25.547	70	1	2.66
REMAP-UH	2.907	29.285	-26.378	95	0	5.15

Study[a]	SEM (μmol/g)	AVS (μmol/g)	SEM-AVS (μmol/g)	Survival[b] %	Significance[c] %	TOC %
REMAP-UH	0.852	1.591	-0.739	93	0	2.03
REMAP-UH	2.294	53.955	-51.661	15	1	4.37
REMAP-UH	2.995	33.995	-31.000	88	0	3.55
REMAP-UH	2.981	44.910	-41.929	94	0	2.97
REMAP-UH	0.677	10.323	-9.646	91	0	3.32

[a] *Sources*: EMAP-VA is U.S. EPA, 1996. NOAA-LI is Wolfe et al., 1994. NOAA-BO is Long et al., 1996. NOAA-HR is Long et al., 1995b. REMAP is Adams et al., 1996.

[b] Conclusion of significance varies for three databases. EMAP significance based on percent survival of control. NOAA significance based on percent survival less than 80%. REMAP significance based on percent survival less than 80%.

[c] Significance: 0, no significant toxicity; 1, significant toxicity.

Appendix C

Quality Assurance Summary for the ESB Document: Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: Metal Mixtures (Cadmium, Copper, Lead, Nickel, Silver, and Zinc)

All data were obtained either from the WQC document for the metals cadmium, copper, lead, nickel, silver, and zinc (USEPA, 1980, 1985b, c, d, 1986, 1987) or from a comprehensive literature search completed in 1999 and updated in 2004. Data for the chromium appendix was obtained from a comprehensive literature search completed in 2004.

All data used in the example benchmark calculations were evaluated for acceptability using the procedures outlined in the Stephan et al. (1985): *Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses*. Data not meeting the criteria were rejected. The approach for deriving the values in this document were also reviewed by the U.S. EPA SAB (U.S. EPA, 1994a; 1995a; 1999). All calculations were made using the procedures in Stephan et al. (1985). This document was reviewed for scientific quality assurance by U.S. EPA Office of Water and Office of Research and Development scientists.

Hard copies of all literature cited in this document reside at ORD/NHEERL Atlantic Ecology Division - Narragansett, Rhode Island.

Appendix D

Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmark (ESBs) for the Protection of Benthic Organisms: Chromium

Executive Summary

Chromium exists in sediments primarily in two oxidation states: Cr(III), which is relatively insoluble and nontoxic, and Cr(VI), which is much more soluble and toxic. Cr(VI) is thermodynamically unstable in anoxic sediments and AVS is formed only in anoxic sediments; therefore sediments with measurable AVS concentrations should not contain toxic Cr(VI). If this "chromium hypothesis" holds true, measuring AVS could form the basis for an ESB for chromium in sediments.

A review of the literature and recently performed experiments with both freshwater and saltwater sediments support the chromium hypothesis.

In saltwater:

1) Survival of amphipods was decreased by waterborne Cr(VI), with a 10-day median lethal concentration (LC50) of 1850 µg/L Cr(VI).
2) Survival of amphipods was not decreased by waterborne Cr(III) at concentrations well above saturation.
3) In both laboratory-spiked sediments with Cr(III) and Cr(VI) and field-contaminated sediments, in sediments where detectable AVS was present, chromium concentrations in interstitial water were very low (<100 µg/L) and no significant lethality to *A. abdita* was observed. In sediments in which AVS was not significantly greater than zero, chromium concentrations in interstitial waters increased significantly, with greater than 90% of the chromium present as Cr(VI), and the mortality of *A. abdita* was elevated.

In freshwater:

1) Survival of amphipods was decreased by waterborne Cr(VI), with a 42-day LC50 of 40 µg/L.
2) Cr(VI) spiked into test sediments with differing levels of AVS resulted in graded decreases in AVS.
3) Sediments with low AVS concentrations (<1 µmol/g) after spiking with Cr(VI) caused 100% mortality of amphipods, but no toxic effects were observed in Cr(VI)-spiked sediments that maintained higher AVS concentrations.
4) Waterborne Cr(III) levels near solubility limits caused decreased survival of amphipods at pH 7 and pH 8, but not at pH 6.
5) Sediments spiked with high levels of Cr(III) had no effect on amphipod survival, but caused significant decreases in reproduction and/or growth.
6) Interstitial waters of some Cr(III)-spiked sediments contained measurable concentrations of Cr(VI), but observed toxic effects did not correspond closely to concentrations of aqueous Cr species.

Thus, although both Cr(VI) and Cr(III) could be toxic to *H. azteca* in water and sediment, risks of Cr toxicity were low in sediments containing substantial concentrations of AVS. Results presented in this appendix suggest that measurements of AVS and interstitial water chromium can be useful in predicting the absence of acute effects from chromium contamination in both freshwater and saltwater sediments. In sediments with substantial AVS, risks of chromium toxicity should be low, because the chromium will be present in the form of Cr (III). This should apply to any sediment with SEM-AVS < 0.0. Sediments with SEM-AVS > 0.0, but which have substantial AVS present may be toxic due to copper, cadmium, lead nickel, or zinc, but should not be toxic due to chromium or silver. The relationship, (SEM-AVS)/f_{OC}, should be used with caution (with regard to chromium toxicity) in sediments with little or no AVS, because a sediment with no appreciable AVS or SEM and substantial chromium might be toxic due to chromium, even though no toxicity due to the other metals would be expected. These findings form the basis for a chromium ESB.

Section 1

Introduction

Chromium is often found in contaminated sediments (Pawlitz et al., 1977). Elevated chromium concentrations in sediments are usually associated with tanneries, smelters, and plating facilities. However, without a good understanding of the adverse biological effects of chromium in sediments, it is difficult to know what concentration of chromium in sediment may present ecological risk to benthos.

Although there have been several studies on the bioaccumulation of chromium from laboratory-spiked sediments (Wang et al., 1997; Griscom et al., 2000; Fan and Wang., 2001), there are few published studies on biological effects of chromium in laboratory-spiked sediments other than uptake of chromium. There are also very few reports on effects of chromium in field sediments. Leslie et al. (1999) found that a tributary below a chromium salt processing plant was incapable of supporting benthic macrofauna, presumably because of chromium leaching from stock piles along the banks of the tributary, but concluded that much of the chromium might be coming from the water rather than the sediment. In a study of sediments associated with a tannery, some toxicity was observed in ten-day static toxicity tests with several sediments with chromium in excess of 4000 µg/g; the same sediments, however, exhibited no toxicity in 28-day flow-through tests, suggesting that the toxicity observed in the 10-day static test was related to test conditions and duration and not sediment chromium (HydroQual, 1994). Several other studies have found elevated chromium concentrations in the tissues of benthos from sediments contaminated with high levels of chromium from mining activities (Bervoets et al., 1998) or tannery wastes (Catsiki et al., 1994), but these tissue concentrations were not linked to biological effects.

Part of the difficulty in understanding the biological effects of chromium in sediment is that chromium exists in sediments in two oxidation states, Cr(III) and Cr(VI), each with very different geochemical properties and toxicological effects. Cr(VI) is highly oxidized and unstable in reducing and even moderately oxidizing environments (DeLaune et al., 1998, Masscheleyn et al., 1992). Cr(VI) is also very soluble and highly toxic, while Cr(III) has very low solubility at environmentally relevant pH (DeLaune et al., 1998; Barnhart., 1997) and is generally thought to have relatively low toxicity (Wang et al., 1997; Thompson et al., 2002). For example, Leslie et al. (1999) assumed that the effects they saw due to chromium must have been caused by Cr(VI). However, they did not measure the chromium speciation.

This appendix provides the technical basis for the derivation of an ESB for chromium analogous to the ESB for the cationic metals cadmium, copper, lead, nickel, silver, and zinc discussed earlier. Determining the relationship between AVS and chromium in sediments would extend the utility of AVS measurements as a part of sediment assessments. Chromium should not necessarily be included among the SEM metals because its interaction with AVS is not via formation of an insoluble sulfide, but rather oxidation of sulfide and concomitant reduction of chromium. However, the geochemical relationship between AVS and chromium and the toxicological differences between oxidation states of chromium might be used to develop a theoretically-derived benchmark through what is called the "chromium hypothesis." The hypothesis is based on the concepts that Cr(III) is much less soluble and toxic than Cr(VI) and that Cr(VI) is not stable in reducing environments such as anoxic sediments in which AVS is formed. Thus, in a sediment where AVS is present, chromium will exist solely as Cr(III), and therefore the interstitial water should contain little chromium and the sediment should not be toxic due to chromium.

