346SERBSF10,619

346SERBSF10,619

Site Name (Subject):	SOUTHERN WOOD PIEDMONT COMPANY
Site ID (Document ID):	NCD058517467
Document Name (DocType):	Contractor Report (CONTR)
Report Segment:	
Description:	Briefing Report to the EPA Science Advisory Board
Date of Document:	12/1/1994
Date Received:	5/29/1996
Box: *Enter SF and # with no spaces*	SF10,619
Access Level:	PUBLIC
Division:	WASTE MANAGEMENT
Section:	SUPERFUND
Program (Document Group):	SERB (SERB)
Document Category:	FACILITY

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BRIEFING REPORT

to the

EPA SCIENCE ADVISORY BOARD

on the

EQUILIBRIUM PARTITIONING APPROACH TO PREDICTING METAL BIOAVAILABILITY IN SEDIMENTS AND THE DERIVATION OF SEDIMENT QUALITY CRITERIA FOR METALS

December 1994

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF WATER AND
OFFICE OF RESEARCH AND DEVELOPMENT

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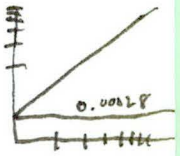
K_{oc} PARTITION COEFFICIENT between (PORE H_2O [redacted]), (SEDIMENT CARBON)

EqP Equilibrium Partitioning

K_{ow} octanol/water partition coefficient

f_{oc} particle % organic Carbon

$\log_{10} K_{oc} = 0.00028 + 0.983 \log_{10} K_{ow}$



so $K_{oc} \approx K_{ow}$

$K_d = f_{oc} K_{oc}$

K_d sediment/pore water partition coefficient

C_s ~~solid phase~~ concentration on sed particles

$C_s = f_{oc} K_{oc} C_d$

$C_{s,oc} = \frac{C_s}{f_{oc}}$

$= K_{oc} C_d$

C_d = free diss concentration

when $C_{s,oc}$ = organic carbon-normalized sed conc

for any sed when $f_{oc} > 0.2$?

DOC dissolved (colloidal) organic C.

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DISCLAIMER

This document is a compilation of data and analyses from scientific investigations into the bioavailability of metals in sediments to benthic organisms with the intent of proposing an approach to assessing metals contamination of sediments for the protection of benthic organisms.

This document does not establish or affect legal rights or obligations. It does not establish a binding norm and is not finally determinative of the issues addressed. Agency decisions in any particular case will be made applying the law and regulations on the basis of specific facts when permits are issued or regulations promulgated.

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CONTENTS

Chapter		Page
1	INTRODUCTION	1-1
	Overview	1-1
	Legal Basis	1-1
	Definition of Sediment Criteria (aquatic life)	1-2
	Methodology Selection	1-2
	Application of Sediment Criteria	1-3
	Document Outline	1-6
2	EQUILIBRIUM PARTITIONING	2-1
	Bioavailability	2-1
	Pore Water Normalization	2-5
	Sorption of Nonionic Organic Chemicals	2-9
	Effects Concentration	2-13
3	METAL TOXICITY IN WATER AND SEDIMENT EXPOSURES	3-1
	Toxicity Correlates to Metal Activity	3-2
	Interstitial Water And Metal Toxicity	3-4
4	METAL PARTITIONING	4-1
	Metal Sorption Phases	4-1
	Titration Experiments	4-2
	Amorphous FeS	4-3
	Sediments	4-4
	Correlation to Sediment AVS	4-5
	Solubility Relationships and Displacement Reactions	4-7
	Application to Mixtures of Metals	4-10
5	LABORATORY SPIKING EXPERIMENTS	5-1
	Results	5-2
	Saltwater Amphipod Tests	5-2
	Water-Only Tests	5-3
	Spiked Sediment tests	5-4
	Sediment Chemistry	5-4
	Day 0 vs Day 10 Chemistry Values	5-4
	Interstitial Water Metal Versus SEM/AVS	5-4
	Sediment Toxicity	5-12
	Discussion	5-20
6	FIELD COLLECTED SAMPLES	6-1
	Saltwater Field Sites	6-2
	Description of Field Sites and Toxicity Test Results	6-2
	Freshwater Field Sites	6-10

Description of Field Sites and Toxicity Test Results 6-10
Discussion 6-17
Saltwater Field Sites 6-17
Saltwater and Freshwater Field Sites 6-23
Field Sites and Spiked Sediments 6-30
Summary 6-32

7 COLONIZATION EXPERIMENTS 7-1
Results 7-2
Exposure 7-2
Effects 7-8
Discussion 7-14

8 BIOACCUMULATION OF METALS 8-1
Laboratory Spiking Experiments-Freshwater 8-3
Laboratory Spiking-Marine 8-5
Field Sediments-Freshwater 8-9
Field Sediments-Marine 8-13
Field Spiking-Freshwater 8-14
Summary and Conclusions 8-17

9 AVS AND OTHER BINDING PHASES 9-1
Vertical and Seasonal AVS Distributions 9-1
The Correlation of AVS to Sediment Organic Carbon 9-9
Oxidation of Metal Sulfides 9-11
FeS(s) and CdS(s) Oxidation Kinetics 912
Sediment Metals Oxidation Model 9-16
Conclusions 9-28
Organic Carbon Binding 9-28
Analysis Framework 9-29
Sorption Isotherm Results 9-31
Least Sorptive Phase 9-44
Pore Water and AVS/SEM Sampling 9-47
Pore Water Sampling 9-47
AVS/SEM Sampling 9-50

10 CONSIDERATIONS FOR ASSESSING METAL BIOAVAILABILITY IN SEDIMENTS 10-1
Interstitial Water 10-1
Acid Volatile Sulfide and SEM 10-2

11 PROPOSED SEDIMENT QUALITY CRITERIA 11-1
Introduction 11-1
Single Metal Sediment Quality Criteria 11-3
AVS Criteria 11-3
Interstitial Water Criteria 11-4

AVS and Organic Carbon Criteria 11-6
AVS and Minimum Partitioning Criteria 11-7
Multiple Metals Criteria 11-8
AVS Criteria 11-8
Interstitial Water Criteria 11-9
AVS and Organic Carbon Criteria 11-10
AVS and Minimum Partition Coefficient Criteria 11-13
Criteria Summary 11-13
Sediment Quality Criteria Uncertainty 11-14
Research Recommendations 11-17
Conclusions 11-18

CHAPTER 1

INTRODUCTION

Overview

This briefing document for the Science Advisory Board (SAB) describes the methodology that the EPA is proposing to use to establish a national sediment quality criteria for metals. It is based on the Equilibrium Partitioning (EqP) method. EqP was originally developed and adopted to derive national sediment criteria for non-ionic organic chemicals. This document presents the methodology and supporting information for deriving sediment criteria for cadmium, copper, lead, nickel, and zinc.

Legal Basis

Responding to environmental problems with corrective action frequently requires proving that something negative has occurred. "Innocent until proven guilty," the standard of the American judicial system, works well for many legal activities; but applying this logic to environmental protection efforts (an activity is environmentally acceptable until it can be proven unacceptable) presents a unique set of strengths and limitations. Regulatory agencies frequently are called upon to prove environmental or human health degradation has or could occur prior to taking any corrective or preventive action. Scientifically sound and legally defensible measures that demonstrate potential or actual impacts are imperative. Fundamental to any effort to ensure environmental protection is to define the party upon whom the burden of proof lies. Chemical specific criteria are one tool developed by regulatory and non-regulatory agencies that is frequently used to meet the burden of proof requirements. Criteria define when a release of a substance into the environment is acceptable and when the release is causing or has potential to cause adverse impacts to aquatic life, wildlife, or human health. EPA initiated efforts to develop national sediment quality criteria under the authority of the Clean Water Act to protect the chemical, physical, and biological integrity of the country's water resources, aquatic life, and water dependent resources. The sediment criteria are intended to be used to prevent

clean sediments from becoming contaminated and to assist in making regulatory and remediation decisions on sediments that are already contaminated.

Definition of Sediment Criteria (aquatic life)

Sediment Quality Criteria are the U.S. Environmental Protection Agency's best recommendation of the concentration of a substance in sediment that will not unacceptably affect benthic organisms.

Methodology Selection

A detailed methodology has been developed to derive sediment quality criteria for metals. This document presents the supporting logic and specifies the numerical procedures to be used to calculate the criteria values.

The use of total sediment metal concentration as a measure of bioavailable - or even potentially bioavailable - concentration is not supported by the available data. Experimental results indicate that different sediments can differ in toxicity significantly for the same total metal concentration. Without accounting for this difference one cannot set a national sediment quality criteria that depends only on the total sediment metal concentration. Therefore, the variation in the bioavailability of metals in various sediments must be explicitly considered in the establishment of defensible sediment quality criteria. This is a significant obstacle; since without some quantitative estimate of the bioavailable metal concentration in a sediment, it is impossible to predict a sediment's toxicity based on chemical measurements. This is true regardless of the methodology used to assess biological impact - be it laboratory toxicity experiments or field data sets comprising benthic biological and chemical sampling.

The EqP approach was selected to establish sediment quality criteria because it incorporates the most useful technical aspects of a variety of approaches. Specific reasons for selecting the approach are as follows:

(1) It was likely that the EqP approach would yield sediment criteria that were predictive of biological effects in the field and would be defensible when used in a regulatory context. These criteria would directly address the issue of bioavailability and for the most part are based on the extensive biological effects data base used to establish national water quality criteria.

(2) Sediment criteria could be readily incorporated into existing regulatory operations since a unique numerical sediment specific criteria can be established for a chemical and compared to field measurements to assess the likelihood of significant adverse effects.

(3) Sediment criteria could provide a simple and cost effective means of assessing sediment measurements to identify areas of concern and could quickly provide regulators with information on potential incremental impacts on benthic organisms as a function of the extent of criteria excedences.

(4) The method takes advantage of the large amount of data and expertise that went into the development of the National Water Quality Criteria.

(5) The methodology could be used as a regulatory predictive tool to link sources to sediment sinks to ensure uncontaminated sites would be protected from attaining unacceptable levels of contamination.

Application of Sediment Criteria

Persistent contaminants discharged into the surface waters of the U.S. end up primarily in the water column and in sediments. Technology based controls, whole effluent toxicity tests, and chemical specific water quality criteria provide the basis for controlling water column contamination. For sediment contamination a similar approach is being adopted. Technology based controls, sediment biological tests, and sediment criteria are intended to control, prevent, and manage sediment contamination.

Over the past two years EPA has been preparing a draft Agency wide sediment management strategy to coordinate and focus EPA's resources on contaminated sediment problems. An outline of this draft strategy has been released to the public for review and a final draft was announced in the Federal Register this past summer as available for formal public comment. The draft strategy is designed around three major principals:

1) In-place sediment should be protected from contamination to ensure that the beneficial uses of the nation's surface waters are maintained for future generations;

2) Protection of in-place sediment should be achieved through pollution prevention and source controls;

3) Natural recovery is often the preferred remedial technique. In-place sediment remediation will be limited to high risk sites where natural recovery will not occur in an acceptable time period and where the cleanup process will not cause greater problems than leaving the site alone.

The draft strategy has six components: assessment, prevention, remediation, dredged material management, research, and outreach. Sediment quality criteria are integrated into this strategy. However, their specific role will be outlined in a "User's Guide" currently under development. The Guide will be based on the comments received on the criteria and strategy and will incorporate the management strategies of a variety of program offices on a program specific basis.

Even though the specific applications of sediment criteria are under development, in general the primary use of sediment criteria will be to prevent sediment contamination and assess risks associated with contaminant levels in sediments. Various EPA programs concerned with contaminated sediment have different regulatory mandates and thus, have different needs and areas for potential application of sediment criteria. Because each

regulatory need is program specific, sediment criteria have to be implemented in a variety of ways to meet the needs of diverse offices and programs.

A likely application of EqP sediment criteria would be in a tiered approach. In such an application, when contaminants in sediments exceed the sediment quality criteria, the sediments would be considered to be causing unacceptable impacts. Further testing may or may not be required depending on site specific conditions and the degree to which a criteria has been violated. (At locations where contamination significantly exceeds a criterion, no additional testing would be required. Where sediment contaminant levels are close to a criteria, additional testing may be necessary). Contaminants in a sediment at concentrations less than the sediment criteria would not be of concern. However, the sediment could not necessarily be considered acceptable for benthic organisms because they may contain other contaminants above safe levels for which no sediment criteria exist. In addition the synergistic, antagonistic, or additive effects of several contaminants in the sediments may be of concern. Sediment criteria can provide a basis for determining whether contaminants are accumulating in sediments to the extent that an unacceptable contaminant level is being approached or has been exceeded. By monitoring sediment contaminants in the vicinity of a discharge, contaminant levels can be compared to sediment criteria to assess the likelihood of impact.

Sediment criteria will be particularly valuable in site monitoring applications where sediment contaminant concentrations are gradually approaching a criteria over time. Comparison of field measurements to sediment criteria will be a reliable method for providing early warning of a potential problem. Such an early warning would provide an opportunity to take corrective action before adverse impacts occur.

The safe removal and treatment or disposal of contaminated sediments can be difficult, expensive, and in some case not the environmentally preferred option (e.g., resuspension of contaminated sediments may cause greater harm than leaving them where they are). Leaving sediments in place and allowing source controls and natural processes to reduce or remove the contamination has proven to be an effective option in some cases.

In some situations, the high cost of clean-up activities has eliminated clean-up as an option. In other situations the spatial extent of the site and site-specific conditions may warrant remediation beyond identified clean-up levels, an additional margin of safety can be provided at little or no extra cost. For these reasons it is not anticipated that mandatory clean-up to a nationally designated level is appropriate in most situations.

Document Outline

This document contains ten additional chapters in which are presented the experimental data and the methods to be employed in deriving sediment quality criteria.

Chapter 2 reviews the Equilibrium Partitioning methodology which is used to understand the relationships between sediment and interstitial water concentrations and observed biological effects.

Chapter 3 examines metal toxicity and bioavailability first in water only exposures and then as a function of interstitial water concentrations. This chapter presents the data that suggest that metal toxicity is best correlated to metal activity in water only exposures. It also presents the correlations of organism response to interstitial water concentrations in sediment exposures.

Chapter 4 reviews the state of the art for predicting metal partitioning in sediments. This is important because it connects the solid phase sediment chemistry to the resulting interstitial water concentrations - both of which set the metal activity of the sediment - interstitial water system. The importance of the cold acid extractable sulfide in sediments, which for historical reasons is called acid volatile sulfide (AVS), is demonstrated. An equilibrium model is analyzed to establish the relationship between metal activity in the sediment - interstitial water system, the extractable solid phase metal concentration - which is called the SEM for reasons discussed below - and the ratio of the metal to iron sulfide solubility constants.

Chapter 5 presents the data from laboratory sediment spiking experiments. Uncontaminated sediments are spiked with varying metal concentrations, and the resulting toxicity is measured using sediment-dwelling animals. The results are analyzed using the SEM and AVS method and the interstitial water concentrations.

Chapter 6 presents a similar set of results but these sediments are from field sites with metal contamination. These experiments address the question: can the SEM, AVS, and interstitial water methods explain the toxicity observed in field collected samples.

Chapter 7 presents the results of colonization experiments. These are designed to mimic the field setting as closely as possible while still retaining a measure of laboratory control over the exposures. A series of sediments are spiked with various concentrations of metals. These are exposed either to raw flowing seawater or are placed on lake bottoms for a period of time. The biological response that is monitored is the quality and quantity of the benthic animals that colonize the sediments.

Chapter 8 examines the extent of metal bioaccumulation from sediment exposures. The biological response in this case is different than that of the previous experiments. The results are analyzed using the same methods based on SEM, AVS, and interstitial water concentrations.

Chapter 9 presents information on a number of topics that influence the variation of AVS, temporally, spatially, and with respect to organic carbon in sediments. The oxidation kinetics of iron sulfide and, more importantly, cadmium and zinc sulfide are examined in order to answer the question: what is the importance of seasonal variations and how do they affect criteria. The experimental information related to organic carbon binding and the resulting partition coefficients are presented.

Chapter 10 presents the strengths and limitations of the various methods that have been discussed in the previous chapters. Recommendations are included for situations where more study is required.

Chapter 11 presents a proposed sediment quality criteria for the five metals: Cd, Cu, Ni, Pb, and Zn. Single metal criteria are not technically supportable since the binding of each of these metals interact with each other, thus affecting their mutual toxicity. A discussion of the limitations of these criteria and their proposed utility is also included.

CHAPTER 2

EQUILIBRIUM PARTITIONING

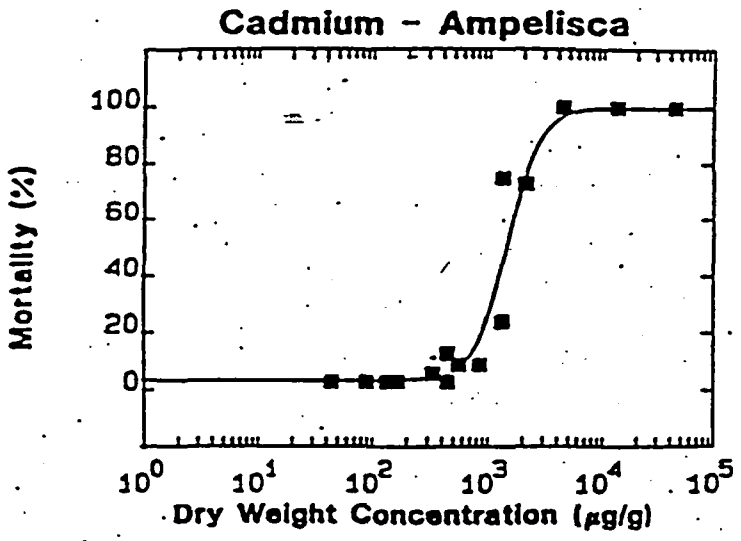
The development and application of the Equilibrium Partitioning (EqP) method for deriving SQC for nonionic organic chemicals has previously been presented to the EPA Science Advisory Board and has been published in the Federal Register for public comment. A full discussion of this work is presented elsewhere [1,2] as well as the derivation of SQC for five nonionic organic chemicals [3,7]. The development of sediment quality criteria for metals also utilizes the EqP method. This chapter presents a summary of the technical basis for establishing sediment quality criteria for nonionic organic chemicals using EqP. Cadmium data is also presented. The purpose of presenting this summary for nonionic organic chemicals is to briefly define the EqP method and to demonstrate its utility in determining the bioavailability of sediment chemicals.

Bioavailability

Establishing a SQC requires a determination of the extent of the bioavailability of sediment associated chemicals. It has frequently been observed that similar concentrations of a chemical, in units of mass of chemical per mass of sediment dry weight (e.g. micrograms chemical per gram sediment), can exhibit a range in toxicity in different sediments. An example is presented in Figure 2-1. These are the results of two sediment toxicity tests of cadmium using amphipods of similar sensitivity [8,9]. One sediment is from Central Long Island Sound and the other is from Yaquina Bay, Oregon. The LC50 for cadmium for these two sediments differ by approximately two orders of magnitude. Because the purpose of SQC is to establish chemical concentrations that apply to sediments of differing types, it is essential that the reasons for this varying bioavailability be understood and be explicitly included in the criteria. Otherwise the criteria cannot be presumed to be applicable across sediments of differing properties.

The importance of this issue cannot be overemphasized. For example, if 20 μg/g of cadmium is the LC50 for an organism in one sediment and 1,500 μg/g is the LC50 in

Dry Weight Normalization



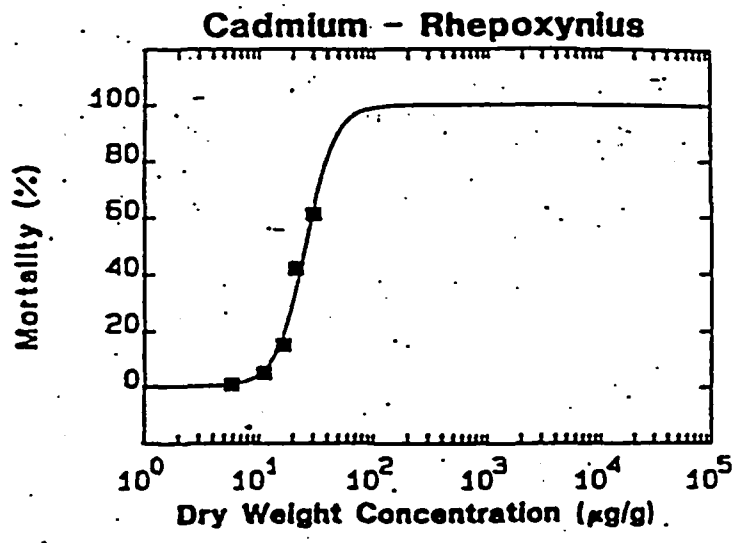


Figure 2-1. Comparison of percent mortality of Ampelisca abdita and Rhepoxynius abronius to concentrations of cadmium in bulk sediment.

another sediment (Figure 2-1), then unless the cause of this difference can be associated with some explicit sediment properties it is not possible to decide what would be the LC50 of a third sediment. The results of toxicity tests used to establish the toxicity of chemicals in sediments would not be generalizable to other sediments. Imagine the situation if the results of toxicity tests in water depended strongly on the particular water source - for example, water from Lake Superior versus well water. Until the source of the differences was understood, it would be fruitless to attempt to establish water quality criteria. It is for this reason that understanding bioavailability is a principal focus in establishing sediment quality criteria.