Although there is literature discussing chromium toxicity and geochemistry, no studies were available which had tested the "chromium hypothesis" directly. To this end, recently, experiments have been carried out with both freshwater (Besser et al., *in press*) and saltwater sediments (Berry et al., *in press*) to verify the chromium hypothesis. In the saltwater test series ten-day water-only and ten-day spiked sediment toxicity tests with the amphipod *Ampelisca abdita* were performed with Cr(VI) and Cr(III). Ten-day sediment tests with saltwater sediments collected from a site contaminated with high concentrations of chromium were also performed. In freshwater sediments, chronic (28- to 42-d) water-only and spiked sediment toxicity tests with the amphipod *Hyalella azteca* were performed with Cr(VI) and Cr(III).

Section 2

Chemistry of Chromium in Sediment

2.1 Valence States of Chromium in Sediments

Studies by many researchers have provided a generalized model of the cycling of chromium between redox states in various aquatic soils/ sediments and their interstitial and overlying waters (Masscheleyn et al., 1992; Kozuh et al., 2000; Hassan and Garrison., 1996; Mattuck and Nikolaidis., 1996). This model is characterized by the relative stability of Cr(VI) in oxygenated overlying waters, particularly in marine waters, and rapid removal of Cr(III) through precipitation of the insoluble hydroxide and adsorption onto particulate matter. In freshwater systems with elevated dissolved organic carbon concentrations, such as in wetland soils and waters, a considerable amount of Cr(III) may be organically complexed, which slows the rate of removal to the particulate matter. In some circumstances, Cr(III) may be oxidized to Cr(VI) by Fe/Mn-rich films on the air-water interface where reduced Mn(II) and Fe(II) diffuses from sediments into oxic overlying water (Masscheleyn et al., 1992).

In sediments and soils, the reactivities of Cr(III) and Cr(VI) are somewhat reversed. Cr(III) may be oxidized to Cr(VI) in soils or sediments with high concentrations of MnO_2 and low organic content apparently by oxidation at MnO_2 surfaces (Hassan and Garrison., 1996). Similar oxidation by resuspended sediments rich in manganese oxides has also been postulated as the cause for relatively higher concentrations of Cr(VI) in deep ocean seawater relative to seawater overlying reduced coastal sediments (Nakayama et al., 1981). If organic content is elevated, however, Cr(III) is not oxidized, even in highly oxidizing sediments (Masscheleyn et al., 1992; Kozuh et al., 2000). On the other hand, Cr(VI) is reduced to Cr(III) and almost completely removed from solution in even moderately oxidizing sediments (redox potential $E_h < 300$ mV). In more reducing sediments ($E_h < 200$ mV), reduction is significantly more rapid due to reaction with ferrous ionic Fe(II). In such reduced sediments, very high partitioning constants indicate that almost all chromium is bound to the sediment, presumably as Cr(III), with very little mobile in interstitial waters (Mattuck and Nikolaidis., 1996). In wetland sediments, much of the dissolved chromium may be organically complexed Cr(III) (Icopini and Long, 2002). Once the reductive capacity of soils or sediments is exceeded, concentrations of dissolved Cr(VI) increase sharply and remain stable. Although the reductive capacity of sediments is generally proportional to organic content, the primary reductant is more likely Fe(II) or, in sulfidic sediments, sulfide.

2.2 Geochemical Distribution of Chromium in Toxicological Exposures

The geochemical distributions found in the recent experiments with marine sediments (Berry et al., *in press*) amended with Cr(VI) and Cr(III) reflected the behavior described in the previous section. Although the sediments had differing characteristics such as silt/clay and organic contents, they were both reducing sediments, as evidenced by the presence of AVS. Cr(III) added to these sediments in massive quantities was essentially inert to redox transformation: no Cr(VI) was evident in sediments, interstitial waters or overlying waters throughout the experiment, as was the case with organic-rich peat soils and wetland sediments. Cr(VI) added to the sediments was reduced completely and rapidly (<1 day), regardless of the amount added, up to the reductive capacity of the sediments. No significant amount of chromium was evident in either interstitial or overlying waters, indicating that Cr(III) complexed by dissolved organic carbon was not important in these sediments. Once the capacity of the sediments were exceeded, very high concentrations of chromium, almost entirely Cr(VI), were evident in interstitial waters (Figure D-1). Concentrations of chromium in overlying waters decreased throughout the experiment and remained primarily as Cr(VI). These geochemical controls on the concentrations and redox speciation of chromium in sediments constrain exposure and consequent biological effects of the chromium on benthic organisms, such as the amphipods used in the saltwater tests.

In a recent study, spiking of freshwater sediments (Besser et al., *in press*) with several levels of Cr(VI) resulted in graded decreases in AVS concentrations and changes in POC concentrations in sediment and interstitial water. For example, mean AVS concentrations decreased by up to 97% in study sediments on day 0 of the test. Sediment TOC also decreased slightly in Cr(VI)-spiked sediments. Cr(VI) spikes were associated with increased DOC, increased alkalinity, and decreased hardness in interstitial waters.

Overlying and interstitial water Cr(VI) concentrations reflected differences in AVS concentrations among treatments. Initial concentrations of Cr(VI) in interstitial water samples were greater than 10,000 µg/L in treatments with the lowest AVS concentrations while interstitial water Cr(VI) concentrations remained low (≤20 µg/L) in treatments with higher AVS concentrations. In all three treatments with quantifiable Cr(VI) in interstitial water, concentrations decreased during the test. Cr(VI) concentrations in overlying water were much lower than those in interstitial water, but followed similar trends among treatments and over time. Decreases in Cr(VI) concentrations during the course of the study may have resulted from reactions with AVS and POC and from dilution due to replacement of overlying water. The smallest proportional decrease of Cr(VI) in interstitial and overlying water occurred in the treatment which had no AVS and low POC.

These results are consistent with the hypothesis that Cr(VI) concentrations remain low in sediments containing substantial concentrations of AVS. Berry et al. (*in press*), in studies with Cr(VI)-spiked marine sediments, did not detect Cr(VI) in interstitial waters of sediments spiked with Cr(VI) at Cr:AVS ratios of 2.2 or less. In contrast, substantial Cr(VI) concentrations were measured in sediments spiked at 3:1 Cr:AVS ratios (Besser et al., *in press*). AVS may have persisted in these treatments due to regeneration of AVS during the test, at least in some treatments. However, the data also suggested that some added Cr(VI) reacted with sediment POC, as has been reported in several previous studies (Wittbrodt and Palmer., 1995; Elovitz and Fish., 1995; U.S.EPA., 2002; Poleo., 1995). The relationship between Cr(VI) spikes and AVS depletion in one freshwater sediment was similar to the 2:1 ratio reported by Berry et al. (*in press*). However, AVS concentrations in a high-POC sediment decreased in a proportion of about one mole of AVS per eight moles of added Cr(VI). Reaction of Cr(VI) spikes with sediment POC is also suggested by decreases in organic carbon in several sediments and increases in interstitial water DOC in all three sediments. These results suggest that sediment POC also provides protection against Cr(VI) lethality in benthic environments, although Cr(VI) lethality occurred in some of the spiked sediments despite high levels of OM.

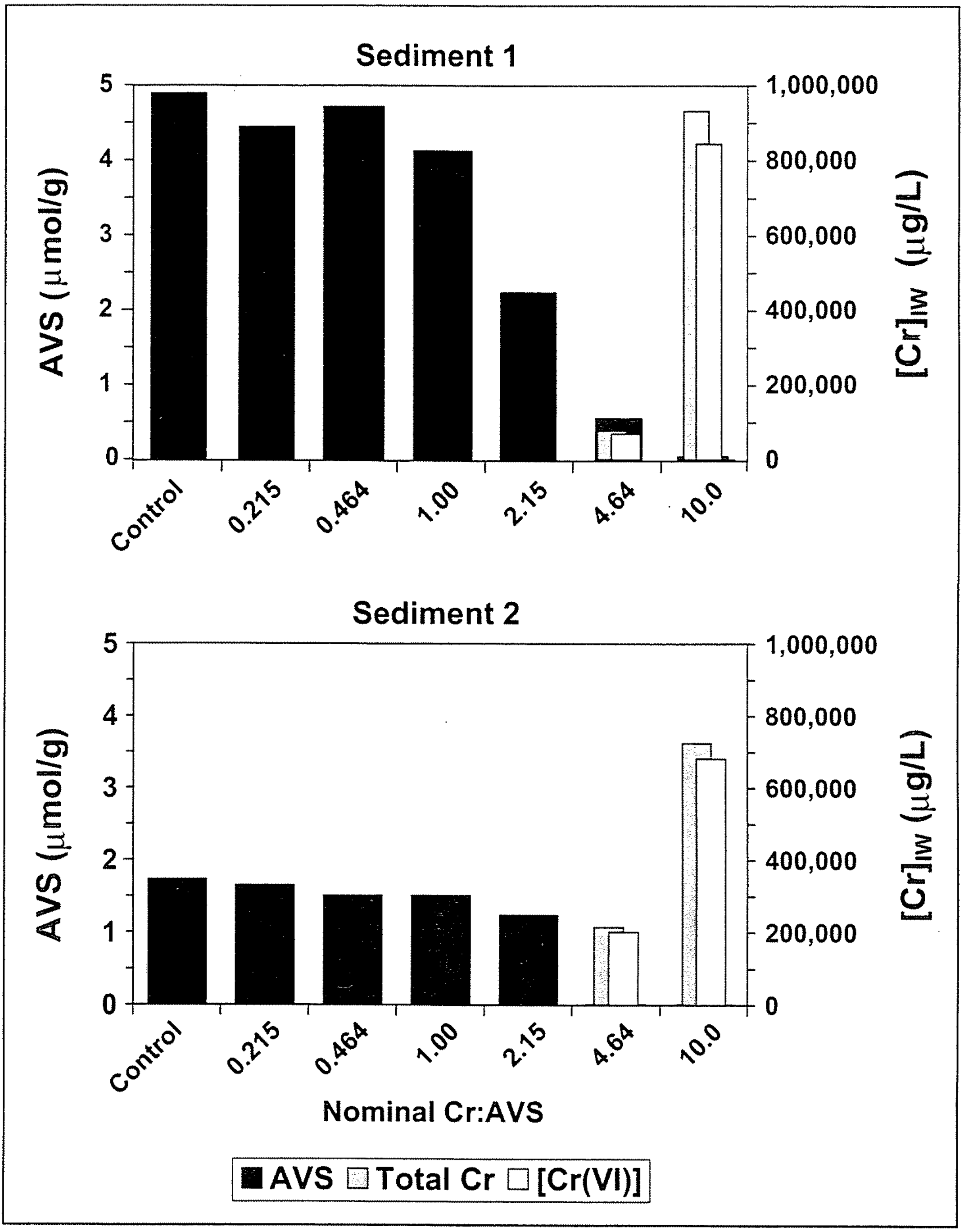

Figure D-1. Concentrations of AVS in sediment, and total Cr and Cr(VI) in interstitial waters of two saltwater sediments spiked with Cr (VI).

Section 3

Chromium Toxicity in Water and Sediment

3.1 Chromium Toxicity in Water-only Tests

Water-only tests were performed to complement the sediment toxicity tests conducted by Berry et al. (*in press*) and Besser et al. (*in press*). Survival of amphipods was decreased by Cr(VI) in water-only tests in saltwater, calculated 10-day LC50s were 1980 and 1854 µg Cr/L based on dissolved and hexavalent concentrations, respectively (Berry et al., *in press*). Survival of amphipods was not decreased by Cr(III) in water-only tests in saltwater at concentrations well above saturation.

Exposure to water-only Cr(VI) in freshwater caused decreased survival of *H. azteca* (Besser et al., *in press*) (Table D-1). Identical LC50s (40 µg/L) were determined for the 28- and 42-d exposure periods suggesting that lethal effects of Cr(VI) occurred early in the exposure. Evidence of sublethal effects of Cr(VI) on amphipods was less conclusive. Amphipod growth was not significantly decreased at any Cr(VI) exposure level, but reproduction in all Cr(VI) treatments was at least one-third less than controls. These results indicate that *H. azteca* is highly sensitive to chronic toxicity of Cr(VI). Excluding the reproduction data, the threshold for chronic Cr(VI) toxicity to *H. azteca* was 15 µg/L (geometric mean of Cr concentrations bracketing the lowest significant toxic effect) slightly greater than the current U.S.EPA water quality criterion for Cr(VI) of 10 µg/L (Richard and Bourg., 1991, U.S.EPA., 1995). Previous studies have reported chronic values for Cr(VI) between 6 µg/L and 40 µg/L for crustacean zooplankton and between 264 µg/L and 1987µg/L for fish (U.S.EPA, 1986).

Toxicity of Cr(III) in freshwater water-only tests was measured at 3 pHs: 6,7, and 8 (Besser et al., *in press*). Cr concentrations in the Cr(III) water-only test were less than the nominal concentration of 100 µg/L, indicating that Cr(III) concentrations were limited by solubility (Table D-2). Filterable Cr concentrations were highest at

Table D-1. Results of a toxicity test with the amphipod *H. azteca* exposed to Cr(VI) in water. Means with standard error in parentheses. Asterisks indicate significant difference between treatment and control ($p<0.05$; ANOVA and Dunnett's test with log-transformed data). From Besser et al. (*in press*).

Cr (ug/L) (n=4)	Survival (%) Day 28 (n=12)	Survival (%) Day 42 (n=8)	Length (mm) Day 42 (n=8)	Reproduction (young per female) (n=8)
<2.0	100 (0)	100 (0)	4.87 (0.11)	8.4 (2.4)
2.0 (0.3)	90 (7)	90 (7)	4.90 (0.07)	2.3 (1.1)*
4.7 (1.1)	95 (3)	95 (5)	4.84 (0.09)	2.9 (1.1)
10 (1.0)	98 (3)	95 (3)	5.27 (0.08)	5.4 (1.5)
18 (6)	88 (5)*	80 (4)*	5.05 (0.07)	3.3 (1.0)
48 (2)	38 (5)*	40 (9)*	5.22 (0.17)	1.6 (1.0)*

pH 6 and lowest at pH 8. Amphipod survival was high (≥90%) in controls at all three pH levels, but control growth and reproduction were significantly lower in pH 6 and pH 8 as compared to pH 7. Poor performance of amphipods in the pH 6 controls may indicate that this is near the lower limit of pH tolerance for this species, but growth and reproduction were also significantly decreased at pH 8, relative to the pH 7 control.

3.2 Spiked Sediments: Saltwater

Mortality of amphipods exposed to Cr(VI) in saltwater sediments increased with increasing chromium concentration, but the response was sediment dependent (Figure D-2a) (Berry et al., *in press*). In sediments where detectable AVS was present, chromium concentrations in interstitial water were very low (<100 µg/L). No significant lethality to *A. abdita* was observed in sediments with less than 0.5 interstitial water toxic units (IWTU) (Figure D-2b). In sediments in which AVS was not significantly greater than zero, chromium concentrations in interstitial waters increased significantly, with greater than 90% of the chromium present as Cr(VI), and *A. abdita* mortality was elevated (Figure D-2c). In a single treatment spiked with a high concentration of Cr(III) there was no chromium in the interstitial water, and the sediment was not toxic (Figures D-2a and D-2b). The results in these tests are consistent with the chromium hypothesis, and are similar to those for the other metals discussed in the main document.

3.3 Field Sediments: Saltwater

Berry et al. (*in press*) exposed amphipods for ten days to field sediments collected from Shipyard Creek, a tidal creek adjacent to a former ferrichromium alloy production facility in Charleston, SC, USA (Breedlove et al., 2002). The relationship between geochemical fractions and amphipod mortality in the field sediments was similar to that found with spiked sediments. AVS was measured at concentrations well above detection limits in all sediments, and despite some exceptionally high concentrations of total chromium (> 3000 µg Cr/g), only traces of Cr(VI) were detected (<4 µg/g) in sediments, and these concentrations were likely artifacts of the Cr(III)/

Table D-2. Results of toxicity test with the amphipod *H. azteca* exposed to Cr(III) in water at three pHs. Means with range (for pH) or standard error in parentheses. Within a pH level, asterisks indicate significant decreases in test endpoints in the Cr(III) treatment, relative to the control. For control sediments, means followed by the same letter are not significantly different ($p \leq 0.05$; ANOVA and Fisher's LSD test with log-transformed data). From Besser et al. *(In press)*.