The observations that provided the key insight to the problem of quantifying the bioavailability of chemicals in sediments were that the concentration-response curve for the biological effect of concern could be correlated not to the total sediment chemical concentration (micrograms chemical per gram sediment), but to the interstitial water (i.e., pore water) concentration (micrograms chemical per liter pore water). The results of toxicity tests of kepone using Chironomus tentans in three sediments is shown in Figure 2-2a. The sediments have quite different LC50s on a sediment dry weight basis: from approximately 1 ug/g to approximately 35 ug/g. However if the mortality is examined as a function of the concentration of kepone in the interstitial or pore water of the sediment, Figure 2-2b, then the mortality-concentration responses are similar for the three sediments. In addition, the LC50s on a porewater basis are the same as the LC50 obtained from a water only exposure toxicity test. Thus the water only LC50 can be used to predict the toxicity of these sediments using their porewater concentrations.

Organism mortality, growth rate, and bioaccumulation data are used to demonstrate this correlation, which is a critical part of the logic behind the EqP approach to developing SQC. For nonionic organic chemicals, it is shown, subsequently, that the concentration - response curves correlate equally well with the sediment chemical concentration on a sediment organic carbon basis. Figure 2-2c presents the same mortality data as a function of the organic carbon normalized sediment kepone concentration (ug kepone/gm sediment organic carbon). The responses for the two sediments with the higher organic carbon

Acute Toxicity of Kepone

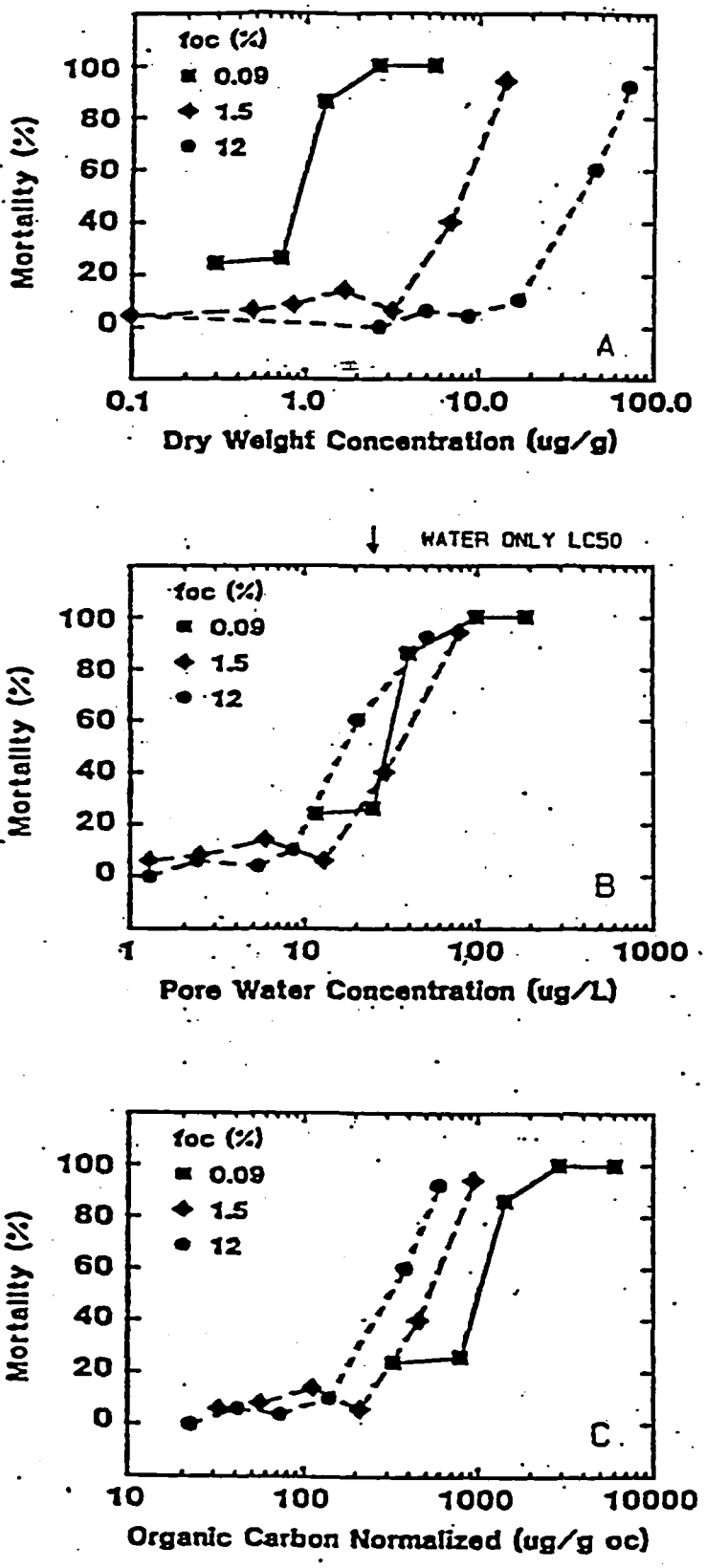


Figure 2-2. Comparison of percent mortality of Chironomus tentans to kepone concentration in bulk sediment (top), pore water (center) and bulk sediment using organic carbon normalization (bottom) for three sediments with varying organic carbon concentrations [9].

fractions (f_{oc}) display the same response. The sandy sediment (with low organic carbon) has a larger LC50, probably because the f_{oc} for this sediment is too small for organic carbon to be the only sorption phase. The range of f_{oc} values for which carbon normalization is appropriate has been examined in more detail [1].

These observations (Figures 2-2b and 2-2c) can be rationalized by assuming that the pore water and sediment carbon are in equilibrium and that the concentrations are related by a partition coefficient, K_{oc}, as shown in Figure 2-3 (right). The name "Equilibrium Partitioning" (EqP) describes this assumption of partitioning equilibrium between sediment carbon and pore water. The rationalization for the equality of water-only and sediment-exposure effects concentrations on a pore water basis is that the sediment - pore water equilibrium system (Figure 2-3, right) provides the same exposure as a water-only exposure (Figure 2-3, left). The reason is that the chemical activity is the same in each system at equilibrium. These results do not imply that pore water or sediment organic carbon is the primary route of exposure because all exposure pathways are at equal chemical activity in an equilibrium experiment and the route of exposure cannot be determined.

It should be pointed out that the EqP assumptions are only approximately true and, therefore, the predictions from the model have an inherent uncertainty. A discussion and quantification of uncertainty is found in the EPA SQC Technical basis document [2].

Pore Water Normalization

A substantial amount of data has been assembled that addresses the relationship between toxicity and pore water concentration [1,2]. The data presented below examines the use of the water-only LC50 to predict the pore water LC50. Figure 2-4 presents mortality data for various chemicals and sediments compared to pore water concentrations when normalized on a toxic unit basis. Three different sediments are tested for each chemical as indicated. Predicted pore water toxic units are the ratio of the measured pore water concentration to the LC50 obtained from an independent water only toxicity test.

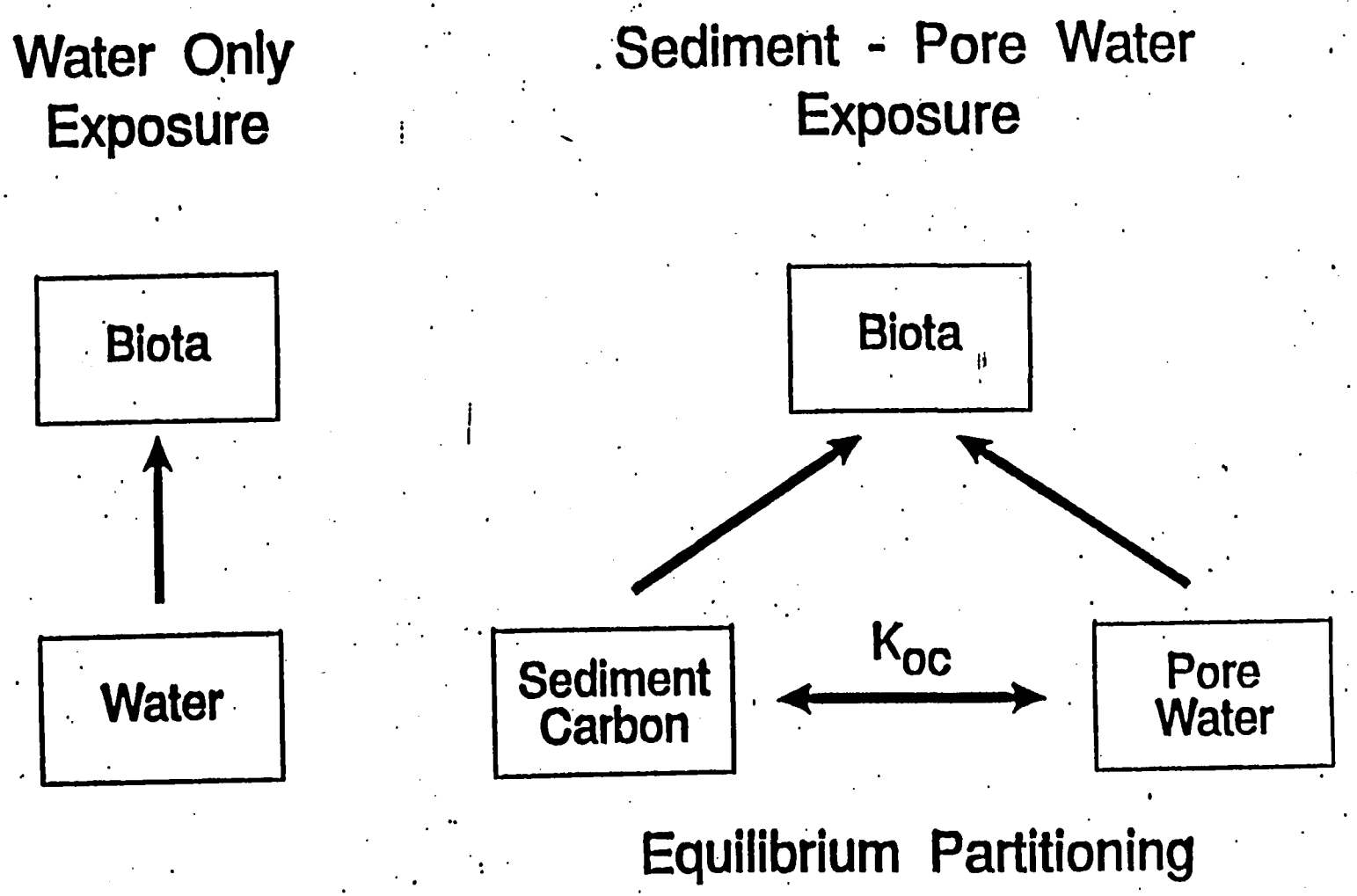


Figure 2-3. Diagram of the organism exposure routes for a water-only exposure (left) and a sediment exposure (right). *Equilibrium partitioning* refers to the assumption that an equilibrium exists between the chemical sorbed to the particulate sediment organic carbon and the pore water. The partition coefficient is K_{oc}.

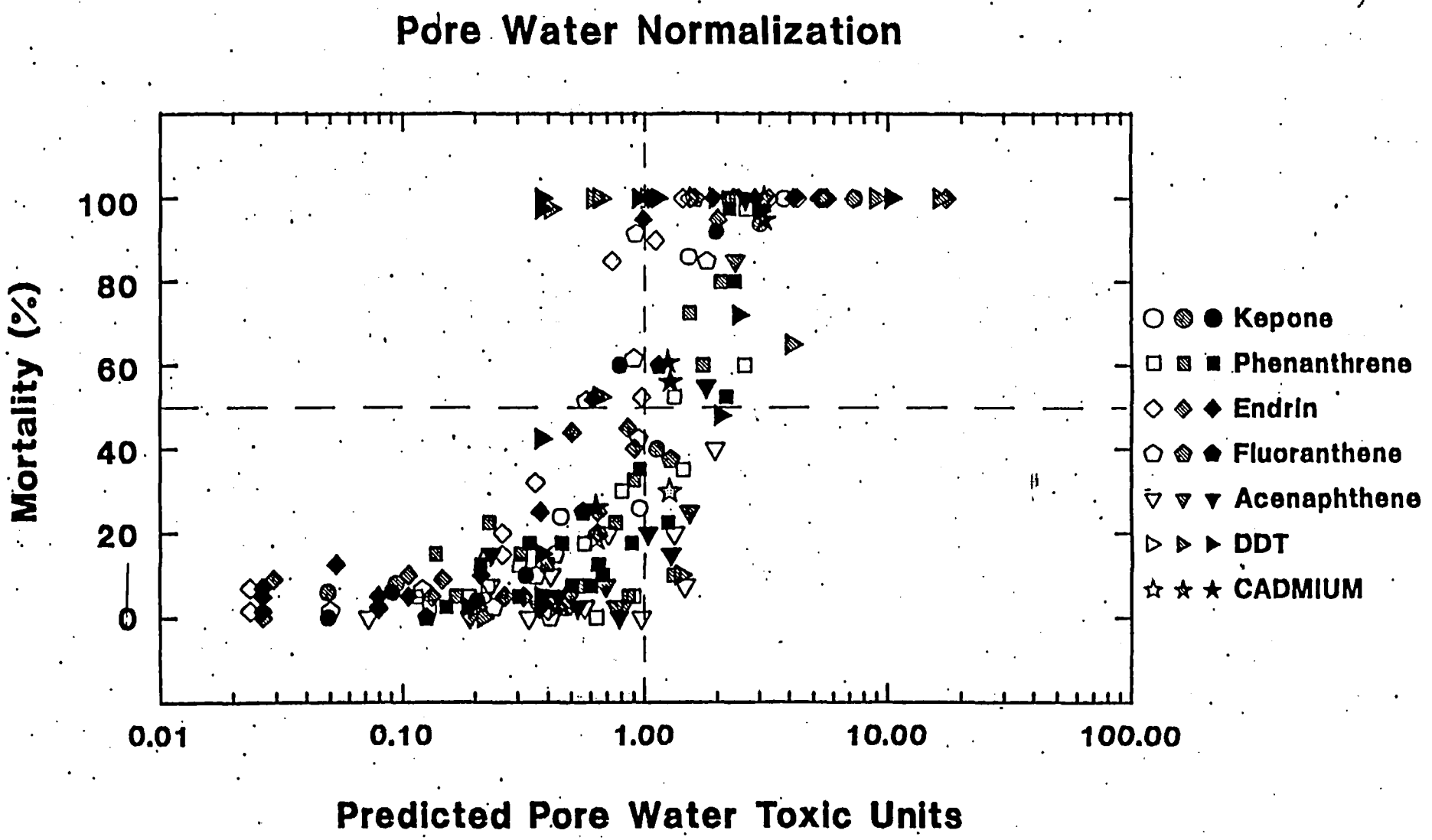


Figure 2-4. Mortality versus predicted pore water toxic units for seven chemicals and up to three organic carbon content sediments per chemical. Sediment types are indicated by the single hatching (lowest organic carbon content), cross hatching (intermediate organic carbon content) and filled symbols (highest organic carbon content). See [2] for more detailed descriptions of these data sets. Predicted pore water toxic units are the ratio of the pore water concentration to the water-only LC_{50} (Eqn. 2-1).

The EqP model predicts that the pore water LC50 will equal the water only LC50. Define:

$$\text{predicted pore water toxic unit} = \frac{\text{(pore water concentration)}}{\text{(water only LC50)}} \qquad (2\text{-}1)$$

A toxic unit of one occurs when the pore water concentration equals the water-only LC50, at which point it would be predicted that 50 percent mortality would be observed. In addition, normalization of these data to pore water toxic units allows all chemical-to-chemical differences to be removed so that all data from these tests with these seven chemicals can be coplotted. The correlation of observed mortality to predicted pore water toxic units in Figure 2-4 demonstrates (a) the efficacy of using pore water concentrations to remove sediment to sediment differences and (b) the applicability of the water-only effects concentration and, by implication, the validity of the EqP model. By contrast, it has been shown [1,2], that the mortality versus sediment chemical concentration on a dry weight basis varies dramatically from sediment to sediment.

The equality of the effects concentration on a pore water basis suggests that the route of exposure is via pore water. However, the equality of the effects concentration on a sediment organic carbon basis, which will be presented in Figure 2-5, suggests that the ingestion of sediment organic carbon is the primary route of exposure. Neither of these references can be supported by the data presented in Figures 2-4 and 2-5 subsequently. It is important to realize that if the sediment and pore water are in equilibrium, then the effective exposure concentration is the same regardless of exposure route. Therefore, it is not possible to determine the primary route of exposure from equilibrated experiments.

Whatever the route of exposure, the correlation of toxicity to pore water suggests that if it were possible to either measure the pore water chemical concentration, or predict it from the total sediment chemical concentration and the relevant sediment properties such as the sediment organic carbon concentration, then that concentration could be used to quantify the exposure concentration for an organism. Thus, understanding the

partitioning of chemicals between the solid and the liquid phase in a sediment becomes a necessary component for establishing SQC for any substance, including metals.

Sorption of Nonionic Organic Chemicals

For nonionic hydrophobic organic chemicals sorbing to natural soils and sediment particles, a number of empirical models have been suggested [10]. The chemical property that indexes hydrophobicity is the octanol/water partition coefficient, K_{ow}. The important particle property is the weight fraction of organic carbon, f_{oc}. Another important environmental variable appears to be the particle concentration itself [11]. A detailed discussion of the particle concentration effect has been presented [1,2].

A number of explanations have been offered for the particle concentration effect. However it is not necessary to decide which of these mechanisms is responsible for the effect if all the possible interpretations yield the same result for sediment/pore water partitioning. Each suggest that the proper partition coefficient to be used in order to relate the free dissolved chemical concentration to the sediment concentration is the partition coefficient to sediment organic carbon, K_{oc}, which is approximately equal to the octanol-water partition coefficient K_{ow}, that is, $K_{oc} \approx K_{ow}$ by the following equation [12].

$$\text{Log}_{10} K_{OC} = 0.00028 + 0.983 \text{ Log}_{10} K_{ow} \qquad (2\text{-}2)$$

The unifying parameter that permits the development of SQC for nonionic hydrophobic organic chemicals that are applicable to a broad range of sediment types is the organic carbon content of the sediments. This can be shown as follows. The sediment/pore water partition coefficient, K_d, is given by

$$K_d = f_{oc} K_{oc} \qquad (2\text{-}3)$$

and the solid phase concentration is given by

$$C_s = f_{oc} K_{oc} C_d \tag{2-4}$$

where C_s is the concentration on sediment particles. An important observation can be made that leads to the idea of organic carbon normalization. Equation 2-3 indicates that the partition coefficient for any nonionic organic chemical is linear in the organic carbon fraction, f_{oc}. Data have presented [1,2,12] to support the linearity of partitioning above a value of f_{oc} = 0.2 percent. This result and the toxicity experiments [1,2] suggest that for $f_{oc} \geq 0.2$ percent, organic carbon normalization is valid.

As a consequence of the linear relationship of C_s and f_{oc}, the relationship between sediment concentration, C_s, and free dissolved concentration, C_d, can be expressed as

$$\frac{C_s}{f_{oc}} = K_{oc} C_d \tag{2-5}$$

If we define

$$C_{s,oc} = \frac{C_s}{f_{oc}} \tag{2-6}$$

as the organic carbon normalized sediment concentration (ug chemical/g organic carbon), then from Equation (2-5):

$$C_{s,oc} = K_{oc} C_d \tag{2-7}$$

Therefore, for a specific chemical with a specific K_{oc}, the organic carbon normalized total sediment concentration, $C_{s,oc}$, is proportional to the dissolved free concentration, C_d, for any sediment with $f_{oc} \geq 0.2$ percent. This latter qualification is judged to be necessary because at $f_{oc} < 0.2$ percent the other factors that influence partitioning (e.g., particle size and sorption to nonorganic mineral fractions) become relatively more important [8]. Using the proportional relationship given by Equation 2-7, the concentration of free dissolved chemical can be predicted from the normalized sediment concentration and K_{oc}. The free concentration is of concern as it is the form that is bioavailable.