			Survival (%)		Length (mm)		Reproduction
Treatment	Chromium (µg/L)	pH	Day 28 (n=12)	Day 42 (n=8)	Day 28 (n=4)	Day 42 (n=8)	(young/female) (n=8)
Control - pH 6	<2	6.44 (6.00-7.12)	94 (1) ab	93 (2)	3.8 (0.1) b	3.3 (0.03) c	0 (0) c
Cr(III) - pH 6	76 (63-90)	6.41 (6.00-7.00)	98 (2)	95 (3)	4.3 (0.4)	4.3 (0.4)	1.0 (0.3)
Control - pH 7	<2	7.11 (6.90-7.34)	90 (2) b	93 (3)	4.4 (0.1) a	3.9 (0.04) a	1.4 (0.2) a
Cr(III) - pH 7	48 (38-54)	7.24 (6.96-7.42)	63 (5) *	60 (7) *	4.1 (0.1)	4.1 (0.1)	1.3 (0.6)
Control - pH 8	<2	7.98 (7.79-8.20)	95 (3) a	93 (4)	4.0 (0.2) b	3.6 (0.04) b	0.8 (0.2) b
Cr(III) - pH 8	29 (23-35)	7.94 (7.81-8.12)	63 (4) *	53 (5) *	3.9 (0.1)	3.9 (0.1)	2.0 (0.6)

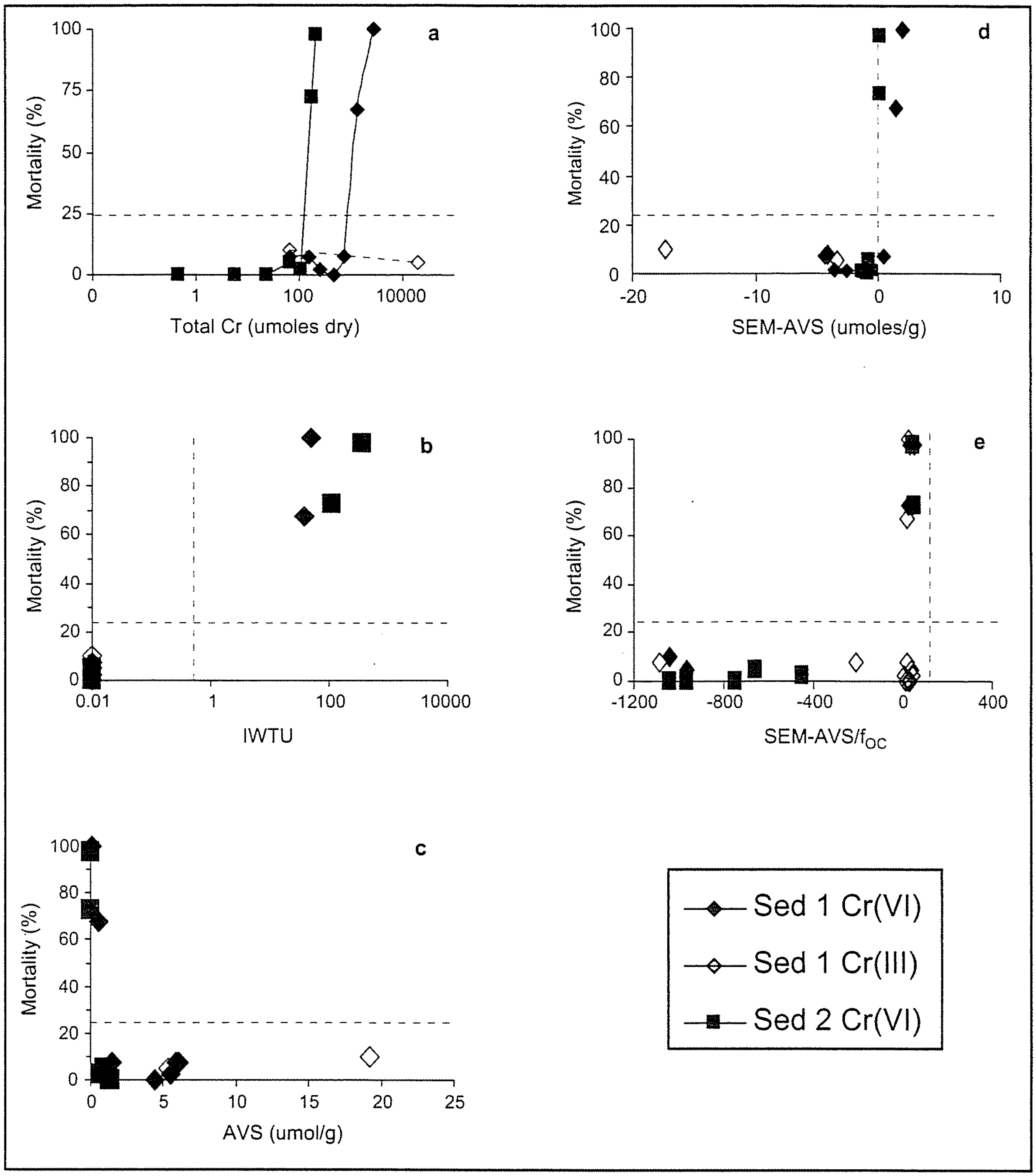

Figure D-2. Mortality in chromium-spiked saltwater sediment experiments (Berry et al., *in press*) vs. total chromium (a), IWTU (b), AVS (c), SEM – AVS (d), and SEM –AVS/f_{OC} (e). Where IWTU = interstitial water toxic units, AVS = acid volatile sulfide, SEM = simultaneously extracted metal, and f_{OC} = fraction of organic carbon. For illustrative purposes, sediments which caused greater than 24% mortality were classified as toxic (horizontal line), (Mearns et al., 1986). Vertical lines are drawn at 0.5 IWTU (b), 0.0 SEM-AVS (d), and 130 (SEM-AVS)/f_{OC} (e).

Cr(VI) separation technique (Berry et al., *in press*). No metals, including Cr(VI), were detected in interstitial waters of any of the sediments, which was expected given the large excess of AVS over SEM measured in all of the sediments. Despite concentrations of chromium exceeding 1700 to 3000 µg/g in some Shipyard Creek sediments, amphipod mortality in those sediments (5-25%) was no greater than in sediments from reference sites (5-20%) or a control sediment performed in conjunction with them (5-15%) (Berry et al., *in press*). These results are also consistent with the chromium hypothesis.

3.4 Spiked Sediments: Freshwater

The 28 and 42-day mortality results from the freshwater Cr(VI)-spiked sediment tests from Besser et al. (*in press*) were very similar to those from the 10-day saltwater Cr(VI) and Cr(III)-spiked sediment tests described by Berry et al. (*in press*). Mortality of amphipods exposed to Cr(VI) in freshwater sediments increased with increasing chromium concentration, but the response was sediment dependent (Figure D-3a) (Besser et al., *in press*). In sediments where detectable AVS was present, chromium concentrations in interstitial water were generally very low (Besser et al., *in press*). No significant toxicity to *H. azteca* was observed in sediments with less than 0.5 interstitial water toxic units (IWTU) (Figure D-3b). In sediments in which AVS was not significantly greater than zero, chromium concentrations in interstitial waters increased significantly (Besser et al., *in press*), with greater than 90% of the chromium present as Cr(VI), and mortality of *H. azteca* was elevated (Figure D-3c). Growth and reproduction were not significantly affected in any Cr(VI) -spiked treatment that did not show significant effects on survival (Besser et al., *in press*) (Figures D-3a ,D-3b, and D-3c)

The 28 and 42-day mortality results from the freshwater spiked sediment tests from Besser et al. (*in press*) with Cr(III) were also similar to those from the 10-day saltwater spiked sediment tests described by Berry et al. (*in press*) in that there was no increased mortality, even at high concentrations of Cr(III). However, the chemistry and sublethal results from the freshwater spiked sediment tests were different from the 10-day saltwater spiked sediment tests and the exposures with Cr(VI)-spiked freshwater sediment in several important respects. First, there was measurable chromium in the interstitial water of all three sediments spiked with a high concentration of Cr(III) (Figure D-3b). Also, there was significantly reduced growth in three of these sediments (Figures D-4a, D-4b, and D-4c) and reduced reproduction in one (Figures D-5a, D-5b, and D-5c). Finally, the reduced growth and reproduction was seen in some sediments which had less than 0.5 IWTU and/or significant amounts of AVS.

Besser et al. (*in press*) concluded that it was difficult to ascribe growth and reproductive effects in the Cr(III) - spiked sediments to chromium toxicity, because t he measured effects did not correspond with dissolved chromium concentrations, or with amphipod mortality. They hypothesized that the effects may have been a result of the physical effect of large amounts of chromium (presumably hydroxide) precipitate which forms when the Cr(III) solutions are pH-neutralized, prior to spiking (Besser et al., *in press*).

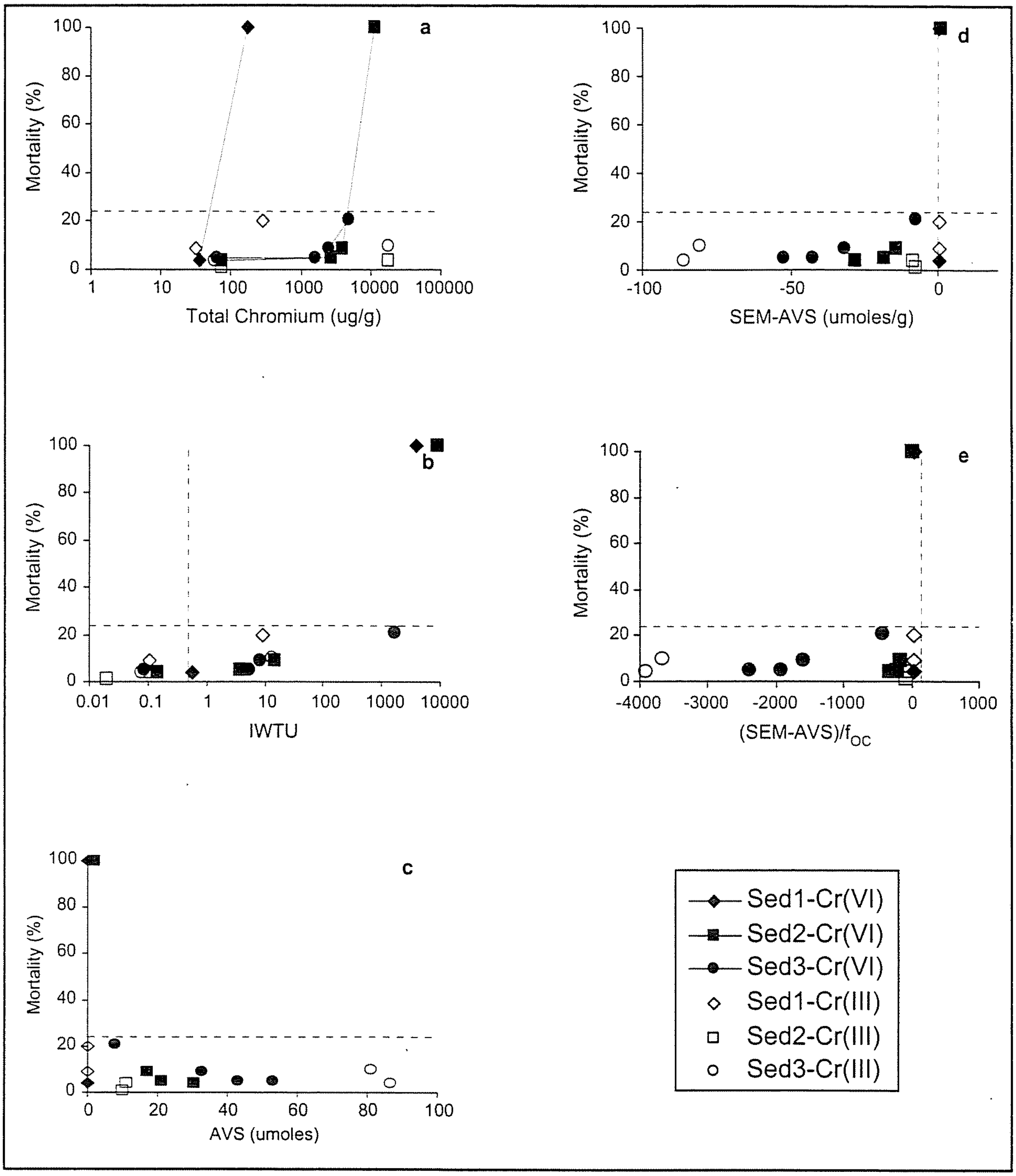

Figure D-3. **Mortality in chromium-spiked freshwater sediment experiments (Besser et al., *in press*) vs. total chromium (a), IWTU (b), AVS (c), SEM – AVS (d), and SEM –AVS/f_{OC} (e). Where IWTU = interstitial water toxic units, AVS = acid volatile sulfide, SEM = simultaneously extracted metal, and f_{OC} = fraction of organic carbon. For illustrative purposes, sediments which caused greater than 24% mortality were classified as toxic (horizontal line) (Mearns et al., 1986). Vertical lines are drawn at 0.5 IWTU (b), 0.0 SEM-AVS (d), and 130 (SEM-AVS)/f_{OC} (e).**