As discussed above, hydrophobic chemicals also tend to partition to colloidal-sized organic carbon particles that are commonly referred to as dissolved organic carbon, or DOC. Although DOC affects the apparent pore water concentrations of highly hydrophobic chemicals, the DOC-bound fraction of the chemical appears not to be bioavailable [1].

Therefore, we expect that toxicity in sediment can be predicted from the water-only effects concentration and the K_{oc} of the chemical. The utility of these ideas can be tested with the same mortality data as these in Figure 2-4 but restricted to nonionic organic chemicals for which organic carbon normalization applies. The concept of sediment toxic units is useful in this regard. These are computed as the ratio of the organic carbon-normalized sediment concentrations, C_s/f_{oc}, and the predicted sediment LC50 using K_{oc} and the water-only LC50. That is:

$$\text{predicted sediment toxic unit} = \frac{C_s/f_{oc}}{K_{oc}\ (\text{water only LC50})} \qquad (2\text{-}8)$$

Figure 2-5 presents the percent mortality versus predicted sediment toxic units. The correlation is similar to that obtained using the pore water concentrations in Figure 2-4. The predicted sediment toxic units for each chemical follow a similar concentration-response curve independent of sediment type. The data demonstrate that 50 percent mortality occurs at about one sediment toxic unit, independent of chemical, organism or sediment type, as expected if the EqP assumptions are correct. If we know the appropriate normalizing phase then the same can be done for metals.

If the assumptions of EqP were exactly true and there were no experimental variability or measurement error, then the data in Figures 2-4 and 2-5 should all predict 50 percent mortality at one toxic unit. There is an uncertainty of approximately a factor of two in the results. This uncertainty associated with sediment quality criteria was obtained from a quantitative estimate of the degree to which the data in Figure 2-5 support the assumptions of EqP [2]. This variation reflects inherent variability in these experiments as

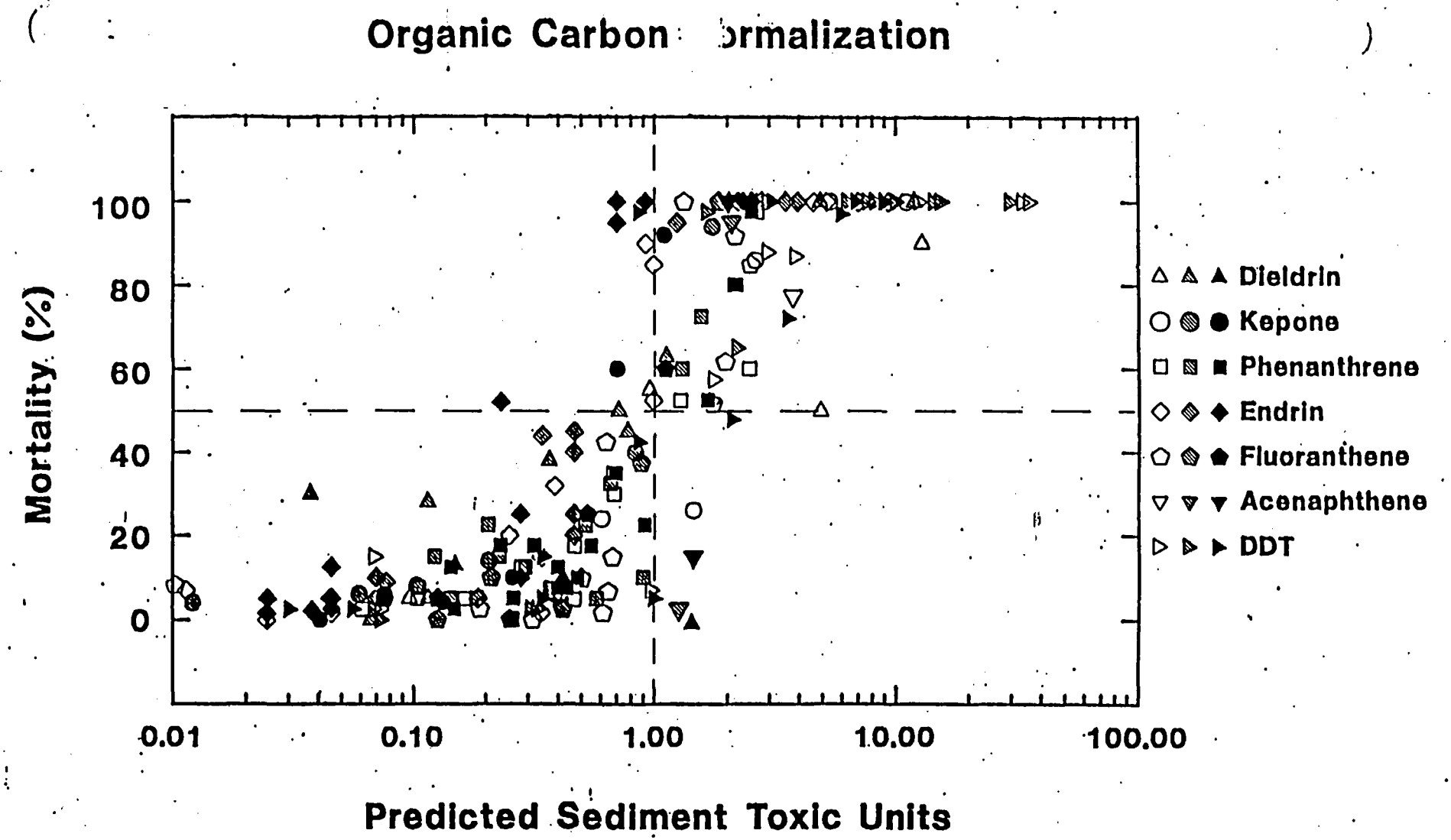


Figure 2-5. Mortality versus predicted sediment toxic units for seven chemicals and up to three organic carbon contents sediments per chemical. Sediment types are indicated by the single hatching (lowest organic carbon content), cross hatching (intermediate organic carbon content) and filled symbols (highest organic carbon content). See [2] for more detailed descriptions of these data sets. Predicted sediment toxic units are the ratio of the organic carbon-normalized sediment chemical concentration to the predicted sediment LC_{50} (Eqn. 2-8). K_{oc} values are computed from K_{ow} and Equation 2-2. K_{ow} for endrin (4.84), fluoranthene (5.00), dieldrin (5.25), phenanthrene (4.46), and acenaphthene (3.76) were measured by the U.S. EPA, Environmental Research Laboratory, Athens, Georgia. Methods are presented elsewhere [2]. K_{ow} for DDT (5.84) is the log average of the reported values in the LOG P database [13]. The kepone K_{oc} is the log mean of the ratio of organic carbon-normalized kepone concentration to pore water-kepone concentration from the toxicity data set.

well as phenomena that have not been accounted for in the EqP model. This appears to be the limit of the accuracy and precision to be expected.

Effects Concentration

The development of SQC requires an effects concentration for benthic organisms. Since many of the organisms used to establish the water quality criteria (WQC) are benthic, perhaps the WQC are adequate estimates of the effects concentrations for benthic organisms. To examine this possibility, the acute toxicity data base, which is used to establish the WQC was segregated into benthic and water column species, and the relative sensitivities of each group was compared. The data are from the 40 freshwater and 30 saltwater U.S. Environmental Protection Agency (EPA) criteria documents. If it were true that benthic organisms are as sensitive as water column organisms, then SQC could be established using the final chronic value (FCV) from these WQC documents as the effects concentration for benthic organisms. The apparent equality between the effects concentration as measured in pore water and in water-only exposures (Figure 2-4) or as predicted from organic carbon normalization (Figure 2-5) supports using an effects concentration derived from water only exposures.

This use of WQC assumes that (a) the sensitivities of benthic species and species tested to derive WQC predominantly water column species, are similar and (b) the levels of protection afforded by WQC are appropriate for benthic organisms. The assumption of similarity of sensitivity using a comparative toxicological examination of the acute sensitivities of benthic and water column species was presented [1,2]. A comparison of the FCVs and the chronic sensitivities of benthic saltwater species in a series of sediment colonization experiments was done [1,2]. Although there is considerable scatter, these results, a more detailed analysis of all the acute toxicity data, and the results of benthic colonization experiments support the contention of equal sensitivity [2].

The final validation of SQC will come from field studies that are designed to evaluate the extent to which biological effects can be predicted from SQC. Sediment

quality criteria for nonionic organic chemicals can possibility be validated more easily than WQC because determining the organism exposure is more straightforward. The benthic population exposure is quantified by the organic carbon normalized sediment concentration.

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CHAPTER 3

METAL TOXICITY IN WATER AND SEDIMENT EXPOSURES

The equilibrium partitioning methodology for establishing sediment quality criteria requires that the chemical concentration be measured in the bioavailable phase and that the chemical potential of the chemical be determined. In this chapter, two questions are addressed. The first concerns the forms of metals that are bioavailable. The question is addressed using water only exposures. The second concerns the observation that the biological response is the same for water only exposures and for sediment exposures using the pore water concentrations. This equality was demonstrated for non-ionic organic chemicals and it is a fundamental tenent of the Equilibrium Partitioning model.

The data presented below demonstrate that biological effects correlate to the metal activity, and that water only exposures and sediment exposures are equivalent. Therefore for both metals and nonionic chemicals this EqP requirement is satisfied.

A direct approach to establishing sediment quality criteria for metals would be to apply the water quality criteria to measured pore water concentrations. The validity of this approach depends on the degree to which pore water concentration and represents free metal activity and can be accurately measured in both systems. For most metals, free metal activity can not be measured at water quality criteria concentrations and present water quality criteria are not based on activity. Metals readily bind to dissolved (actually colloidal) organic carbon (DOC), and DOC complexes do not appear to be bioavailable. Hence the direct use of pore water concentration is precluded for metals with significant DOC complexing.

By implication this difficulty extends to any complexing ligand that is present in sufficient quantity. The decay of sediment organic matter can cause substantial changes in interstitial water chemistry. In particular bicarbonate increases due to sulfate reduction. This increases the importance of the metal-carbonate complexes and further complicates the question of the bioavailable specie.

The sampling of sediment interstitial water is not a routine procedure. The least invasive technique employs a diffusion sampler which has cavities covered with a filter membrane [2,3,4,5]. The sampler is inserted into the sediment and the concentrations on either side of the membrane equilibrate. When the sampler is removed the cavities contain filtered pore water samples. The time required for equilibration depends on the pore size of the membrane and the geometry of the cavity and usually exceeds one day.

An alternate technique is to obtain a sediment core, slice it, and filter or centrifuge the slice to separate the pore water. For anaerobic sediments this must be done in a nitrogen atmosphere to prevent the precipitation of iron hydroxide which would scavenge the metals and yield artificially low dissolved concentrations [5,6].

Although either of these techniques are suitable for research investigations they require more than the normally available sampling capabilities. If solid phase chemical measurements were available from which pore water metal activity could be deduced it would obviate the need for pore water sampling and analysis and it would circumvent the need to deal with complexing ligands.

Toxicity Correlates to Metal Activity

A substantial number of water only exposure experiments disscussed below point to the fact that biological effects can be correlated to the divalent metal activity $\{M^{2+}\}$. The claim is not that the only bioavailable form is M^{2+} - for example MOH^{+} may also be bioavailable - but that the DOC and certain other ligand complexed fractions are not bioavailable.

The acute toxicity of cadmium to grass shrimp (Palaemonetes) has been determined at various concentrations of chloride and NTA, both of which form cadmium complexes [7]. The results are shown in Figure 3-1. The top panels are concentration response curves as a function of total cadmium. The response is quite different at different concentrations of chloride, indexed by salinity, and NTA. However if the concentration

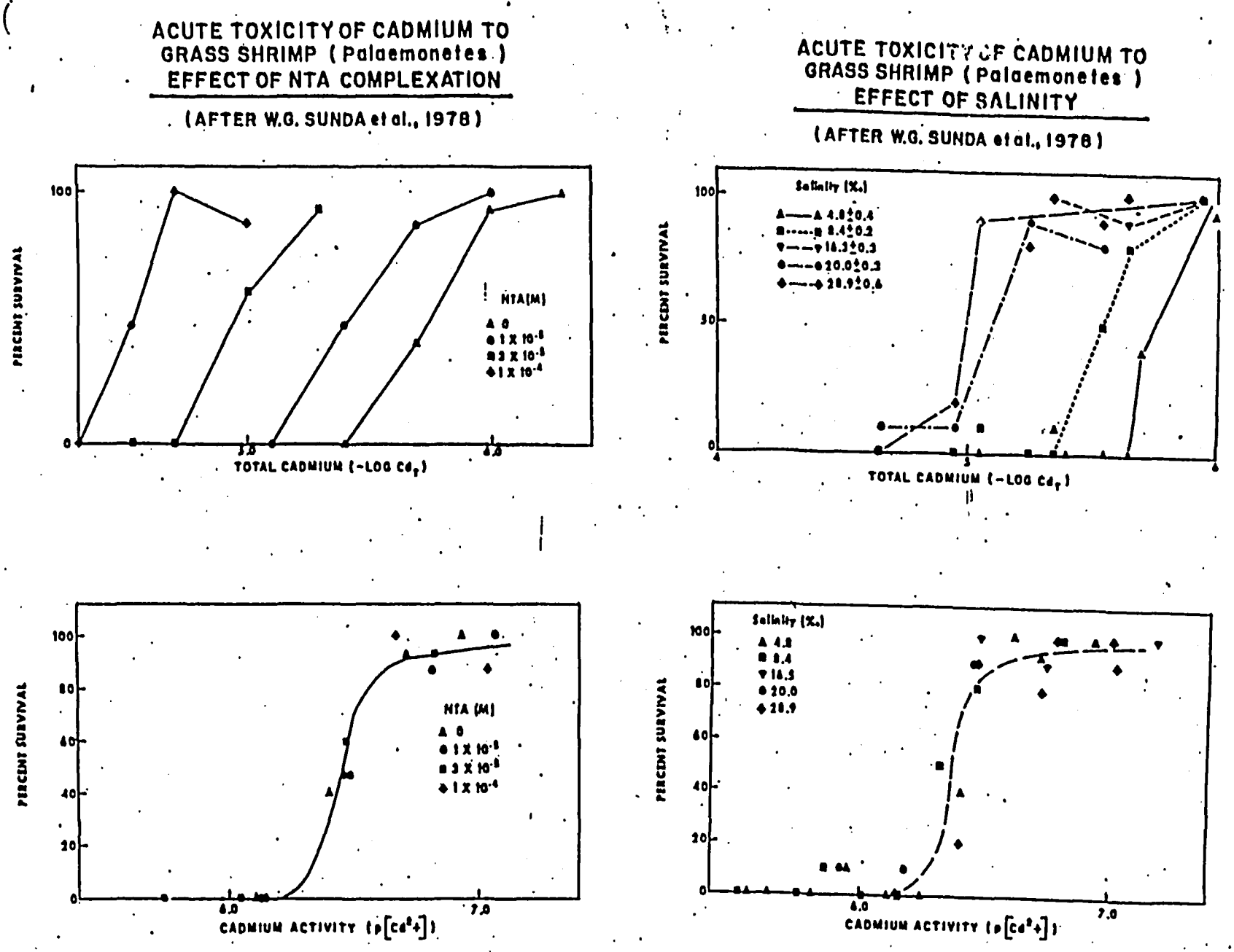


Figure 3-1. Acute toxicity to palaemonetes of total cadmium (top) and cadmium activity (bottom) with different concentrations of the complexing agents NTA (left) and chloride as salinity (right).

response is evaluated with respect to Cd^{2+} activity in the solution, then the curves all collapse into the same single curve (bottom panels). Comparable results have been reported for copper-EDTA complexes [8] for which concentration response correlates to Cu^{2+} activity (Figure 3-2, left top and bottom).

Chronic toxicity of zinc, with phytoplankton growth as the endpoint, has also been examined. The results of an experiment in which the metal concentration is held constant and the complexing ligand is varied are shown in Figure 3-2, right top and bottom [9]. As NTA is added the toxicity of zinc to *Microcystis* decreases. The cell density increases rather than decreases in time and reaches control levels at the highest NTA concentration (left top and bottom panel). The data can all be correlated to free zinc activity as shown (right top and bottom panel). Similar results for diatoms exposed to copper and the complexing ligand Tris are shown in Figure 3-3 (top) [10]. Variations in Tris concentrations and pH produce markedly different growth rates (left top and bottom) which can all be correlated to the Cu^{2+} activity (right). A similar set of results have been obtained by Sunda and Lewis [11] with DOC from river water as the complexing ligand, Figure 3-3 (right top and bottom).

Metal bioavailability as measured by organism uptake can also be examined [12]. Uptake of copper by oysters is correlated not to total copper concentration (Figure 3-4 top) but to copper activity (bottom).

The implication to be drawn from these experiments is that the partitioning model required for establishing sediment quality criteria should predict $\{M^{2+}\}$ in the pore water. The following section examines the utility of this idea.

Interstitial Water And Metal Toxicity

This section presents some early data that first indicated the equivalence of pore water concentrations and water only exposures. Much more data of this sort are presented subsequently in Chapters 5 and 6. Swartz [13] tested the acute toxicity of

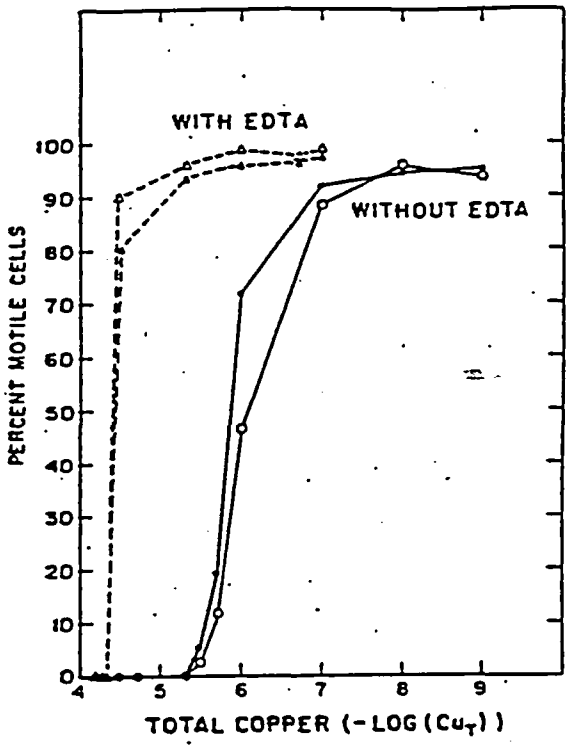
TOXICITY DEPENDS
RESPONSE
ON H_2O cd, NOT
Sel Cd. Other
Variables affect
partitioning of
$Sel_{cd} \rightarrow PtH_2O_{cd}$

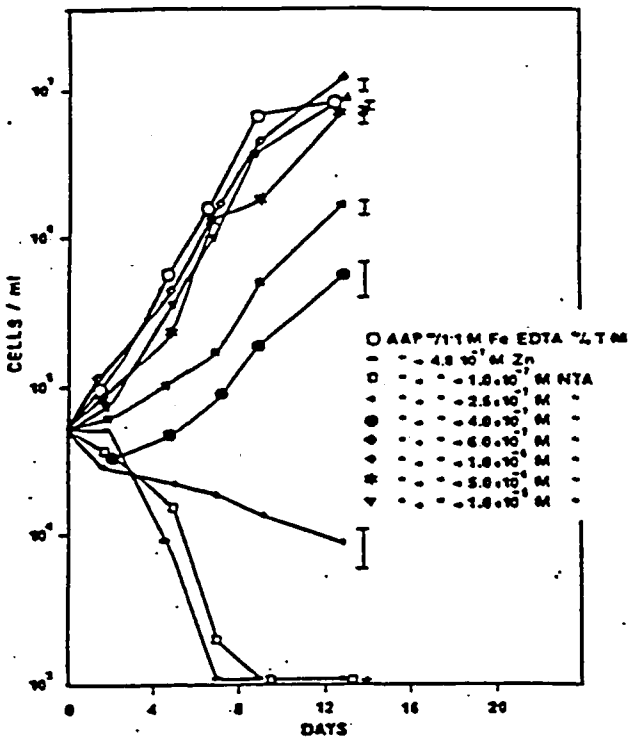
ACUTE TOXICITY OF COPPER TO A DINOFLAGELLATE

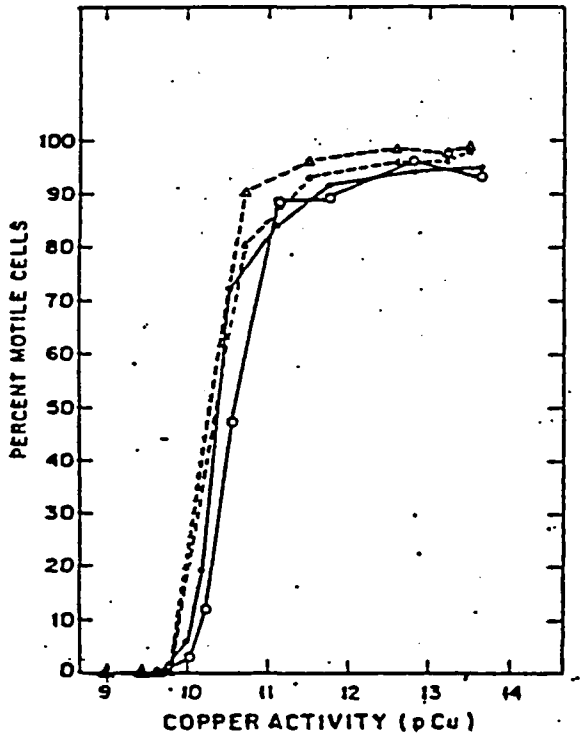
(FROM ANDERSON AND MOREL, 1978)

CHRONIC TOXICITY OF ZINC ON MICROCYSTIS AERUGINOSA

(FROM ALLEN, et.al., 1980).