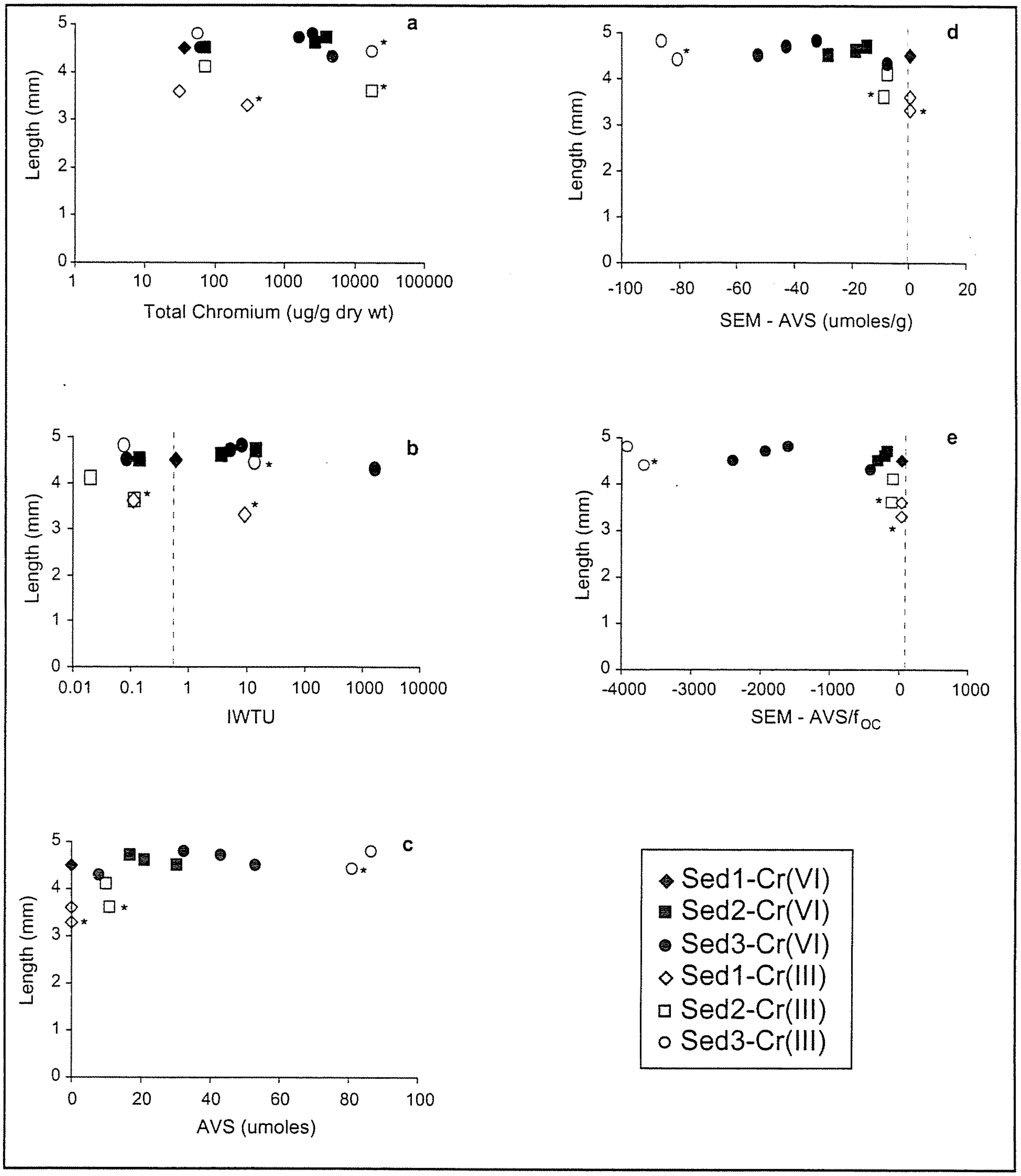

Figure D-4 Growth (length in mm) in chromium-spiked freshwater sediment experiments (Besser et al., *in press*) vs. total chromium (a), IWTU (b), AVS (c), SEM – AVS (d), and SEM –AVS/f_{OC} (e). Where IWTU = interstitial water toxic units, AVS = acid volatile sulfide, SEM = simultaneously extracted metal, and f_{OC} = fraction of organic carbon. Treatments significantly different from control are indicated with an asterisk. Vertical lines are drawn at 0.5 IWTU (b), 0.0 SEM-AVS (d), and 130 (SEM-AVS)/f_{OC} (e).

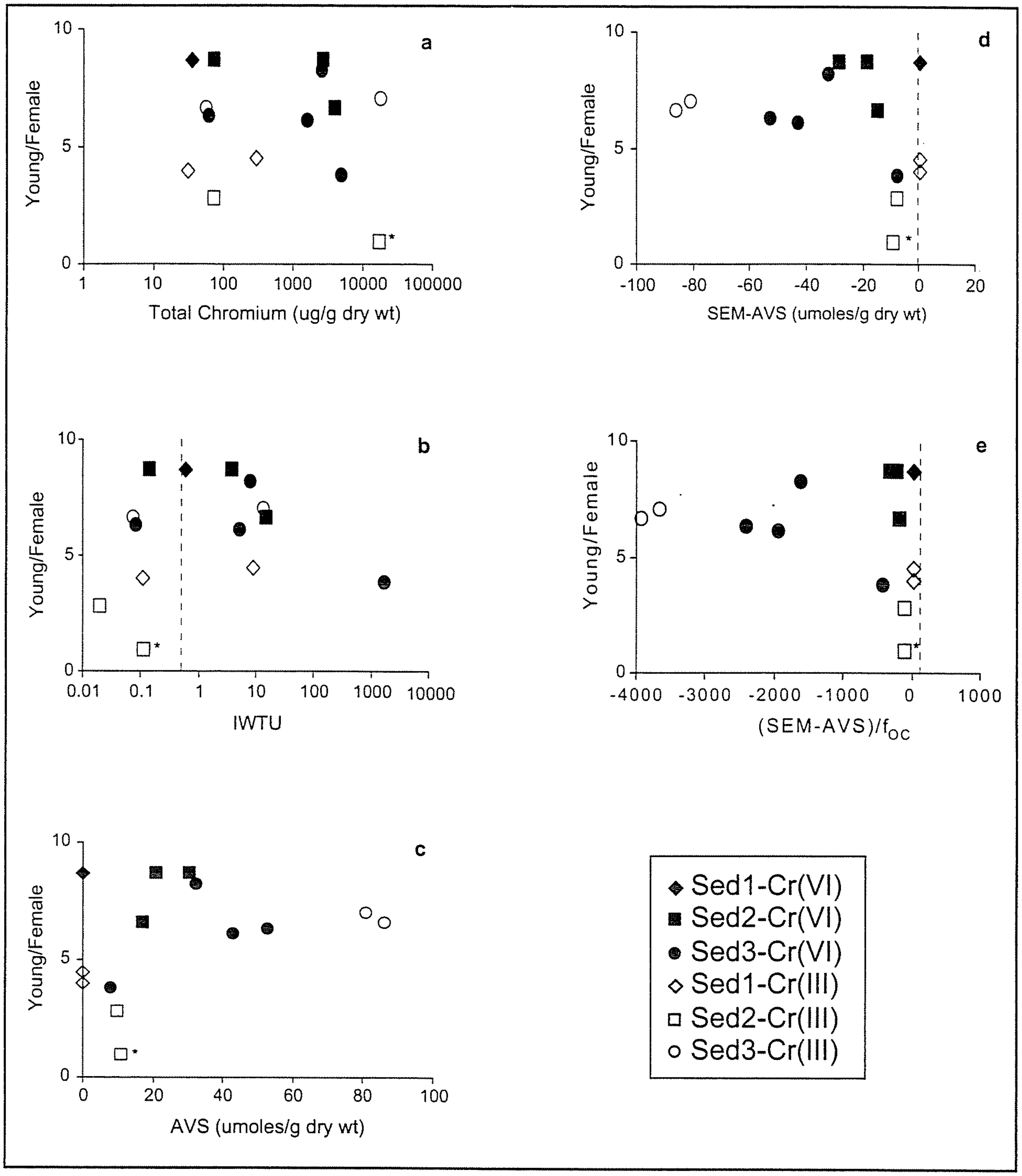

Figure D-5. Reproduction (young per female) in chromium-spiked freshwater sediment experiments (Besser et al., *in press*) vs. total chromium (a), IWTU (b), AVS (c), SEM – AVS (d), and SEM –AVS/f_{OC} (e). Where IWTU = interstitial water toxic units, AVS = acid volatile sulfide, SEM = simultaneously extracted metal, and f_{OC} = fraction of organic carbon. Treatments significantly different from control are indicated with an asterisk. Vertical lines are drawn at 0.5 IWTU (b), 0.0 SEM-AVS (d), and 130 (SEM-AVS)/f_{OC} (e).

Section 4

Derivation of ESB for Chromium

4.1. General Information

Mortality results of the toxicity tests conducted in both fresh and saltwater, with both spiked and field sediments, were generally consistent with the chromium hypothesis. They indicated that sediments with measurable amounts of AVS will not have acute toxicologically significant concentrations of chromium in the interstitial water, and that the sediments will not be acutely toxic due to chromium. Therefore, if measured sediment chemistry is being used as part of a sediment assessment, the presence of measurable AVS could be used to rule out chromium as the cause of observed acute toxicity. The chromium hypothesis can also serve as a foundation for a theoretically-derived sediment ESB for chromium.

The growth and reproduction results of the chronic tests conducted in freshwater with Cr(VI) were also consistent with the chromium hypothesis. The growth and reproduction results of the chronic tests conducted in freshwater with Cr(III) were more ambiguous. It is possible that these effects were observed as a result of the unrealistic conditions in the Cr(III)-spiked sediments, but more testing may have to be performed before the presence of growth and reproductive effects in sediments with large amounts of Cr(III) present can be ruled out.

4.2 Limitations of the chromium hypothesis

For the chromium hypothesis to work, and a Cr ESB to be useful, Cr(III) must not be toxic in interstitial water; however, many studies have reported on the toxic effects of Cr(III). Both the U.S. and Canada have water quality criteria (WQC) for Cr(III), although the criteria for Cr(III) are much higher than those for Cr(VI) (Pawlitz et al., 1997; U.S.EPA., 1985). Confounding factors in many of the tests used to develop these criteria, such as pH values outside of the tolerance range of test organisms (Dorfman., 1997) or reported LC50s orders of magnitude above limits of solubility for Cr(III) (Calabrese et al., 1973), make interpretation of the results of these tests difficult. Nonetheless, some of the tests used to develop the criteria demonstrate biological effects of Cr(III) at environmentally reasonable pH values and within limits of solubility (e.g., Stevens and Chapman (1984) showed chronic effects of Cr(III) on salmonid larvae).

Several recent studies have also shown biological effects due to Cr(III), including DNA damage and other sublethal effects associated with exposure to sediments from some of the same field sites from which Berry et al., (*in press*) collected sediments (Breedlovee et al., 2002), reduced growth of cyanobacteria (Thompson et al., 2002) and reduction in population growth rate of polychaetes (Mauri et al., 2002). Lastly, Besser et al. (2002) report reduced survival of the amphipod *Hyalella azteca* after 28 days in water-only exposures to Cr(III) at concentrations below solubility limits at a range of environmentally reasonable pHs. All of these reported effects are either sublethal or occurred after 10 days, so none of them would be expected to occur in the acute assays of Berry et al., (*in press*).