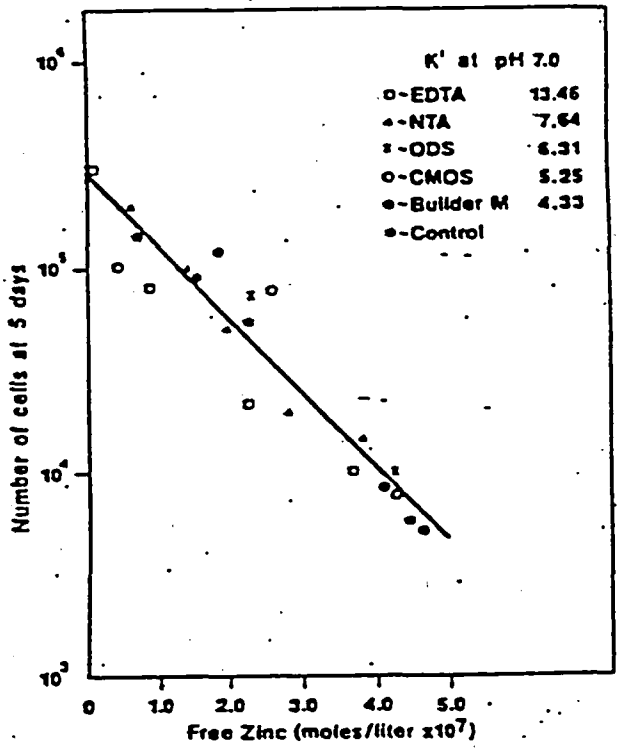


Figure 3-2. Acute toxicity to a dinoflagellate (left) of total copper (top) and copper activity (bottom), with and without EDTA. Chronic toxicity of zinc to Microcystis aeruginosa (right) showing growth as cells/ml versus time with different levels of EDTA and NTA (top) and number of cells at five days as a function of free zinc concentration (bottom).

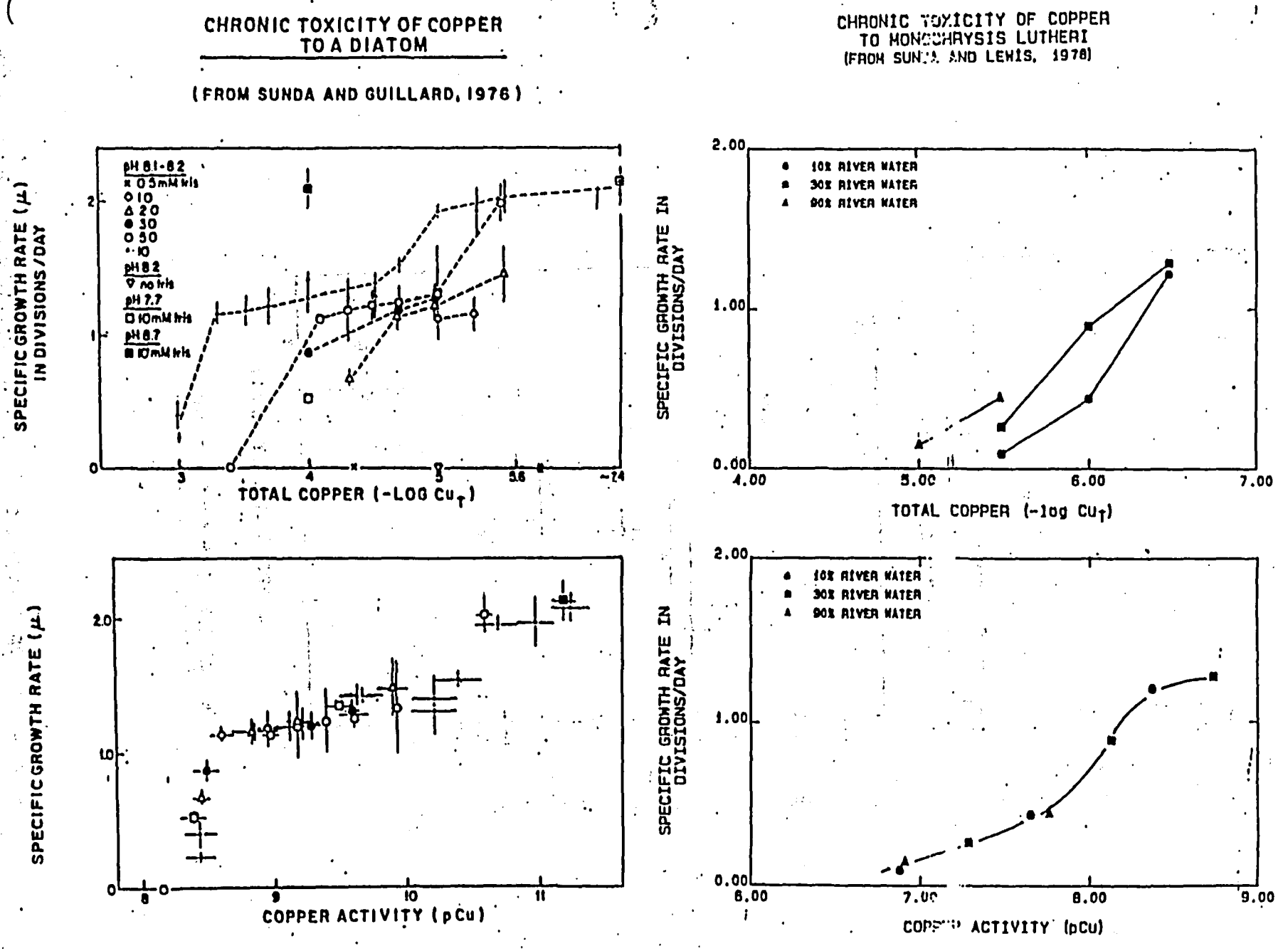


Figure 3-3. Specific growth rate of a diatom (left) and Monochrysis lutheri (right) versus total copper (top) and copper activity (bottom) for a range of concentrations of the complexing ligands Tris and natural DOC.

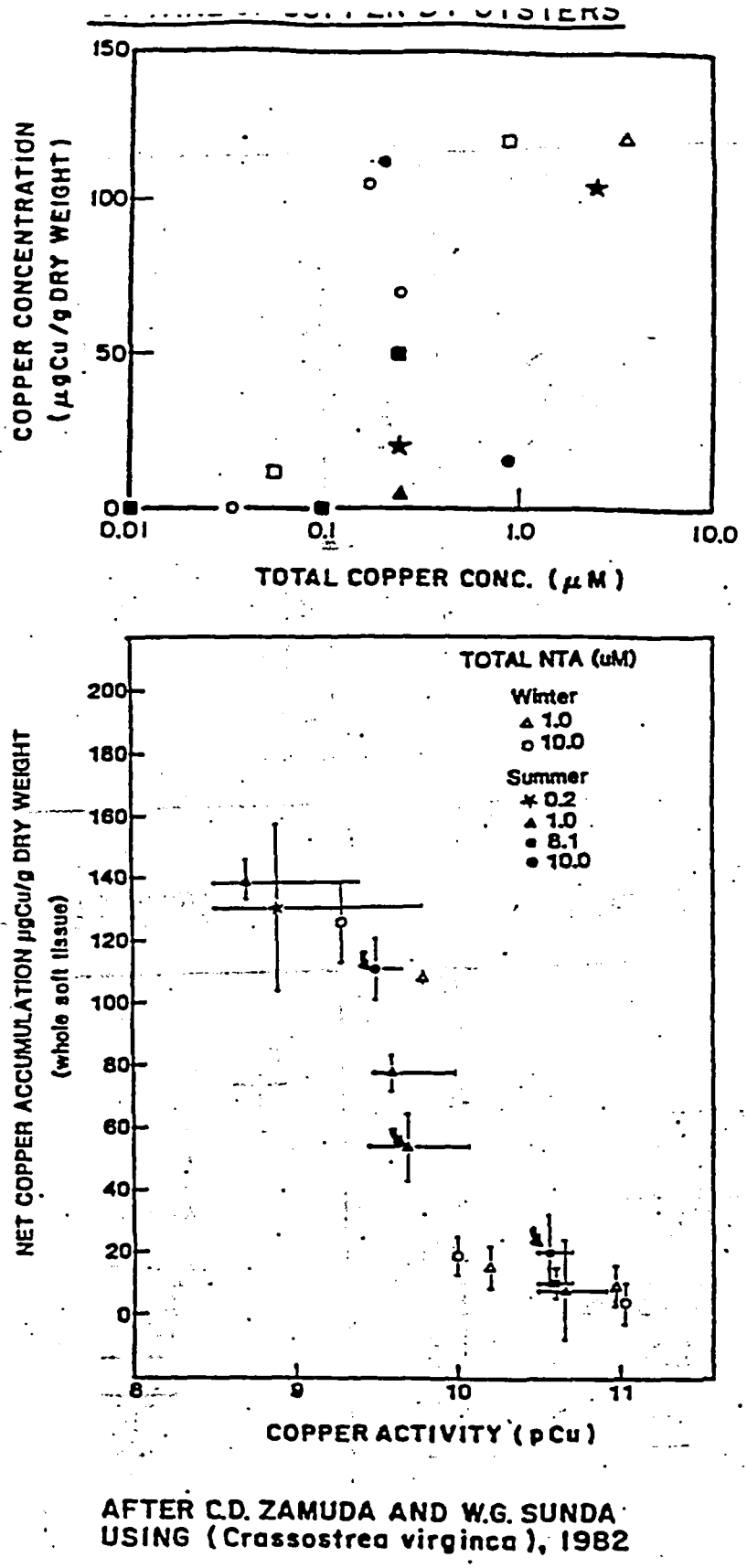


Figure 3-4. Body burden of copper in oysters versus total copper (top) and copper activity (bottom) with different levels of the complexing ligand NTA.

cadmium to the marine amphipod, Rhepoxynius abronius in sediment and seawater. An objective of the study was to determine the contributions of interstitial and particle-bound cadmium to toxicity. Figure 3-5 presents mean survival versus dissolved cadmium concentration for 4-day toxicity tests in seawater and interstitial water. A comparison of the 4-day LC50 of cadmium in interstitial water (1.42 mg/L) with the 4-day LC50 of cadmium in seawater without sediment (1.61 mg/L) resulted in no significant difference between the two.

Experiments were performed to determine the role of acid volatile sulfides in cadmium spiked sediments using the amphipods Ampelisca abdita and Rhepoxynius hudsoni [14]. Three sediments were used, a Long Island Sound sediment with high AVS, Ninigret Pond sediment with low AVS concentration and a 50/50 mixture of the two sediments. Figure 3-6 presents a comparison of the observed mortality to the observed interstitial water cadmium activity, measured with a specific ion electrode, for the three sediments. Four-day water only and 10-day exposure sediment toxicity tests were performed. The water-only response data for *Ampelisca* and *Rhepoxynius* are included for comparison although they represent a shorter duration exposure.

An elegant experimental design was employed by Kemp and Swartz [15] to examine the relative acute toxicity of particule bound and dissolved interstitial cadmium. They circulated water of the same cadmium concentration through different sediments. This result in differing bulk sediment concentrations but the same interstitial water concentrations. They found no statistically significant difference in organisim response for the different sediments. Since the interstitial water concentrations were the same in each treatment - the circulating water concentrations established the interstitial water concentrations - these experiments confirmed the equal concentration hypothesis.

A series of 10-day toxicity tests using the amphipod Hyalella azteca were performed to evaluate the bioavailability of copper in sediments from two sites highly contaminated with this metal: Steilacoom Lake, Washington, and Keweenaw Watershed, Michigan [16]. A water-only, 10-day copper toxicity test was also conducted with the same organism.

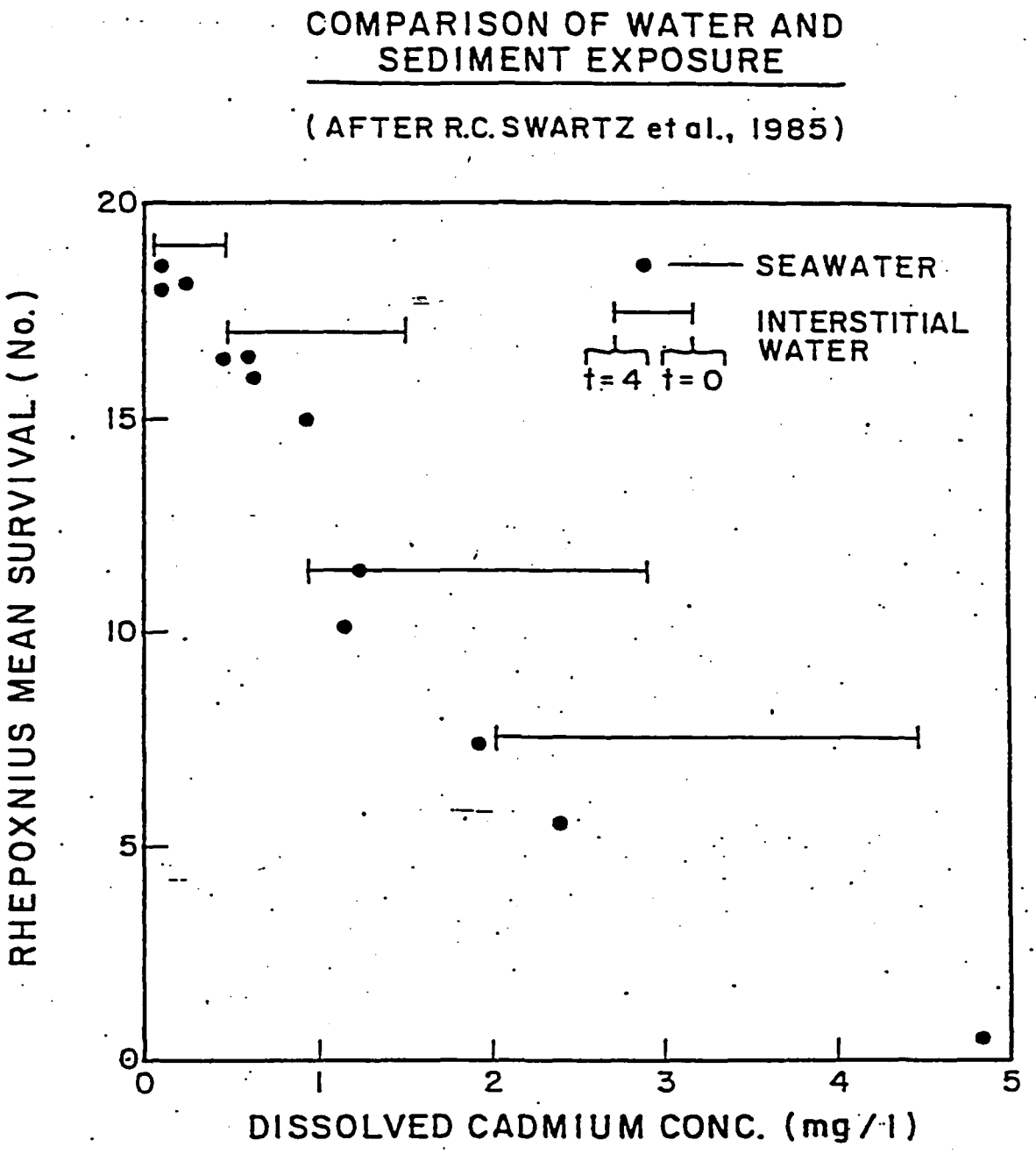


Figure 3-5. Rhepoxynius abronius mean survival versus dissolved cadmium for 4-day toxicity tests in seawater (symbols) and interstitial water at time 0 and 4 days (bars).

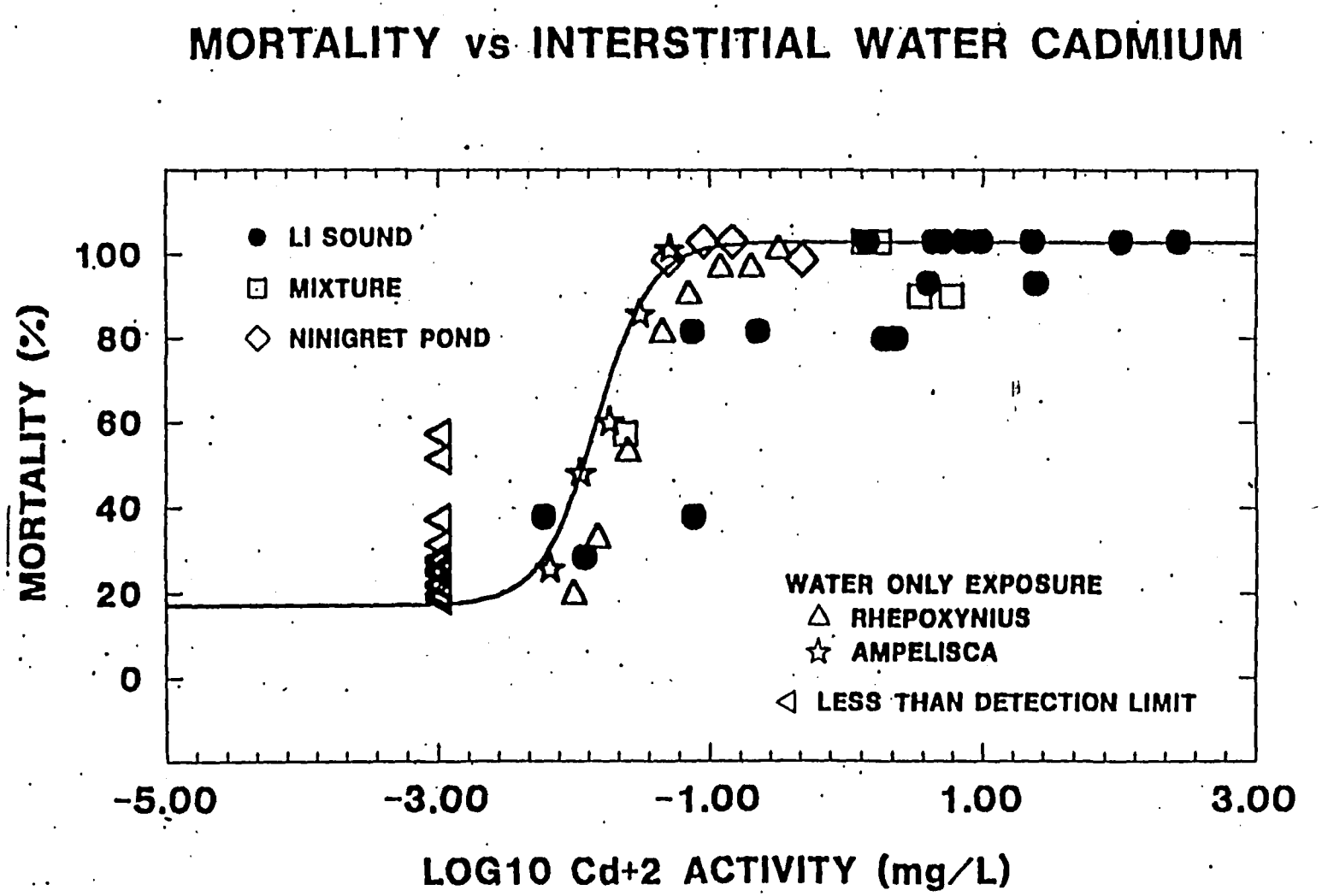


Figure 3-6. Mortality versus interstitial water cadmium activity for three sediments. Water only exposure data for Ampelisca and Rhepoxynius. The line is a joint fit to both water only data sets.

Figure 3-7 presents a comparison of the resulting mortality from the water-only test and interstitial water from the sediment tests. The LC50s for the water-only and the average of day 0 and day 10 pore-water concentration were 31 and 28 ug/L respectively showing strong agreement in predicting toxicity.

The data presented in this chapter demonstrate that in water-only exposures metal activity and concentration can be used to predict toxicity. The results of four experiments demonstrate that mortality data from water-only exposures can be used to predict sediment toxicity using pore water concentrations. The metal activity or concentration in interstitial water therefore would be an important component of a partitioning model that is needed to establish sediment quality criteria. The following chapters present the current developments in determining partitioning and hence bioavailability for sediment metals.

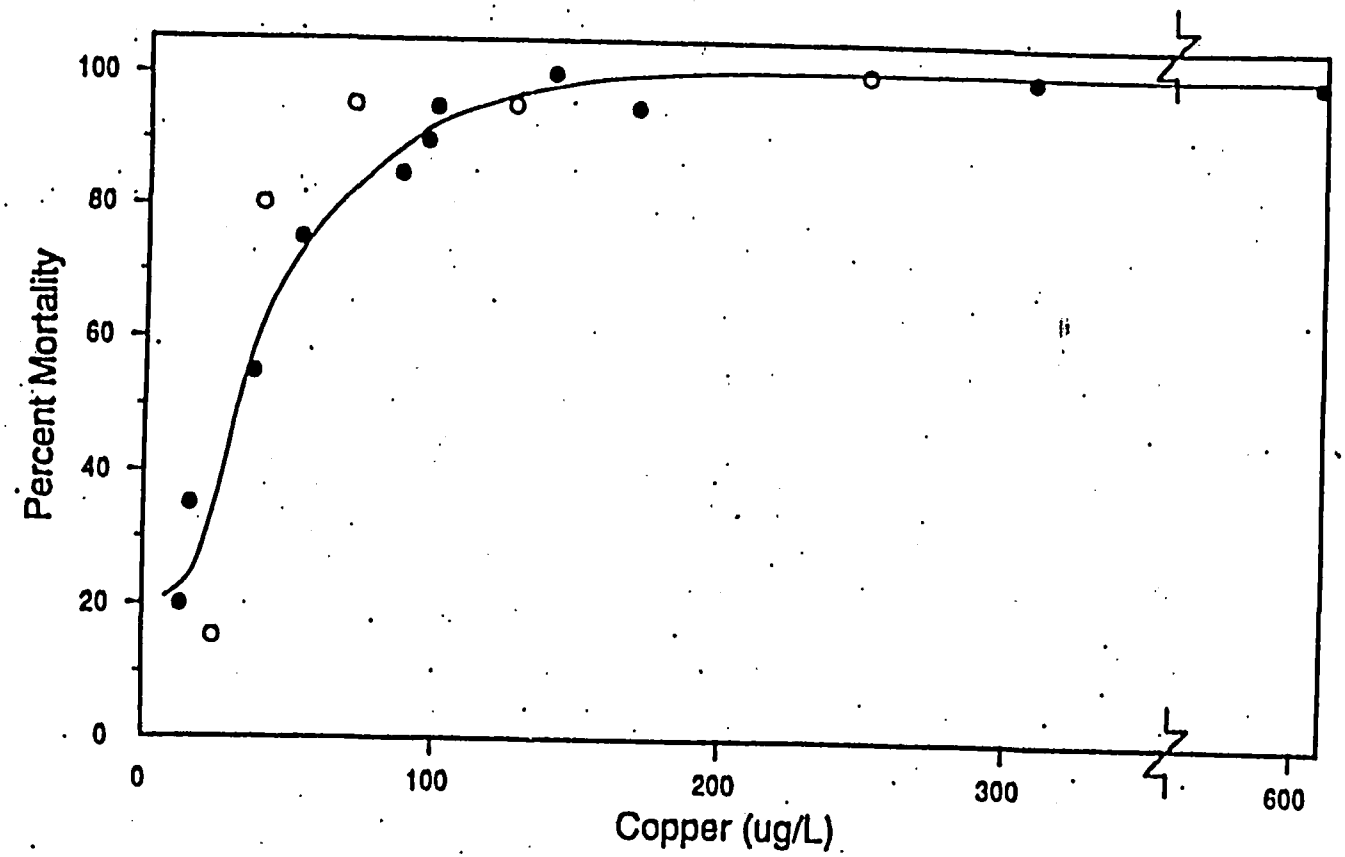


Figure 3-7. Toxicity of copper to Hyallela azteca versus metal concentrations in a water-only exposure (open symbols) and versus porewater copper concentrations in sediments from Keweenaw Waterway (closed symbols).

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CHAPTER 4

METAL PARTITIONING

The state of the art of modeling metal sorption to oxides in laboratory systems is well developed and detailed models are available for cation and anion sorption [see the articles in Stumm, [1] and Dzombak and Morel, [2] for recent summaries]. The models consider surface complexation reactions as well as electrical interactions via models of the double layer. Models for natural soil and sediment particles are less well developed. However, recent studies suggest that similar models can be applied to soil systems [3,4,5,6,7,8,9]. Since the ability to predict partition coefficients is required if pore water metal concentration is to be inferred from the total concentration, some practical model is required. This chapter presents the theoretical development of metals partitioning in sediments.

Metal Sorption Phases

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

A start in this direction was made during a recent conference [10]. A more formal presentation is available [11]. The basic idea was that instead of considering only one sorption phase as is assumed for non-ionic hydrophobic chemical sorption, multiple sorption phases were considered. The conventional view of metals speciation in aerobic soils and sediments is that metals are associated with the exchangable, carbonate, and Fe and Mn oxide forms, as well as that associated with the organic matter and 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 iron and manganese [12,13,14,15]. These phases are important because they have a large

sorptive capacity. Further 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 labile metal sulfide interactions which dominate the speciation in the anaerobic layers of the sediment.

Titration Experiments

The importance of sulfide in the control of metal concentrations in the interstitial water of marine sediments is well documented [16,17,18,19]. Metal sulfides are very insoluble and the equilibrium interstitial water metal concentrations in the presence of sulfides are small. If the interstitial water sulfide concentration in sediments is large, then as metal is added to the sediment, metal sulfide would precipitate following the reaction:

$$M^{2+} + S^{2-} \rightarrow MS(s) \qquad (4\text{-}1)$$

This appeared to be happening during a spiked cadmium sediment toxicity test [20] since a visible bright yellow cadmium sulfide precipitate formed as cadmium was added to the sediment. However, interstitial water sulfide activity, $\{S^{2-}\}$, measured with a sulfide electrode indicated that there was little or no free sulfide in the unspiked sediment. This was, at the time, a most puzzling result.

The lack of 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 this solid phase sulfide initially present. As cadmium is added to the sediment it causes the solid phase iron sulfide to dissolve releasing sulfide which is available for the formation of cadmium sulfide. The reaction is:

$$Cd^{2+} + FeS(s) \rightarrow CdS(s) + Fe^{2+} \qquad (4\text{-}2)$$

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

Amorphous FeS

A direct test of the extent to which this reaction takes place was performed [20]. 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 4-1. The plot of dissolved cadmium versus cadmium added illustrates the increase in dissolved cadmium that occurs near $[Cd]_A / [FeS(s)]_i = 1$. A similar experiment has been performed for amorphous MnS with comparable results. It is interesting to note that these displacement reactions among metal sulfides have been observed by other investigators [21]. The reaction was also postulated by Pankow [22] to explain an experimental result involving copper and synthetic FeS.

These experiments plainly demonstrate that solid phase amorphous iron and manganese sulfide can readily be displaced by adding cadmium. As a consequence it is a source of available sulfide which must be taken into account in evaluating the relationship between solid phase and aqueous phase cadmium in sediments. A direct confirmation that the removal of cadmium was via the displacement of iron sulfide is shown in Figure 4-2. The supernatant from a titration of FeS by Cd^{2+} was analyzed for both cadmium and iron. The solid lines are the theoretical expectation based on the stoichiometry of the reaction (Equation 4-2).

Sediments

A similar titration procedure has been used to evaluate the behavior of sediments taken from four quite different marine environments: the Long Island Sound and Ninigret

CADMIUM TITRATION OF IRON SULFIDE

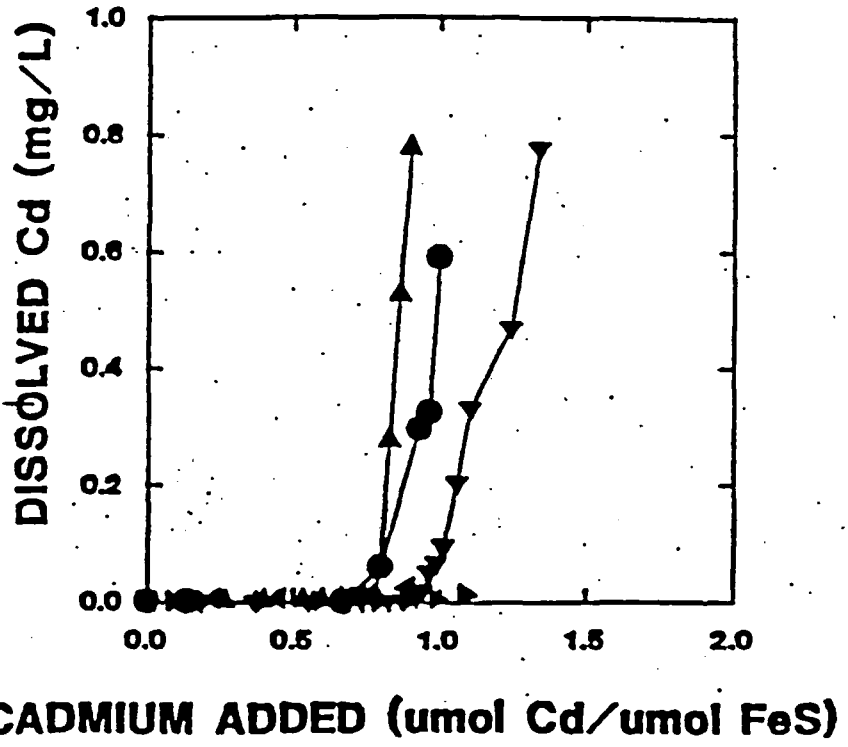

Figure 4-1. Cadmium titrations of amorphous FeS. Abscissa is cadmium added normalized by FeS initially present. Ordinate is total dissolved cadmium. The lines connecting the data points are an aid to visualizing the data.

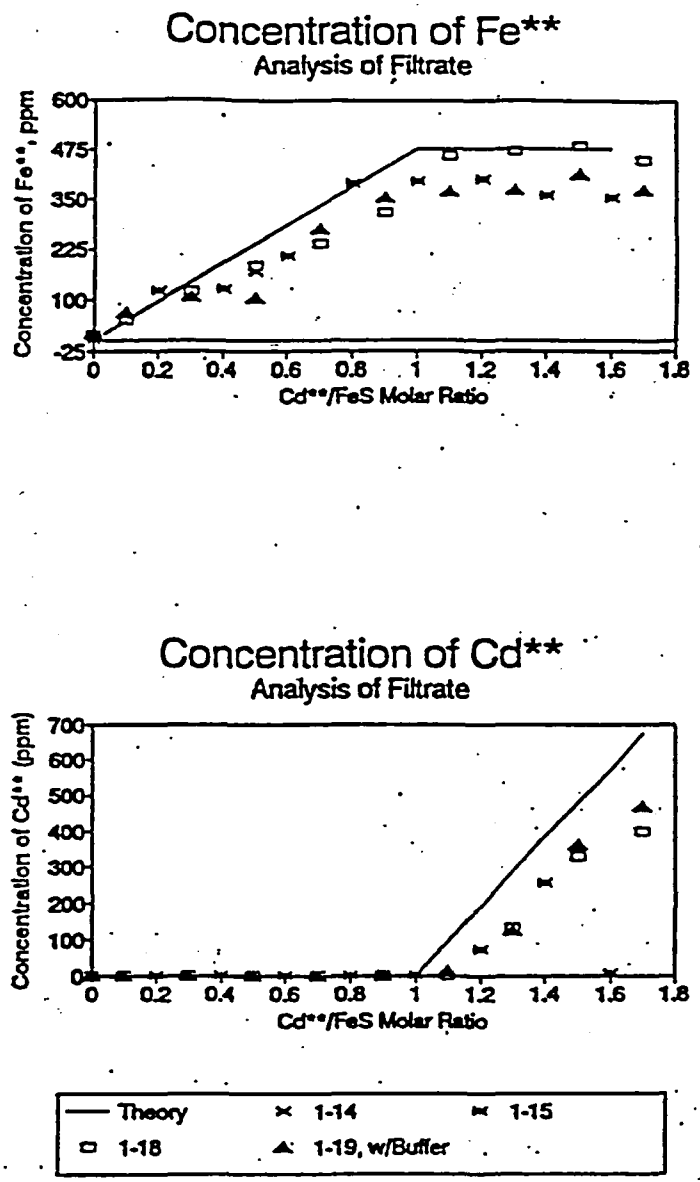

Figure 4-2. Concentrations of Fe^{2+} and Cd^{2+} in supernatent from titration of FeS by Cd^{2+}.

Pond sediments used in the toxicity tests; and sediments from Black Rock Harbor and the Hudson River. The binding capacity for cadmium is estimated by extrapolating a straight line fit to the dissolved cadmium data. The equation is:

$$[\Sigma Cd(aq)] = \max\{0, m([Cd]_A - [Cd]_B)\} \quad (4\text{-}3)$$

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 sediments exhibit quite different binding capacities for cadmium, listed in Table 4-1, ranging from approximately 1 μmol/gm to more than 100 μmol/g. The question is whether this binding capacity is explained by the solid phase sulfide present in the samples.

TABLE 4-1. CADMIUM BINDING CAPACITY AND AVS OF SEDIMENTS

Sediment	Initial AVS (μmol/g)[a]	Final AVS (μmol/g)[b]	Cd Binding Capacity[e] (μmol/g)
Black Rock Harbor	175.(41.)	-	114.(12.1)
Hudson River	12.6(2.8)	-	8.58 (2.95)
LI SoundOe(c)	15.9 (3.3)	13.9 (6.43)	4.57 (2.52)
Mixture[c]	5.45 (-)	3.23 (1.18)	-
Ninigret Pond[c,d]	2.34 (0.73)	0.28 (0.12)	1.12 (0.42)

[a]Average (Standard Deviation) AVS of repeated measurements of the stock
[b]Average (Standard Deviation) AVS after the sediment toxicity experiment
[c]From original cadmium experiment [20]
[d]50/50 mixture of LI Sound and Ninigret Pond
[e]From Equation (4-3)

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 are the most reactive. These sediment sulfides can be classified into three broad classes which reflect the techniques used for quantification [19,23,24]. The most labile fraction, acid volatile sulfide (AVS),

is associated with the more soluble iron and manganese 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 associated with the organic matter in sediments [25].

The possibility that acid volatile sulfide is a direct measure of the solid phase sulfide that reacts with cadmium is examined in Table 4-1 which lists the sediment binding capacity for cadmium and the measured AVS for each sediment and in Figure 4-3 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, Table 4-1, suggests that some AVS is lost during titration experiment. In any case the covariation of sediment binding capacity and AVS is clear in the data in Table 4-1and Figure 4-3. This suggests that AVS is the proper quantification of the solid phase sulfides that can be dissolved by cadmium. The chemical basis for this is examined below.

Solubility Relationships and Displacement Reactions

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

$$FeS(s) \rightleftharpoons Fe^{2+} + S^{2-} \tag{4-4}$$

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

$$Cd^{2+} + FeS(s) \rightleftharpoons Cd^{2+} + Fe^{2+} + S^{2-} \tag{4-5}$$

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 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:

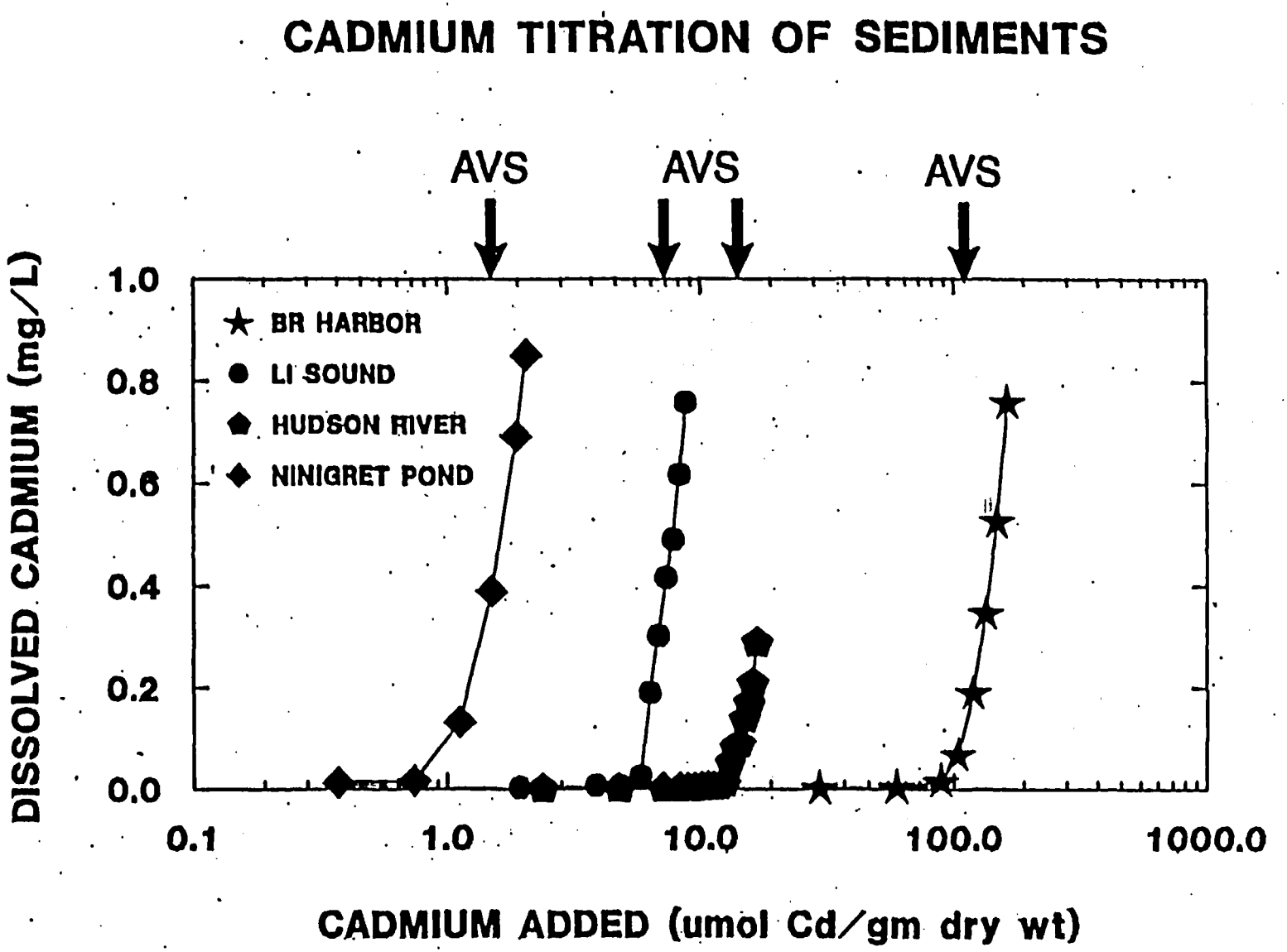

Figure 4-3. Cadmium titration of sediments as indicated in figure legend. Cadmium added per unit dry weight of sediment versus total dissolved cadmium.

$$Cd^{2+} + FeS(s) \rightarrow CdS(s) + Fe^{2+} \quad (4\text{-}6)$$

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 an analysis of the M(II)-Fe(II)-S(-II) system with both MS(s) and FeS(s) present in Appendix 4A. M(II) 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 products:

$$\{M^{2+}\}/[M]_A < K_{MS}/K_{FeS} \quad (4\text{-}7)$$

This is a general result that 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 4-6. However, the ratio is still less than the ratio of the sulfide solubility products.