Another important fact to consider when deriving an ESB for chromium is that benthic animals, particularly tube and burrow dwellers such as *A. abdita*, modify the sediment around them by irrigation of their tubes and burrows, leading to changes in the sediment environment, and particularly in the redox condition of sediments near the animal (Wang et al., 2001). Thus, bulk sediment might have measurable AVS, while Cr(VI) might be present in oxic microenvironments within the sediment. The geochemistry of chromium argues against this, however, because direct oxidation of Cr(III) to Cr(VI) by dissolved oxygen is slow (DeLaune et al., 1998), significant oxidation of Cr(III) to Cr(VI) occurs only in soils and sediments with elevated concentrations of manganese oxides and low organic content, conditions under which AVS would not be formed (Masscheleyn et al., 1992, Kozuh et al., 2000), and Cr(III) is very slow to react even in environments where it is thermodynamically unstable (Barnhart, 1997).

4.3 Incorporation into Multiple Metals Benchmark

In sediments where chromium is the only major metal of concern the AVS and interstitial water ESBs may be used as listed below. However, in many cases chromium will be present along with other metals, and will need to be evaluated along with them. One of the major objectives of this appendix is to expand the utility of the AVS methodology used with cadmium, copper, lead, nickel, silver, and zinc to include chromium. See sections 4 and 6 of the metals ESB for more detail on the benchmarks for cadmium, copper, lead, nickel, silver and zinc, and exact definitions of the AVS and interstitial water benchmarks.

Any sediment in which SEM -AVS < 0.0 should have low risk of adverse biological effects due to chromium, because measurable AVS must be present for this to be true (Figures D-2d, D-3d, D-4d, and D-5d). It should also have low risk of adverse biological effects due to cadmium, copper, lead, nickel, and zinc. Any sediment in which SEM - AVS > 0.0, but AVS > 0.0 should have low risk of adverse biological effects due to chromium or silver, but may have adverse biological effects due to cadmium, copper, lead, nickel or zinc. Sediments with SEM - AVS > 0.0 in which AVS does not exceed 0.0 may have adverse biological effects due to cadmium, copper, lead, nickel, silver, zinc and chromium.

The use of the (SEM - AVS)/f_{OC} benchmark in sediments contaminated with chromium is complicated slightly by the fact that a sediment with a slight excess of SEM - AVS may have AVS = 0.0, and thus be at risk to adverse biological effects of chromium, while at the same time not posing a risk due to cadmium, copper, lead, nickel, or zinc because of organic carbon binding. However, with an understanding of the chemistry of AVS, organic carbon, and metals it is possible to use the benchmark in sediment containing a mixture of metals including chromium. The interpretation of the benchmark with respect to cadmium, copper, lead, nickel, silver, zinc, and chromium is driven by four assumptions:

1) Any sediment with AVS > 0.0 will not cause adverse biological effects due to chromium or silver.
2) Any sediment in which (SEM -AVS)/f_{OC} < 130 µmols/g_{OC} should pose low risk of adverse biological effects due to cadmium, copper, lead, nickel and zinc.
3) Any sediment in which 130 µmols/g_{OC} < (SEM - AVS)/f_{OC} < 3,000 µmols/g_{OC} may have adverse biological effects due to cadmium, copper, lead, nickel or zinc.
4) In any sediment in which (SEM - AVS)/f_{OC} > 3,000 µmols/g_{OC} adverse biological effects due to cadmium, copper, lead, nickel or zinc may be expected.

Section 5

Sampling and Analytical Chemistry

5.1 General Information

All of the issues regarding proper sampling and analytical methods described for other metals (e.g., sampling biologically active zone, seasonal variation) are equally pertinent when chromium is an analyte of interest. Therefore, the guidance given on these topics earlier in this document are similarly appropriate. However, the differing physical and chemical characteristics of chromium in various oxidation states create additional concerns, both in sampling and analysis. For example, samples need to be collected and stored to preserve and minimize disturbance of existing redox conditions and thereby retain the distribution of solid and aqueous phase Cr(III) and Cr(VI) as much as possible. These chromium specific concerns are discussed below.

5.2 Sampling Sediment and IW

Normal procedures used to collect and preserve sediments for analysis of AVS and SEM are sufficient to preserve chromium speciation as well. Potential artifacts of sample handling and storage might include reduction of Cr(VI) or oxidation of Cr(III). The former should be addressed by keeping a sample cold, or even frozen, to inhibit *in situ* microbial reduction, while isolating a sediment sample from air, as well as chilling and freezing the sample, should eliminate the likelihood of oxidation of Cr(III) to Cr(VI) in sediments. Preservation of redox conditions in water samples, however; is significantly more problematic, and requires greater diligence.

As with sediment sampling, the guidance provided earlier in this document regarding collection of interstitial water is appropriate for samples in which chromium is an analyte of interest. Because of the potential of reduction of Cr (VI) to insoluble Cr(III) species within the sampler during the course of the experiment (Berry et al., *in press*), interstitial water samples should be filtered immediately after removal from the sampler, whether collected using centrifugation or *in situ* diffusion samplers (Berry et al., 1996). If centrifugation is used to isolate interstitial water, temperature should be kept low and the overlying atmosphere rendered inert to prevent possible oxidation of Cr(III) to Cr(VI) by Fe/Mn-rich films at the air-water interface (Masscheleyn et al., 1992).

Techniques that separate Cr species of different redox states should be applied to water samples as soon after collection as possible; if such separation cannot be obtained rapidly, samples should be frozen to preserve chemical speciation until such time as separation is practical. For example, Cr(III) and Cr(VI) species in overlying and interstitial water samples can be separated using a modified Fe(OH)3 coprecipitation technique (Berry et al., *in press*, Cranston and Murray, 1978) within hours of collection. Treatment with ion exchange resins to isolate Cr species has also been used (Besser et al., *in press*).

5.3 Chemical Analyses

5.3.1 Sediment Analysis

Techniques recommended for analysis of AVS in sediment samples are appropriate when chromium is a concern, with only slight modification of techniques for analyzing simultaneously extracted metals (SEM). As with water samples, if Cr(VI) is to be measured in the SEM solution, separation of redox species should be conducted as soon after filtration of the extract as possible. If Cr(VI) is expected to be a problem, it should be determined in an aliquot of the SEM extracts by using a modified $Fe(OH)_3$ coprecipitation technique to remove Cr(III) (Wang et al., 1997, Berry et al., *in press*) and analyzing Cr in the supernatent by atomic spectrochemical means (e.g., inductively coupled plasma atomic emission spectrometry (ICP-AES) and graphite furnace atomic absorption spectrophotometry (GFAAS)).

5.3.2 Water analysis

Interstitial waters and overlying seawater from sediment tests may be analyzed for total and dissolved chromium and Cr(VI); however, analysis of chromium in saline waters at low concentrations can be problematic, so separation of redox species should only be conducted when evidence suggests the presence of Cr(VI) (i.e., AVS concentrations are near or below detection limits). Aliquots of water samples to be analyzed for dissolved metals should be filtered through a 0.4-micron polycarbonate membrane and then acidified with concentrated nitric acid (1% v/v), with Cr(VI) determined in subsamples of the dissolved sample using a modified $Fe(OH)_3$ coprecipitation technique (Cranston and Murray, 1978) as appropriate. Analysis of the various fractions may be conducted by GFAAS.

Section 6

Benchmark Sediment Values: Application and Interpretation

6.1 AVS Benchmark

The AVS benchmark for chromium is different from the SEM-AVS used for cadmium, copper, lead, nickel, silver and zinc because chromium does not form an insoluble sulfide. However, an AVS measurement is still useful in predicting the toxicity of chromium in a sediment, because sediments which have measurable AVS should be reducing in nature; therefore, most chromium should be present in the form of Cr(III), and the risk from acute toxicity due to chromium exposure should be low.