This is an important finding since the data presented in Chapter 3 indicates 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 sulfide solubility products and the ratios are listed in Table 4-2. The ratio of cadmium activity to total cadmium is less than $10^{-10.5}$. For nickel the ratio is less than $10^{-5.6}$. 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 4-2, Zn, Cd, Pb, and Cu, indicate that metal activity for these metals will be very small in the presence of excess AVS.

TABLE 4-2. METAL SULFIDE SOLUBILITY PRODUCTS[a]

Metal Sulfide	log $K_{sp,2}$	log K_{sp}	Log (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

[a]Solubility products, $K_{sp,2}$, for the reaction $M^{2+} + H^{s-} \rightarrow MS(s) + H^+$ for CdS (greenockite), FeS (mackinawite), and NiS (millerite) from ref 27. Solubility products for CuS (covellite), PbS (galena), and ZnS (wurtzite), and $pK_2 = 18.57$ for the reaction $HS^- \rightarrow H^+ + S^{2-}$ from [28]. K_{sp} for the reaction $M^{2+} + S^{2-} \rightarrow MS(s)$ is computed from log $K_{sp,2}$ and pK_2.

Application to Mixtures of Metals

A conjecture based on the sulfide solubility products for the metals listed in Table 4-2 is that the AVS normalized toxicity of metals is additive. Since all these divalent metals have lower sulfide solubility parameters than FeS, they would all exist as metal sulfides if their molar sum is less than the AVS. For this case

$$\frac{\Sigma_i[M_T]_i}{[AVS]} < 1 \qquad (4\text{-}8)$$

no metal toxicity would be expected where $[M_T]_i$ is the total cold acid extractable ith metal concentration in the sediment. 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:

$$\frac{\Sigma_i[M_T]_i}{[AVS]} > 1 \qquad (4\text{-}9)$$

These two equations are precisely the formulas that one would employ 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 one discriminates between non toxic 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.

The appropriate quantity of metals to use in the metals/AVS ratio is referred to as "simultaneously extracted metal" or SEM. This is the metal which is extracted in the cold acid used in the AVS procedure. This is the appropriate quantity to use because some metals form sulfides which are not labile in the AVS extraction (e.g., nickel). If a more rigorous extraction were used to increase the fraction of metal extracted which 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 to AVS ratio [26].

The above discussion is predicated on the assumption that all the metal sulfides behave similarly to cadmium sulfide. Results of sediment spiking experiments will be presented in Chapter 5 for cadmium, copper, lead, nickel, zinc, and metals mixtures which demonstrate the similar behavior of these metals. Further 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 can be tested directly using sediment toxicity tests. These are discussed in the next chapters.

Appendix 4A

Solubility Relationships for Metal Sulfides. Consider the following situation: a quantity of FeS is titrated with a metal that forms a more insoluble sulfide. We analyze the result using an equilibrium model of the M-(II)-Fe(II)-S(-II) system. The mass action laws for the metal and iron sulfides are

$$\gamma_{M^{2+}}[M^{2+}]\gamma_{S^{2-}}[S^{2-}] = K_{MS} \tag{A-1}$$

$$\gamma_{Fe^{2+}}[Fe^{2+}]\gamma_{S^{2-}}[S^{2-}] = K_{FeS} \tag{A-2}$$

where $[M^{2+}]$, $[Fe^{2+}]$, and $[S^{2-}]$ are the molar concentrations; $\gamma_{M^{2+}}$, $\gamma_{Fe^{2+}}$, and $\gamma_{S^{2-}}$ are the activity coefficients; and K_{MS} and K_{FeS} are the sulfide solubility products. The mass balance equations for total M(II), Fe(II), and S(-II) are

$$\alpha^{-1}_{M^{2+}}[M^{2+}] + [MS(s)] = [M]_A \tag{A-3}$$

$$\alpha^{-1}_{Fe^{2+}}[Fe^{2+}] + [FeS(s)] = [FeS(s)]_i \tag{A-4}$$

$$\alpha^{-1}_{S^{2-}}[S^{2-}] + [MS(s)] + [FeS(s)] = [FeS(s)]_i \tag{A-5}$$

where

$$\alpha_{M^{2+}} = [M^{2+}]/[\Sigma M(aq)] \tag{A-6}$$

$$\alpha_{Fe^{2+}} = [Fe^{2+}]/[\Sigma Fe(aq)] \tag{A-7}$$

$$\alpha_{S^{2-}} = [S^{2-}]/[\Sigma S(aq)] \tag{A-8}$$

are the ratios of the divalent species concentrations to the total dissolved M(II), Fe(II), and S(-II) concentrations, $[\Sigma M(aq)]$, $[\Sigma Fe(aq)]$, and $[\Sigma S(aq)]$, respectively. [MS(s)] and [FeS(s)] are the concentrations of solid-phase metal and iron sulfides at equilibrium. $[FeS(s)]_i$ is the

initial iron sulfide concentration in the sediment, and $[M]_A$ is the concentration of added metal.

The solution of these five equations can be obtained as follows. the mass balance Equations A-3 and A-4 for M(II) and Fe(II) can be solved for [MS(s)] and [FeS(s)] and substituted in the mass balance Equation A-5 for S(II):

$$-\sigma^{-1}_{S^{2-}}[S^{2-}] + \sigma^{-1}_{Fe^{2+}}[Fe^{2+}] + \sigma^{-1}_{M^{2+}}[M^{2+}] = [M]_A \qquad \text{(A-9)}$$

The mass action Equations A-1 and A-2 can be used to substitute for $[Fe^{2+}]$ and $[M^{2+}]$, which results in a quadratic equation for $[S^{2-}]$:

$$-\sigma^{-1}_{S^{2-}}[S^{2-}] + \frac{1}{\gamma_{S^{2-}}[S^{2-}]}\left[\frac{\sigma^{-1}_{Fe^{2+}}K_{FeS}}{\gamma_{Fe^{2+}}} + \frac{\sigma^{-1}_{M^{2+}}K_{MS}}{\gamma_{M^{2+}}}\right] = [M]_A \qquad \text{(A-10)}$$

The positive root can be accurately approximated by

$$\frac{1}{\gamma_{S^{2-}}[S^{2-}]} = \left[\frac{\sigma^{-1}_{Fe^{2+}}K_{FeS}}{\gamma_{Fe^{2+}}} + \frac{\sigma^{-1}_{M^{2+}}K_{MS}}{\gamma_{M^{2+}}\gamma_{S^{2-}}}\right]^{-1}[M]_A \qquad \text{(A-11)}$$

which results from ignoring the leading term in Equation A-10. This is legitimate because the term in parentheses in Equation A-10 is small relative to $[M]_A$ due to the presence of the sulfide solubility products. As a results, $[S^{2-}]$ is also small since it is in the denominator. Hence, the leading term in Equation A-10 must be small relative to $[M]_A$ and can safely be ignored.

The metal activity can now be found from the solubility equilibrium Equation A-1:

$$\{M^{2+}\} = \gamma_{M^{2+}}[M^{2+}] = K_{MS}\frac{1}{\gamma_{S^{2-}}[S^{2-}]} = K_{MS}\left[\frac{\alpha^{-1}_{Fe^{2+}}K_{FeS}}{\gamma_{Fe^{2+}}} + \frac{\alpha^{-1}_{M^{2+}}K_{MS}}{\gamma_{M^{2+}}}\right]^{-1}[M]_A \quad \text{(A-12)}$$

so that

$$\frac{\{M^{2+}\}}{[M]_A} = \frac{K_{MS}}{\beta_{Fe^{2+}}K_{FeS} + \beta_{M^{2+}}K_{MS}} \quad \text{(A-13)}$$

where

$$\beta_{Fe^{2+}} = 1/(\alpha_{Fe^{2+}}\gamma_{Fe^{2+}}) \quad \text{(A-14)}$$

and

$$\beta_{M^{2+}} = 1/(\alpha_{M^{2+}}\gamma_{M^{2+}}) \quad \text{(A-15)}$$

Equation A-13 can be expressed as

$$\frac{\{M^{2+}\}}{[M]_A} = \frac{K_{MS}}{K_{FeS}}\left[\frac{1}{\beta_{Fe^{2+}} + \beta_{M^{2+}}\frac{K_{MS}}{K_{FeS}}}\right] \quad \text{(A-16)}$$

The magnitude of the term in parentheses can be estimated as follows. The first term in the denominator is always greater than or equal to 1, $\beta_{Fe^{2+}} \geq 1$, because it is the reciprocal of two terms both of which are less than or equal to 1, Equation A-14. They are $\alpha_{Fe^{2+}} \leq 1$, which is the ratio of the divalent to total aqueous concentration, and $\gamma_{Fe^{2+}} \leq 1$, which is an activity coefficient. The second term in the denominator cannot be negative, $\beta_{M^{2+}}K_{MS}/K_{FeS} > 0$, since all of its terms are positive. thus, the denominator of the expression in parentheses is always greater than 1, $\beta_{Fe^{2+}} + \beta_{M^{2+}}K_{MS}/K_{KeS} > 1$. Therefore, the expression in parentheses is always less than 1. Hence, the magnitude of the ratio of metal activity to total added metal is bounded from above by ratio of the sulfide solubility products:

$$\{Me^{2+}\}/[M]_A < K_{MS}/K_{FeS} \tag{A-17}$$

This results applies if $[FeS]_i > [M]_A$ so that excess [FeS(s)] is present.

If sufficient metal is added to exhaust the initial quantity of iron sulfide, then [FeS(s)] = 0. Hence, the iron sulfide mass action equation (A-2) is invalid and the above equation no longer applies. Instead, the only solid-phase sulfide is metal sulfide and

$$[MS] = [FeS]_i \tag{A-18}$$

so that, from the metal mass balance equation

$$\{M^{2+}\} = \gamma_{M^{2+}}\alpha_{M^{2+}}([M]_A - [FeS(s)_i]) \tag{A-19}$$

this completes the derivation of Equations 4-8 and 4-9.

Glossary

[AVS]	acid volatile sulfide concentration (μmol/g)
$\{Fe^{2+}\}$	activity of Fe^{2+} (mol/L)
$[Fe^{2+}]$	concentration of Fe^{2+} (mol/L)
[FeS(s)]	concentration of iron sulfide (mol/L)
$[FeS(s)]_i$	initial iron sulfide concentration in the sediment (mol/L)
K_{FeS}	solubility product for FeS(s) $[(mol/L)^2]$
K_{MS}	solubility product for MS(s) $[(mol/L)^2]$
$\{M^{2+}\}$	divalent metal activity (mol/L)
$[M^{2+}]$	concentration of M^{2+} (mol/L)
$[M]_A$	concentration of added metal (mol/L)
[MS(s)]	concentration of solid-phase metal sulfide (mol/L)
$\{S^{2-}\}$	activity of S^{2-} (mol/L)
$[S^{2-}]$	concentration of S^{2-} (mol/L)
[SEM]	simultaneously extracted metal concentration (μmol/g)
$[SEM]_{Cd}$	simultaneously extracted Cd concentration (μmol/g)
$[SEM]_{Cu}$	simultaneously extracted Cu concentration (μmol/g)
$[SEM]_{Ni}$	simultaneously extracted Ni concentration (μmol/g)
$[SEM]_{Pb}$	simultaneously extracted Pb concentration (μmol/g)
$[SEM]_{Zn}$	simultaneously extracted Zn concentration (μmol/g)
$\alpha_{Fe^{2+}}$	$\{Fe^{2+}\}/[\Sigma Fe(aq)]$
$\alpha_{M^{2+}}$	$\{M^{2+}\}/[\Sigma m(aq)]$
$\alpha_{S^{2-}}$	$\{S^{2-}\}/[\Sigma S(aq)]$
$\beta_{Fe^{2+}}$	$(\alpha_{Fe^{2+}}\gamma_{Fe^{2+}})^{-1}$
$\beta_{M^{2+}}$	$(\alpha_{M^{2+}}\gamma_{M^{2+}})^{-1}$
$\gamma_{Fe^{2+}}$	activity coefficient of Fe^{2+}
$\gamma_{M^{2+}}$	activity coefficient of M^{2+}
$\gamma_{S^{2-}}$	activity coefficient of S^{2-}
$[\Sigma Fe(aq)]$	concentration of total dissolved Fe(II) (mol/L)

[ΣM(aq)]	concentration of total dissolved M(II) (mol/L)
[ΣS(aq)]	concentration of total dissolved S(II) (mol/L)

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CHAPTER 5

LABORATORY SPIKING EXPERIMENTS

The discussion in the previous chapter has highlighted the importance of metal sulfides. Sulfides of Cd, Cu, Ni, Pb, and Zn all have lower sulfide solubility product constants than the sulfides of iron and manganese, which are formed naturally in sediments as a product of the bacterial oxidation of organic matter [1]. As a result, these metals will displace manganese and iron whenever they are present together with manganese and iron monosulfides [2]. Because the solubility product constants of these sulfides are so small, sediments with an excess of AVS will have very low metal activity in the interstitial water, and no toxicity due to these metals should be observed in the sediments. If the metals are present in excess of the sulfides (SEM/AVS > 1.0) and there are no other sediment phases capable of binding the metals (e.g., DOC or TOC) metal will be present in the interstitial water and the sediment may be toxic. The validity of this theory can be demonstrated through experimentation. Results of acute toxicity testing with sediments spiked with metals in the laboratory are presented in this chapter. Predictions of the toxicity of metals-contaminated field sediments using interstitial water concentration of metals and AVS normalization are presented in Chapter 6. Results of chronic toxicity tests using sediment colonization experiments are presented in Chapter 7.

In this chapter results from a series of acute toxicity tests using saltwater sediments spiked with cadmium, copper, lead, nickel, or zinc, and an equimolar mixture of cadmium, copper, nickel, and zinc will be examined in detail. The methodology for these tests is presented in Appendix 5A. These tests will be highlighted because they serve as an example from a single laboratory (Narragansett EPA Research Laboratory) of the methods used in the sediment spiking experiments with metals and represent a series of tests which followed a consistent methodology, performed with a relatively sensitive species unable to avoid the sediment (Ampelisca abdita, the amphipod). A. abdita is an estuarine, tube-building, infaunal amphipod commonly used in sediment toxicity testing. Published results from tests using polychaetes [4,5] and copepods [6] in saltwater sediments, and oligochaetes and snails [7] in freshwater sediments, will be combined with the A. abdita

results. Data from spiked sediment tests in which neither AVS nor interstitial water were measured [8,9] or which used non-standard methods [10] will not be included.

Results: Saltwater Amphipod Tests

The data handling techniques used in this chapter are discussed below. Detection limits were calculated for all chemical analyses based on instrument detection limits and sample size. In those instances where a mean concentration is a summation of measured data and data below the limit of detection, 1/2 the detection limit was used for those values below the limit of detection. Means for which there were no measured values above the detection limit are indicated as n.d. in the appropriate tables and graphs. Only detectable interstitial water metal was included in the calculation of interstitial water toxic units.

Sediments which caused greater than 24 percent mortality were considered toxic. Mearns et al. [8] found that sediments which caused greater than 24 percent mortality in tests with the amphipod Rhepoxynius abronius were not consistently classified as significantly toxic. This criterion is similar to the "80 percent of control survival" criterion used in the EMAP program [13].

Many of the interstitial and overlying water concentrations discussed herein are expressed as toxic units. A toxic unit is the measured water concentration divided by the water-only LC50 concentration for that particular compound for the test organism. For example, a sediment with an interstitial water concentration equal to the water-only LC50 concentration for the test organism would have one interstitial water toxic unit (IWTU). When more than one toxic metal is present, IWTUs are calculated as the sum of the toxic units of the individual metals; e.g., $IWTU_{Cd+Ni}$ = (interstitial water conc $Cd/LC50_{Cd}$) + (interstitial water conc $Ni/LC50_{Ni}$). Thus, if interstitial water is the principal source of metals toxicity, and availability of metals is the same in water of water-only tests and interstitial water in sediment tests, 50 percent mortality would be expected in sediments having 1.0 IWTUs. In this document we use < 0.5 IWTUs to indicate sediments unlikely

to cause significant mortality because on the average water-only LC0 and LC50 values differ by approximately a factor of two [14] and because data in our experiments supports this value as a break-point between nontoxic and toxic sediments.

Dashed lines are used on all figures to indicate predicted break points in mortality and chemical concentration. The dashed lines at SEM/AVS = 1.0 indicate the predicted boundaries between nontoxic sediments and sediments which may be toxic. The dashed line at 24 percent mortality indicates the demarcation between toxic and nontoxic sediments, and the dashed lines at 50 percent mortality and IWTU = 1.0 indicates the theoretical mortality at 1.0 IWTU.

Water-Only Tests

Ten-day static renewal tests were conducted with A. abdita to determine water-only LC50s for Cd, Cu, Ni, Pb, and Zn in seawater. The 10-day LC50 values for the water-only tests were calculated using the trimmed Spearman-Karber method [11]. The LC50 values from the water-only tests are summarized in Table 5-1. There is no 10-day LC50 value for cadmium available for Rhepoxynius hudsoni so the 10-day LC50 value for Ampelisca abdita (36 µg/L) was used for the calculation of toxic units for this species. This assumption is reasonable because these amphipods have similar sensitivities; i.e., the 4-day LC50's for R. hudsoni (640 µg/l) and A. abdita (340 µg/l) differed by less than a factor of two [12]. We assume that the ten-day LC50s for both species will also be similar.

TABLE 5-1. 10-DAY WATER-ONLY LC50 FOR AMPELISCA ABDITA

Metal	LC50 (µg/L)	95 % Confidence Limits
Cadmium	36.0	Not reliable
Copper	20.5	16.5 - 25.5
Lead	3,020	1,980 - 4,610
Nickel	2,400	2,050 - 2,820
Zinc	343	291 - 405

Spiked sediment tests

Amphipods were exposed to control and metal-spiked sediments in 10-day tests with continuous renewal of overlying water. In all experiments two sediments of different AVS concentrations were used: Ninigret Pond (AVS = 1.18-2.25 μmol/g) and Long Island Sound (AVS = 9.72-19.9 μmol/g). In the cadmium test a mixture of these two sediments was also used (AVS = 4.34 μmol/g). The nominal treatments used in most experiments, expressed as the molar ratio of metal to AVS were 0.0 (control), 0.1, 0.3, 1, 3, 10, and 30 (Table 5-2). There were four replicates per treatment in each test: two "biological" replicates were used to assess mortality, and two "chemical" replicates were used for metal and AVS analyses of the sediment at test initiation and termination. Twenty (30 in the cadmium test) amphipods were added to each "biological" and the day 10 "chemical" replicate at the start of the test. Interstitial water samples were collected in diffusion samplers (peepers) from each of these three replicates at the termination of the experiments.

Sediment Chemistry -

Day 0 Versus Day 10 Chemistry Values -

AVS, SEM, and dry weight sediment chemistry measurements varied somewhat from day 0 to day 10, but the variation was generally within 20 percent and did not show a definite time, concentration, or metal-dependent pattern. Therefore, all AVS, SEM, and dry weight sediment chemistry data will be reported as means of day 0 and day 10 values.

Interstitial Water Metal Versus SEM/AVS

In all the individual and mixed metals experiments the interstitial water metal concentrations were usually below the limit of detection in sediments with SEM/AVS ratios below 1.0 (Table 5-2, Figure 5-1). In the cadmium and mixed metals experiments the values for interstitial water appear high because of the high detection limits in these

TABLE 5-2. SUMMARY OF SEDIMENT CHARACTERISTICS, METAL CONCENTRATIONS, AND AMPHIPOD MORTALITY IN SIX SPIKED SEDIMENT EXPERIMENTS.