6.2 Interstitial Water Benchmark

The interstitial water benchmark is similar to that for cadmium, copper, lead, nickel, silver and zinc. If the interstitial water concentration of chromium does not exceed the chronic WQC FCV for Cr(VI) (10 µg/L in freshwater and 50 µg/L in saltwater (U.S.EPA., 1995)), the risk from chromium exposure should be low. The Cr(VI) WQC is used because most of the dissolved chromium in sediments should be in the form of Cr(VI), the freshwater benchmark for Cr(VI) is lower than that for Cr(III), and there is no chronic benchmark for Cr(III) in saltwater.

6.3 Incorporation into Multiple Metals Benchmark

The metals benchmark with respect to cadmium, copper, lead, nickel, silver, zinc and chromium is driven by four assumptions:

1) Any sediment with AVS > 0.0 will not cause adverse biological effects due to chromium or silver.
2) Any sediment in which $(\mathrm{SEM} - \mathrm{AVS})/f_{\mathrm{OC}} < 130$ µmols/g_{OC} should pose low risk of adverse biological effects due to cadmium, copper, lead, nickel and zinc.
3) Any sediment in which 130 µmols/g_{OC} < $(\mathrm{SEM} - \mathrm{AVS})/f_{\mathrm{OC}}$ < 3,000 µmols/g_{OC} may have adverse biological effects due to cadmium, copper, lead, nickel or zinc.
4) In any sediment in which $(\mathrm{SEM} - \mathrm{AVS})/f_{\mathrm{OC}} >$ 3,000 µmols/g_{OC} adverse biological effects due to cadmium, copper, lead, nickel or zinc may be expected.

These four assumptions should prove useful in the application of the chromium ESB in sediment assessments. However, the relationship $(\mathrm{SEM} - \mathrm{AVS})/f_{\mathrm{OC}}$ should be used with caution (with regard to chromium toxicity) in sediments with little or no AVS. This is because a sediment with no appreciable AVS or SEM and substantial chromium might be toxic due to chromium, even though no toxicity due to other metals would be expected. Other potential limitations to the use of the chromium ESB are outlined in Section 4 of this appendix.

Use of an AVS based benchmark for assessing and predicting mortality in sediments due to chromium was successful in both freshwater and saltwater. Assessing and predicting sublethal toxicity in freshwater sediments was hindered by the observation of significant growth and reproductive effects in treatments where such effects were not expected. Causes of these effects remain ambiguous and may reflect sublethal chromium toxicity or experimental artifacts. Further study is needed to resolve these questions. Consequently, consistent with the recommendations of EPA's Science Advisory Board, publication of this document does not imply the use of ESBs as stand-alone, pass-fail criteria for all applications; rather, exceedances of ESBs could trigger collection of additional assessment data.

Arguably, the most important additional data needed for assessing contaminated sediments along with ESBs are the results of toxicity tests. Sediment toxicity tests provide an important complement to ESBs in interpreting overall risk from contaminated sediments. Toxicity tests have different strengths and weaknesses compared to chemical-specific guidelines, and the most powerful inferences can be drawn when both are used together (see U.S. EPA 2003a,b for further discussion of using toxicity testing with ESBs to assess contaminated sediments).

The ESB approaches are intended to protect benthic organisms from direct toxicity associated with exposure to metal-contaminated sediments. They are not designed to protect aquatic systems from metals release associated, for example, with sediment suspension, or the transport of metals into the food web from either sediment ingestion or ingestion of contaminated benthos. Furthermore, the ESBs do not consider the antagonistic, additive or synergistic effects of other sediment contaminants in combination with metal mixtures or the potential for bioaccumulation and trophic transfer of metal mixtures to aquatic life, wildlife or humans.

Section 7

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ATTACHMENT C

SEDIMENT TREATABILITY TESTING

SEDIMENT TREATABILITY TESTING SCOPE OF WORK

INTRODUCTION

The Vanadium Corporation of America Site (Site) is located in the Town of Niagara, Niagara County, New York. The Site currently includes property parcels owned by Airco Properties, Inc., CC and Alloys, Inc., and the New York Power Authority (NYPA) and Niagara Mohawk Power Corporation (NiMo).

In accordance with the FS, up to 80,000 cubic yards of soil/slag and 10,000 cubic yards of sediment will be excavated and consolidated in a landfill on-site. Dewatering and/or stabilization of the sediment may be necessary to ensure that the sediment meets stability requirements for landfilling. The sediment is expected to be suitable for on-Site disposal if the unconfined compressive strength is 1 psi or more.

The following is a work plan for a treatability study to determine the dewatering and/or stabilization procedure that will allow the sediment to meet the above criteria. Dewatering alone will be tested. In addition, stabilization of the sediment with the excavated slag and stabilization of the sediment using solidification agents such as Portland cement, fly ash, quick lime and cement kiln dust will also be tested.

LABORATORY STUDY

1. OBJECTIVE

The objective of this treatability study is to determine the most effective treatment to stabilize sediment in order to allow the material to be consolidated and capped.

2. TASK 1: INITIAL CHARACTERIZATION

A five-gallon sample of representative sediment and a 1 gallon sample of representative slag will be obtained. The samples will be shipped to the CRA Treatability Study Laboratory in Niagara Falls, NY. It is expected that settling of the solids will occur during transit. Before beginning any characterization of the sediment sample, the sample will be mixed to restore the original sediment: water ratio.

The samples will be analyzed for:

- pH; and
- Moisture Content

3. TASK 2: DEWATERING TESTS

A subsample of the sediment will be poured into a settling column. The column will be sampled and total suspended solids (TSS) in the supernatant water will be measured at 0, 15, 30, and 60 minutes. These times may be adjusted, once the settling rate is experimentally observed. After settling has occurred, a sample of the supernatant water will be analyzed for TSS and a pocket penetrometer will be used to estimate the compressive strength of the dewatered sediment. If the pocket penetrometer reading shows that the sediment may have enough compressive strength to meet disposal requirements, the sediment will be analyzed for unconfined compressive strength.

4. TASK 3: SOLIDIFICATION USING EXCAVATED SLAG

Solidification with slag excavated from the Site will also be tested. The amounts of slag to be added to the dewatered sediment will be determined visually based on the characteristics of the dewatered sediment. Several ratios of slag to sediment will be tested. The two substances will be mixed in a mechanical mixer for 5 minutes before being packed into a glass jar and cured in a high humidity chamber for 1 week. After 1 week, pocket penetrometer readings of the compressive strength of the mixtures will be taken. If any of the treatments appear to have enough compressive strength to meet disposal requirements larger quantities of these mixtures will be prepared, cured for 2 weeks and then analyzed for unconfined compressive strength.

5. TASK 4: SOLIDIFICATION USING OTHER AGENTS

Solidification using other reagents will also be tested. The solidification reagents to be tested will include Portland cement, cement kiln dust, fly ash, quick lime and bed ash. After curing for 1 week, the samples will be tested with a pocket penetrometer determine whether the solidification agent is effective at the dose used. The first batch of reagents to be screened would be as follows:

1. 5% Bed Ash;
2. 5% Cement Kiln Dust;
3. 5% Quick Lime;
4. 5% Bed Ash, 5% Cement Kiln Dust;
5. 5% Fly Ash, 5% Cement Kiln Dust; and
6. 5% Portland Cement.

The tests will be prepared by placing 100 g of soil with the appropriate amount of solidification agent(s) in a mechanical mixer. The soil and agent will be mixed for 5 minutes and then placed in a glass jar. The increase in sample volume due to the treatment will be noted. The glass jar will be placed in a high humidity chamber, in an effort to replicate field conditions, for curing. After 1 week the compressive strength of each test will be measured using a pocket penetrometer and the treatments showing the highest compressive strengths will be further tested. Larger quantities of these mixtures will be prepared, cured for 2 weeks and then analyzed for unconfined compressive strength.

6. TASK 5: REPORTING

A study report will be prepared describing the testing conducted in the treatability study and including the results obtained. The report will provide the most cost effective dosage and solidification agent(s) for stabilization of the sediments.

7. SCHEDULE

CRA will implement this work plan following receipt of approval to proceed. The following are milestone events for the Work Plan:

1. Complete Task 1 -1 weeks after receipt of samples;
2. Complete Task 2 -3 weeks after receipt of samples;
3. Complete Task 3 -4 weeks after receipt of samples;
4. Complete Task 4 -4 weeks after receipt of samples; and
5. Complete Task 5 -6 weeks after receipt of samples.