Spiked Metal	Sediment	Nominal Concentration	Percent TOC	Percent Silt/Clay	Dry Weight of Metal (ug/g)					Sum Dry Wt. (umol/g)	Sum SEM*** (umol/g)	AVS (umol/g)	SEM/ AVS	IWTU	Percent Mortality
					Cu	Pb	Cd	Zn	Ni						
Cadmium	LIS	CONT	0.88	94.4	58*	35.89*	ND**	156.29*	27.07*	3.94	0.00	14.9	0.00	ND	1.65
Cadmium	LIS	0.1X	0.88	94.4	58*	35.89*	175.53	156.29*	27.07*	5.50	1.56	14.9	0.10	ND	8.35
Cadmium	LIS	0.3X	0.88	94.4	58*	35.89*	544.77	156.29*	27.07*	8.78	4.85	14.9	0.33	ND	16.7
Cadmium	LIS	1X	0.88	94.4	58*	35.89*	1872.22	156.29*	27.07*	20.59	16.66	14.9	1.12	ND	10
Cadmium	LIS	3X	0.88	94.4	58*	35.89*	5810.61	156.29*	27.07*	55.63	51.69	14.9	3.47	2405.56	100
Cadmium	LIS	10X	0.88	94.4	58*	35.89*	19969.10	156.29*	27.07*	181.60	177.66	14.9	11.92	13444.44	88.4
Cadmium	NIN	CONT	0.15	0.0	ND*	ND*	ND	2.87*	ND*	0.06	0.00	1.3	0.00	ND	5
Cadmium	NIN	0.1X	0.15	0.0	ND*	ND*	17.20	2.87*	ND*	0.21	0.15	1.3	0.12	ND	12.5
Cadmium	NIN	0.3X	0.15	0.0	ND*	ND*	71.79	2.87*	ND*	0.70	0.64	1.3	0.49	ND	12.5
Cadmium	NIN	1X	0.15	0.0	ND*	ND*	287.15	2.87*	ND*	2.61	2.55	1.3	1.95	ND	40
Cadmium	NIN	3X	0.15	0.0	ND*	ND*	638.19	2.87*	ND*	5.74	5.68	1.3	4.33	263.89	95
Cadmium	NIN	10X	0.15	0.0	ND*	ND*	2727.93	2.87*	ND*	24.33	24.27	1.3	18.53	81.11	100
Cadmium	MIX	CONT	0.57	47.2	29.04*	18.28*	ND	77.56*	14*	1.97	0.00	4.3	0.00	ND	16.7
Cadmium	MIX	0.1X	0.57	47.2	29.04*	18.28*	31.08	77.56*	14*	2.25	0.28	4.3	0.06	ND	11.7
Cadmium	MIX	0.3X	0.57	47.2	29.04*	18.28*	196.49	77.56*	14*	3.72	1.75	4.3	0.40	ND	23.4
Cadmium	MIX	1X	0.57	47.2	29.04*	18.28*	1082.71	77.56*	14*	11.60	9.63	4.3	2.22	ND	46.7
Cadmium	MIX	3X	0.57	47.2	29.04*	18.28*	2325.82	77.56*	14*	22.66	20.69	4.3	4.77	966.67	100
Cadmium	MIX	10X	0.57	47.2	29.04*	18.28*	5443.61	77.56*	14*	50.40	48.43	4.3	11.16	3277.78	85
Copper	LIS	CONT	0.88	94.4	58.00	35.89	0.21	156.29	27.07	3.94	0.27	13.3	0.02	0.07	12.5
Copper	LIS	0.1X	0.88	94.4	177.12	36.55	0.21	157.46	27.07	5.84	0.99	12.2	0.08	0.09	7.5
Copper	LIS	0.3X	0.88	94.4	408.41	36.15	0.24	159.37	27.06	9.50	1.54	4.4	0.35	0.13	17.5
Copper	LIS	1X	0.88	94.4	1234.76	35.91	0.23	157.41	26.56	22.47	11.46	1.2	9.43	0.87	100
Copper	LIS	3X	0.88	94.4	3323.07	35.08	0.18	151.37	25.53	55.22	46.23	1.9	23.89	264.00	100
Copper	LIS	10X	0.88	94.4	11165.67	35.74	0.17	150.08	23.12	178.59	173.23	1.7	103.73	1319.53	100
Copper	LIS	30X	0.88	94.4	23369.54	23.15	ND	148.01	9.96	370.34	300.87	1.8	163.07	19768.63	100
Copper	NIN	CONT	0.15	0.0	ND	ND	ND	2.87	ND	0.06	0.00	1.2	0.00	0.06	22.5
Copper	NIN	0.1X	0.15	0.0	4.60	ND	ND	2.38	ND	0.12	0.05	1.4	0.04	0.29	5
Copper	NIN	0.3X	0.15	0.0	11.09	ND	ND	2.27	ND	0.22	0.08	1.1	0.08	0.14	15
Copper	NIN	1X	0.15	0.0	71.68	ND	ND	2.34	ND	1.18	0.42	0.6	0.67	0.39	30
Copper	NIN	3X	0.15	0.0	213.31	ND	ND	2.41	ND	3.41	2.05	0.3	6.36	2.08	100
Copper	NIN	10X	0.15	0.0	428.60	ND	ND	2.38	ND	6.79	5.32	0.3	15.41	415.16	100
Copper	NIN	30X	0.15	0.0	724.98	ND	ND	2.67	ND	11.46	10.28	0.6	16.31	7920.93	100
Lead	LIS	CONT	0.99	94.4	50.32	43.52	ND	165.69	24.17	3.95	0.23	19.9	0.01	ND	10
Lead	LIS	0.1X	0.99	94.4	52.96	202.94	ND	178.71	24.55	4.97	1.25	18.6	0.07	ND	5
Lead	LIS	0.3X	0.99	94.4	52.57	595.01	ND	165.17	24.50	6.64	4.16	12.8	0.33	ND	12.5
Lead	LIS	1X	0.99	94.4	52.16	2297.99	ND	169.50	24.50	14.92	14.58	16.4	0.89	0.16	7.5
Lead	LIS	3X	0.99	94.4	49.86	8803.36	ND	161.58	23.50	46.14	28.49	14.9	1.92	0.26	22.5
Lead	LIS	10X	0.99	94.4	42.73	23108.45	ND	184.43	17.13	115.31	68.26	15.5	4.41	1.09	42.5
Lead	LIS	30X	0.99	94.4	41.49	90441.39	ND	148.43	18.07	439.72	78.61	14.2	5.52	18.44	100

TABLE 5-2. SUMMARY OF SEDIMENT CHARACTERISTICS, METAL CONCENTRATIONS, AND AMPHIPOD MORTALITY IN SIX SPIKED SEDIMENT EXPERIMENTS.
(continued)

Spiked Metal	Sediment	Nominal Concentration	Percent TOC	Percent Silt/Clay	Dry Weight of Metal (ug/g) Cu	Pb	Cd	Zn	Ni	Sum Dry Wt (umol/g)	Sum SEM*** (umol/g)	AVS (umol/g)	SEM/AVS	IWTU	Percent Mortality
Lead	NIN	CONT	0.15	0.0	ND	7.53	ND	8.56	ND	0.18	0.02	1.2	0.02	ND	10
Lead	NIN	0.1X	0.15	0.0	ND	27.70	ND	6.36	ND	0.24	0.17	1.9	0.09	0.02	17.5
Lead	NIN	0.3X	0.15	0.0	0.43	100.46	ND	9.46	ND	0.65	0.59	2.2	0.26	ND	15
Lead	NIN	1X	0.15	0.0	0.67	353.51	ND	9.38	ND	1.87	1.87	3.1	0.60	0.03	5
Lead	NIN	3X	0.15	0.0	0.35	1218.28	ND	3.25	ND	5.94	7.14	5.8	1.24	0.21	17.5
Lead	NIN	10X	0.15	0.0	2.44	11448.69	ND	1.32	ND	55.32	16.73	4.1	4.10	2.48	55
Lead	NIN	30X	0.15	0.0	ND	9519.39	ND	1.51	ND	45.98	20.27	3.4	6.01	43.26	92.5
Nickel	LIS	CONT	0.88	94.4	54.26	35.17	0.28	144.47	25.39	3.67	0.66	12.6	0.05	ND	0
Nickel	LIS	0.1X	0.88	94.4	54.67	35.13	0.30	143.66	84.48	4.67	1.12	12.0	0.09	ND	7.5
Nickel	LIS	0.3X	0.88	94.4	55.19	36.37	0.27	146.93	209.13	6.86	2.90	10.7	0.27	ND	2.5
Nickel	LIS	1X	0.88	94.4	55.73	36.35	0.29	149.45	636.29	14.18	9.82	6.2	1.59	ND	10
Nickel	LIS	3X	0.88	94.4	54.73	36.04	0.28	151.94	1638.94	31.28	26.47	3.9	6.81	9.44	95
Nickel	LIS	10X	0.88	94.4	54.61	36.00	0.34	156.97	4254.09	75.90	70.93	4.0	17.70	163.98	100
Nickel	LIS	30X	0.88	94.4	55.00	36.30	0.41	168.67	9565.33	166.55	266.04	2.7	99.27	843.73	100
Nickel	LIS	100X	0.88	94.4	53.65	37.25	0.65	205.85	25169.49	432.89	574.22	1.9	303.26	2979.15	100
Nickel	NIN	CONT	0.15	0.0	ND	1.47	ND	2.48	1.39	0.07	0.17	1.9	0.09	0.04	5
Nickel	NIN	0.1X	0.15	0.0	ND	ND	ND	2.16	5.89	0.14	0.35	1.9	0.18	ND	7.5
Nickel	NIN	0.3X	0.15	0.0	ND	ND	ND	2.47	20.45	0.39	0.25	1.8	0.13	ND	2.5
Nickel	NIN	1X	0.15	0.0	ND	ND	ND	2.46	50.20	0.90	0.54	1.0	0.53	0.06	7.5
Nickel	NIN	3X	0.15	0.0	ND	ND	ND	2.44	94.20	1.65	1.21	0.6	2.02	1.47	2.5
Nickel	NIN	10X	0.15	0.0	ND	ND	ND	2.82	162.23	2.81	2.63	0.7	4.03	55.23	97.5
Nickel	NIN	30X	0.15	0.0	ND	ND	ND	3.36	473.75	8.13	7.64	0.9	8.74	271.94	100
Nickel	NIN	100X	0.15	0.0	ND	ND	ND	6.07	1399.45	23.93	22.95	0.5	49.35	762.81	97.5
Zinc	LIS	Cont	0.88	94.4	61.34	36.37	0.25	156.73	29.20	4.04	1.20	11.3	0.11	0.12	15
Zinc	LIS	0.1X	0.88	94.4	61.73	36.63	0.26	284.10	29.22	5.99	2.82	11.7	0.24	0.08	7.5
Zinc	LIS	0.3X	0.88	94.4	62.46	38.62	0.29	529.70	29.06	9.77	5.60	13.4	0.42	0.07	17.5
Zinc	LIS	1X	0.88	94.4	60.38	37.44	0.28	1369.89	28.67	22.58	20.71	15.1	1.37	0.02	15
Zinc	LIS	3X	0.88	94.4	60.97	38.16	0.27	3404.96	28.97	53.73	75.77	18.2	4.17	10.18	77.5
Zinc	LIS	10X	0.88	94.4	87.49	51.60	3.87	6877.02	32.29	107.41	158.43	15.0	10.53	344.62	100
Zinc	LIS	30X	0.88	94.4	84.30	48.74	3.32	13319.66	30.79	205.87	142.29	14.0	10.16	8283.21	100
Zinc	NIN	Cont	0.15	0.0	0.35	1.24	0.02	2.56	ND	0.06	0.01	2.3	0.00	ND	5
Zinc	NIN	0.1X	0.15	0.0	ND	1.28	ND	17.04	ND	0.28	0.27	2.5	0.11	ND	12.5
Zinc	NIN	0.3X	0.15	0.0	ND	1.39	ND	42.05	ND	0.66	0.71	3.0	0.24	ND	12.5
Zinc	NIN	1X	0.15	0.0	ND	1.28	ND	96.49	ND	1.49	1.51	2.7	0.55	0.03	5
Zinc	NIN	3X	0.15	0.0	ND	1.16	ND	178.69	ND	2.75	2.02	1.8	1.11	23.27	35
Zinc	NIN	10X	0.15	0.0	0.32	1.35	ND	256.79	ND	3.95	4.21	1.3	3.21	754.56	95
Zinc	NIN	30X	0.15	0.0	ND	1.30	ND	542.44	ND	8.32	8.99	1.9	4.63	2909.37	100
Cd, Cu, Ni, Zn	LIS	Cont	0.99	94.4	43.31	ND	0.47	121.50	18.82	2.86	3.21	9.7	0.33	ND	5

TABLE 5-2. SUMMARY OF SEDIMENT CHARACTERISTICS, METAL CONCENTRATIONS, AND AMPHIPOD MORTALITY IN SIX SPIKED SEDIMENT EXPERIMENTS. (continued)

Spiked Metal	Sediment	Nominal Concentration	Percent TOC	Percent Silt/Clay	Dry Weight of Metal (ug/g) Cu	Pb	Cd	Zn	Ni	Sum Dry Wt. (umol/g)	Sum SEM*** (umol/g)	AVS (umol/g)	SEM/AVS	IWTU	Percent Mortality
Cd, Cu, Ni, Zn	LIS	0.1X	0.99	94.4	70.58	ND	45.40	150.17	41.19	4.51	4.38	11.3	0.39	ND	2.5
Cd, Cu, Ni, Zn	LIS	0.3X	0.99	94.4	120.02	ND	128.65	199.90	81.55	7.48	8.68	6.9	1.25	ND	2.5
Cd, Cu, Ni, Zn	LIS	1X	0.99	94.4	287.67	ND	427.89	367.06	203.79	17.42	19.56	3.4	5.83	1.91	15
Cd, Cu, Ni, Zn	LIS	3X	0.99	94.4	927.79	ND	1457.76	962.64	560.80	51.85	53.67	1.7	31.26	142.45	100
Cd, Cu, Ni, Zn	LIS	10X	0.99	94.4	2797.69	ND	2034.90	1970.39	1322.42	114.80	115.37	0.2	536.60	16154.85	100
Cd, Cu, Ni, Zn	NIN	Cont	0.15	0.0	0.39	ND	0.26	2.33	ND	0.05	0.08	2.0	0.04	ND	5
Cd, Cu, Ni, Zn	NIN	0.1X	0.15	0.0	1.14	ND	1.68	3.15	1.21	0.10	0.20	1.3	0.15	ND	17.5
Cd, Cu, Ni, Zn	NIN	0.3X	0.15	0.0	3.27	ND	5.29	5.19	3.63	0.24	0.28	1.4	0.19	ND	5
Cd, Cu, Ni, Zn	NIN	1X	0.15	0.0	6.64	ND	14.98	13.90	10.11	0.62	0.62	0.6	1.12	5.53	22.5
Cd, Cu, Ni, Zn	NIN	3X	0.15	0.0	26.43	ND	94.03	39.17	17.53	2.15	2.45	0.9	2.83	23.66	30
Cd, Cu, Ni, Zn	NIN	10X	0.15	0.0	203.18	ND	108.72	48.24	18.78	5.22	2.88	ND	32.93	2011.72	100

*Values not available for this test. Values from similar control sediments were substituted.
**ND = Not detectable.
***SEM was measured for only the metals spiked in the experiment. SEM was not available for the cadmium experiment. Bulk values have been substituted.

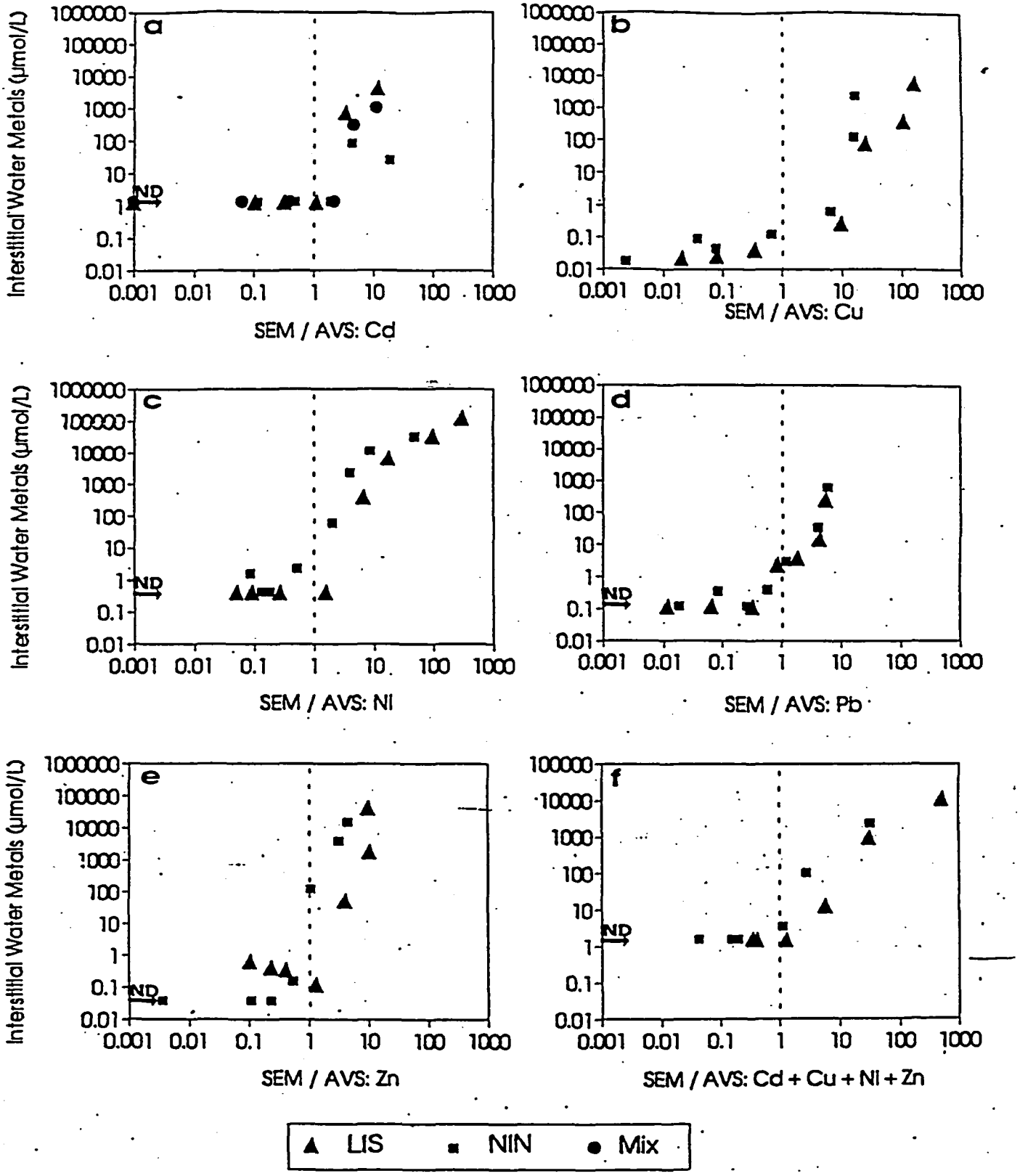


Figure 5-1. Interstitial water metals (IW) concentration (µM/l) as a function of SEM/AVS ratio in three sediments: Long Island Sound (LIS), Ninigret Pond (NIN), and a 50/50 mixture of these two sediments (Mix). Each panel represents data from a separate experiment. Data from the mixed metals experiment represents the molar sum of cadmium, copper, nickel, and zinc. Data below the IW detection limit are plotted at one half the detection limit, indicated by arrows. All IW data in the copper experiment were above the limit of detection. Data below the SEM detection limit are plotted at SEM/AVS = 0.001.

experiments. In the cadmium experiment one-half the detection limit of the cadmium electrode used to measure cadmium ion concentrations was 1.33 μmol/L. For the mixed metals experiment the sum of one-half of the detection limits of the four metals spiked in this test was 1.54 μmol/L. Above an SEM/AVS ratio of 1.0 the interstitial water concentration increased up to five orders of magnitude with increasing SEM/AVS ratio. In each experiment there were usually one or more sediments with SEM/AVS ratios of only slightly greater than 1.0 having interstitial water concentrations below or near detection limits. This indicates that there are other binding phases in the sediment. In some sediments spiked with copper, nickel, and a mixture of metals, AVS decreased with increasing metals concentration (Table 5-2), presumably due to the formation of copper and nickel sulfides not soluble in the AVS extraction. This underscores the importance of using SEM rather than total metal in the calculation of metals/AVS ratios.

When the results of all the experiments are plotted together (Figure 5-2) the relationship between interstitial water concentration and SEM/AVS is confirmed. In most cases interstitial water concentrations were below the detection limit in sediments with SEM/AVS < 1.0, increasing with increasing SEM/AVS ratio at SEM/AVS ratios > 1.0.

The relationship between interstitial water concentration and SEM/AVS ratio in the mixed metals experiment was similar to that in the individual metal experiments when the molar concentrations of all of the metals are summed (Figures 5-1f and 5-2). Further insight into the partitioning of the metals in the interstitial water from the mixed metals experiment can be gained by plotting the interstitial water concentrations for each individual metal (Figure 5-3). In the LIS sediment all four metals were below the limit of detection in treatments with SEM/AVS ratios of 1.25 or lower (Figure 5-3). As the SEM/AVS ratio of the treatments increased, detectable concentrations of metal began to appear. The most soluble sulfide (nickel) appeared first and at the highest interstitial water concentration. As SEM/AVS ratios increased the other metals appeared in order of their sulfide solubility product constants. The metal with the least soluble sulfide (copper) appeared last and at the lowest concentration. The relationship between interstitial water concentration and SEM/AVS ratio in the NIN sediments was similar to that

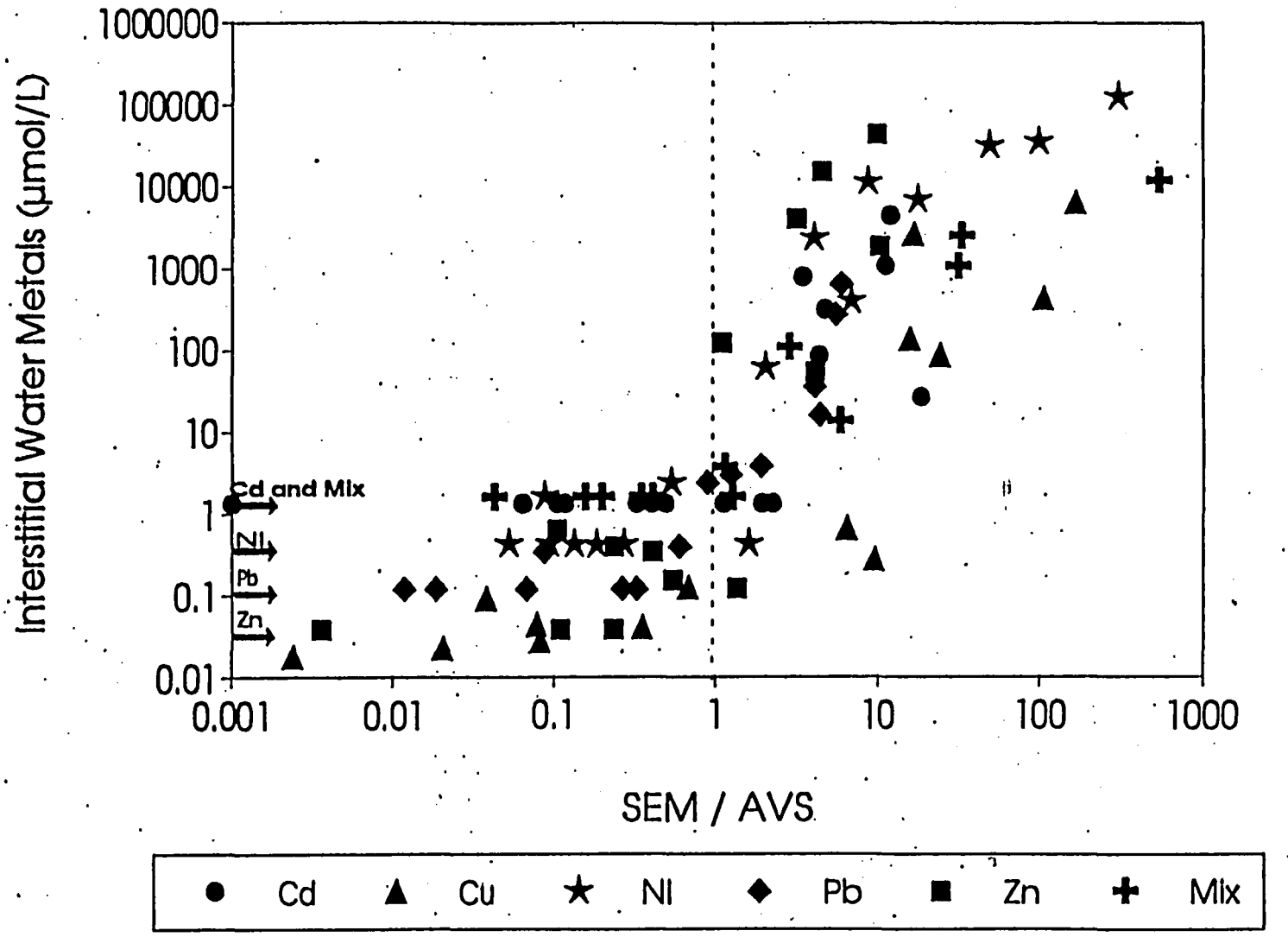
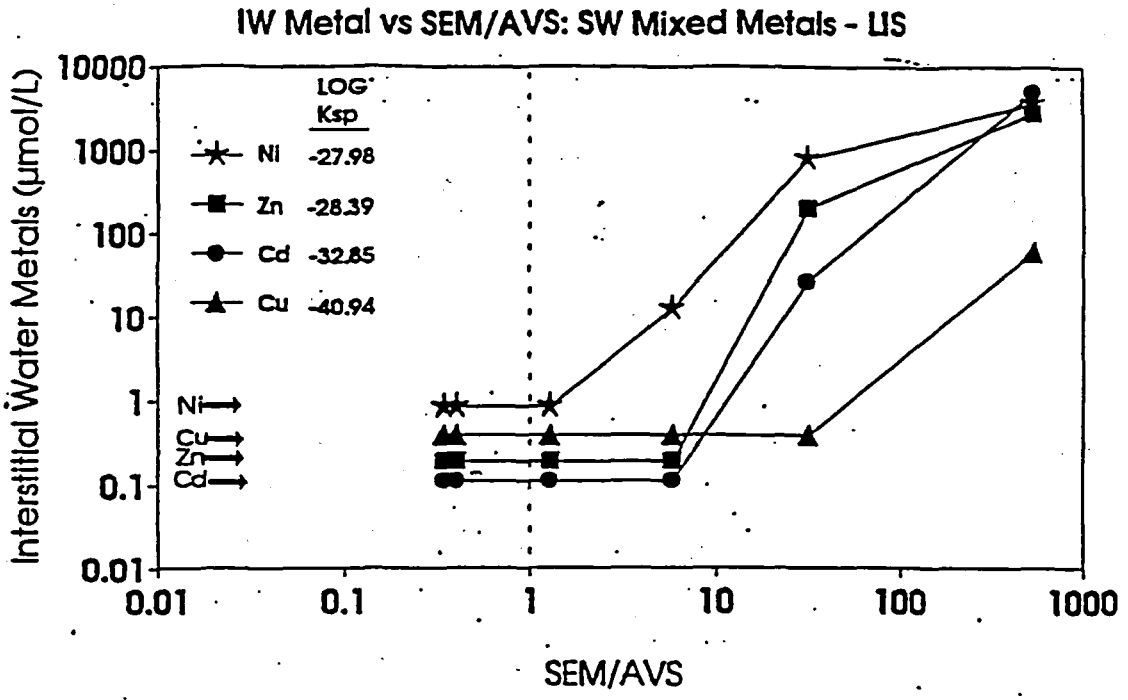


Figure 5-2. Interstitial water metals (IW) concentration (µM/l) as a function of SEM/AVS ratio. Data from the mixed metals experiment represents the molar sum of cadmium, copper, nickel, and zinc. All experiments combined. Data below the IW detection limit are plotted at one half the detection limit and indicated by arrows. All data in the copper experiment were above the limit of detection. Data below the SEM detection limit are plotted at SEM/AVS = 0.001.



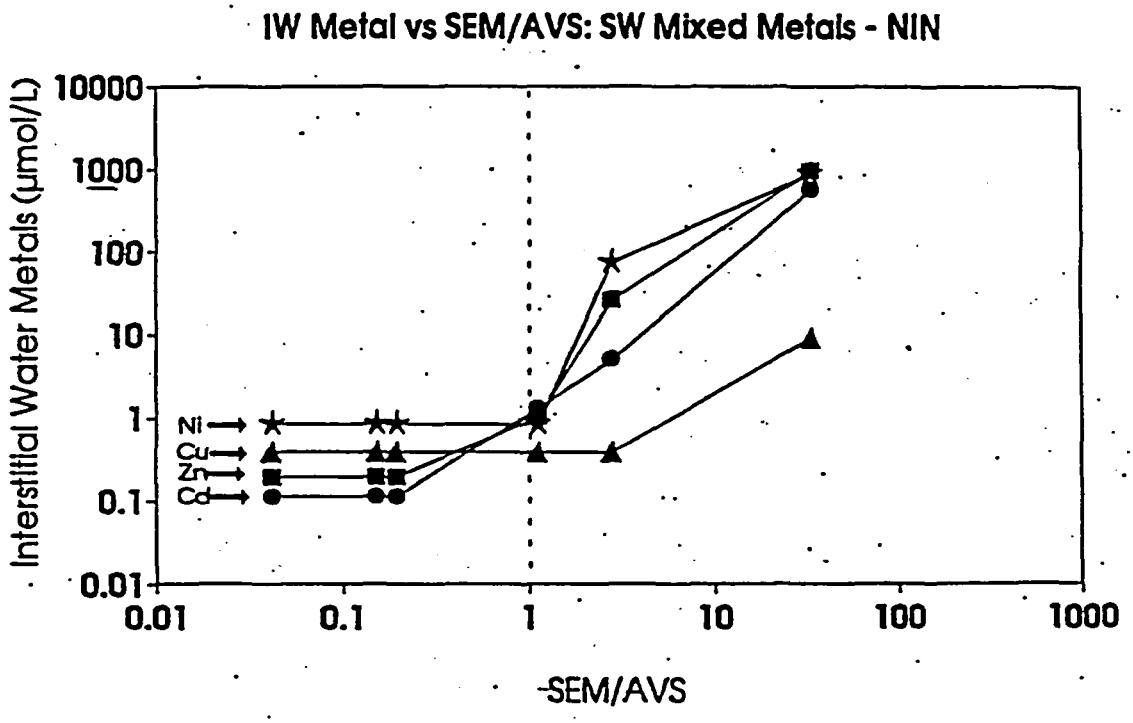


Figure 5-3. Individual interstitial water metals (µM/l) concentration in the mixed metals experiment as a function of SEM/AVS ratio. The top panel represents data from the LIS sediment, the bottom panel data from the NIN sediment. Data below the IW detection limit are plotted at one half the detection limit, indicated by arrows.

in the LIS sediments (Figure 5-3). In the sediment treatments with SEM/AVS ratios of less than 1.0 there was no detectable metal in the interstitial water. In one sediment with an SEM/AVS ratio slightly greater than 1.0 (1.12) there was measurable zinc and cadmium, but only in low concentrations. In the sediment treatment with the next higher ratio there was measurable nickel, zinc, and cadmium, with the concentrations decreasing in the that order. Only in the sediment with the highest SEM/AVS ratio was measurable copper found in the interstitial water.

Sediment Toxicity

The mortality of amphipods as a function of dry weight metals concentrations followed a similar pattern in each of the five individual metals and the mixed metals toxicity tests. Mortality appeared sediment-dependent when plotted on a metals basis (Figure 5-4). Mortality increased with increasing metals concentration (ug/g dry wt.) for each sediment, but in each experiment there were treatments in low AVS sediments (Ninigret Pond) which caused 100 percent mortality at dry weight concentrations which did not cause appreciable mortality in treatments from the high AVS sediment (Long Island Sound). Thus, although mortality is concentration dependent for both sediments, the concentration-response curves do not overlap. Therefore it is not possible to predict sediment toxicity on the basis of dry weight metals concentration alone (Figure 5-4, Figure 5-5a). Mortality did not appear to be metal-specific when plotted on a molar dry weight metal basis (Figure 5-5a), indicating that some factor in the sediment was affecting the toxicity of all five metals similarly. Within one sediment the results from all five metals were very similar (Figure 5-5b).

Mortality in the individual and mixed metals experiments was sediment independent when plotted on an SEM/AVS basis (Figure 5-6). Sediments with an SEM/AVS ratio $\leq$ 1.0 did not cause mortality significantly different from the control; i.e., greater than 24 percent. In sediments with SEM/AVS > 1.0, mortality increased with increasing SEM/AVS ratio, although in each experiment there were usually one or two sediments with SEM/AVS ratios slightly greater than 1.0 (and in one instance 5.8; Table 5-2) which did

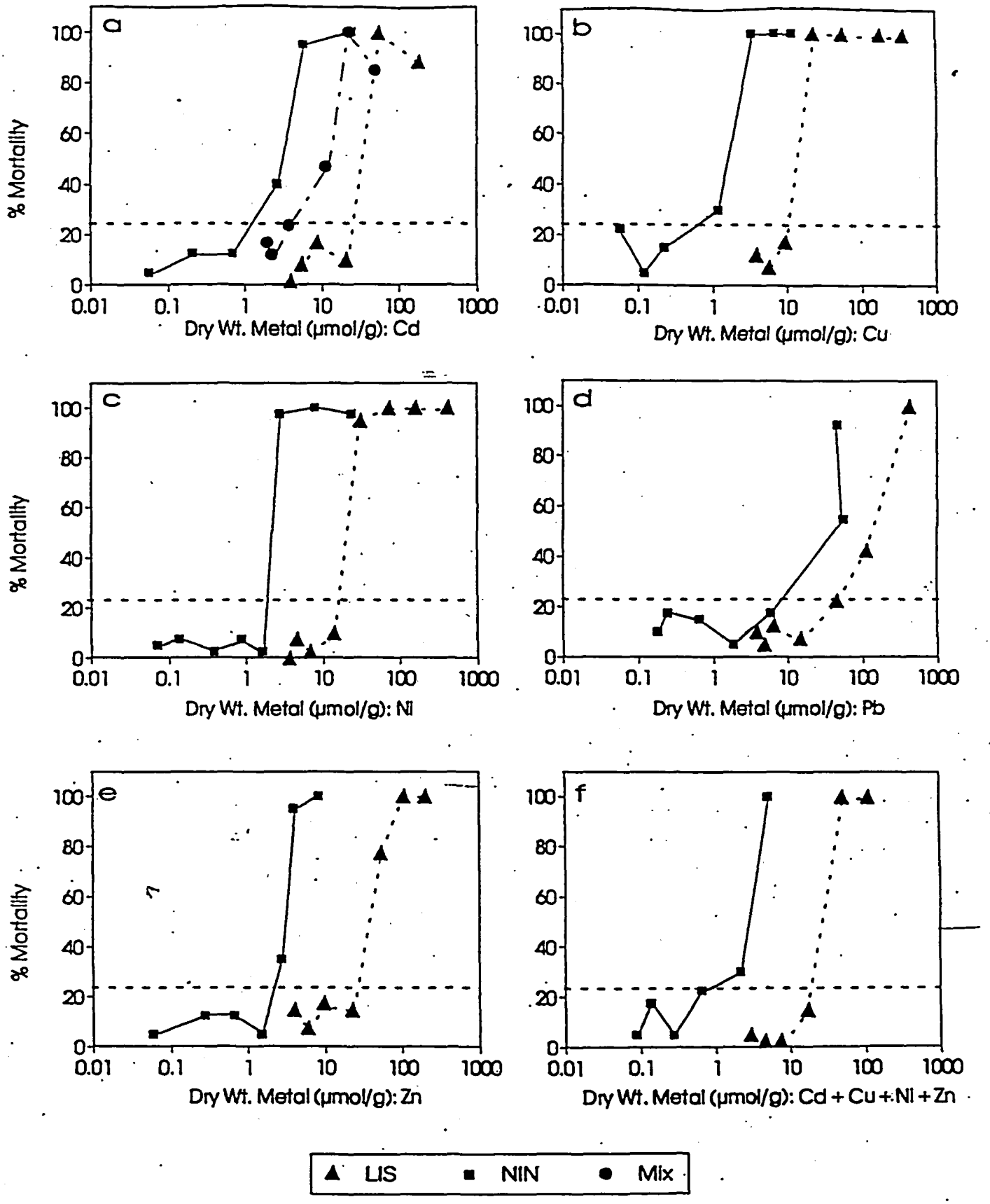


Figure 5-4. Percentage mortality of Ampelisca abdita as a function of the sum of the concentrations of cadmium, copper, lead, nickel, and zinc in μM divalent metal per gram dry weight sediment in three sediments: Long Island Sound (LIS), Ninigret Pond (NIN), and a 50/50 mixture of these two sediments (Mix). Each panel represents data from a separate experiment.

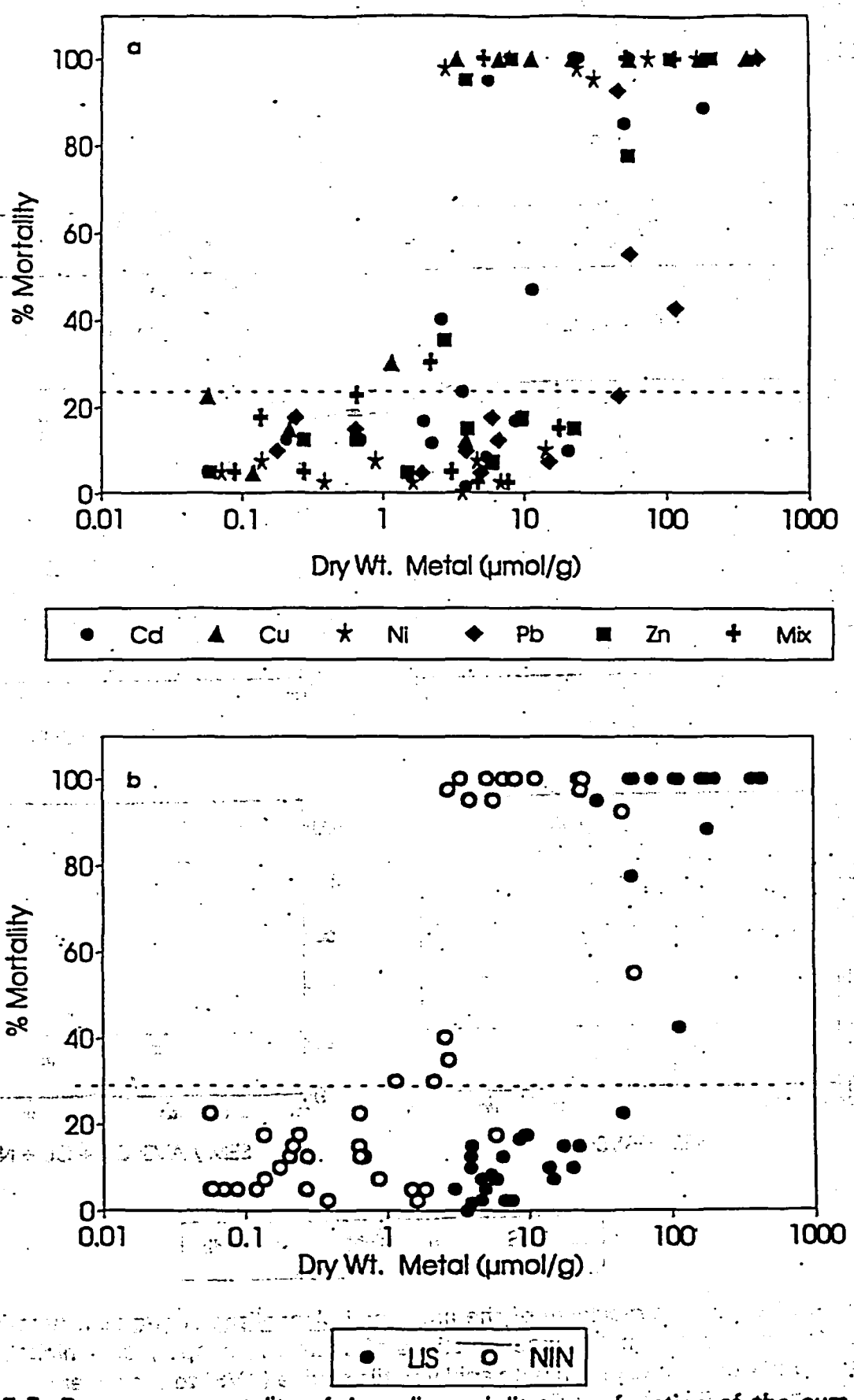


Figure 5-5. Percentage mortality of Ampelisca abdita as a function of the sum of the concentrations of cadmium, copper, lead, nickel, and zinc in μM divalent metal per gram dry weight sediment. All experiments combined. Upper panel plots data by metal, lower panel plots data by sediment: Long Island Sound (LIS) and Ninigret Pond (NIN).

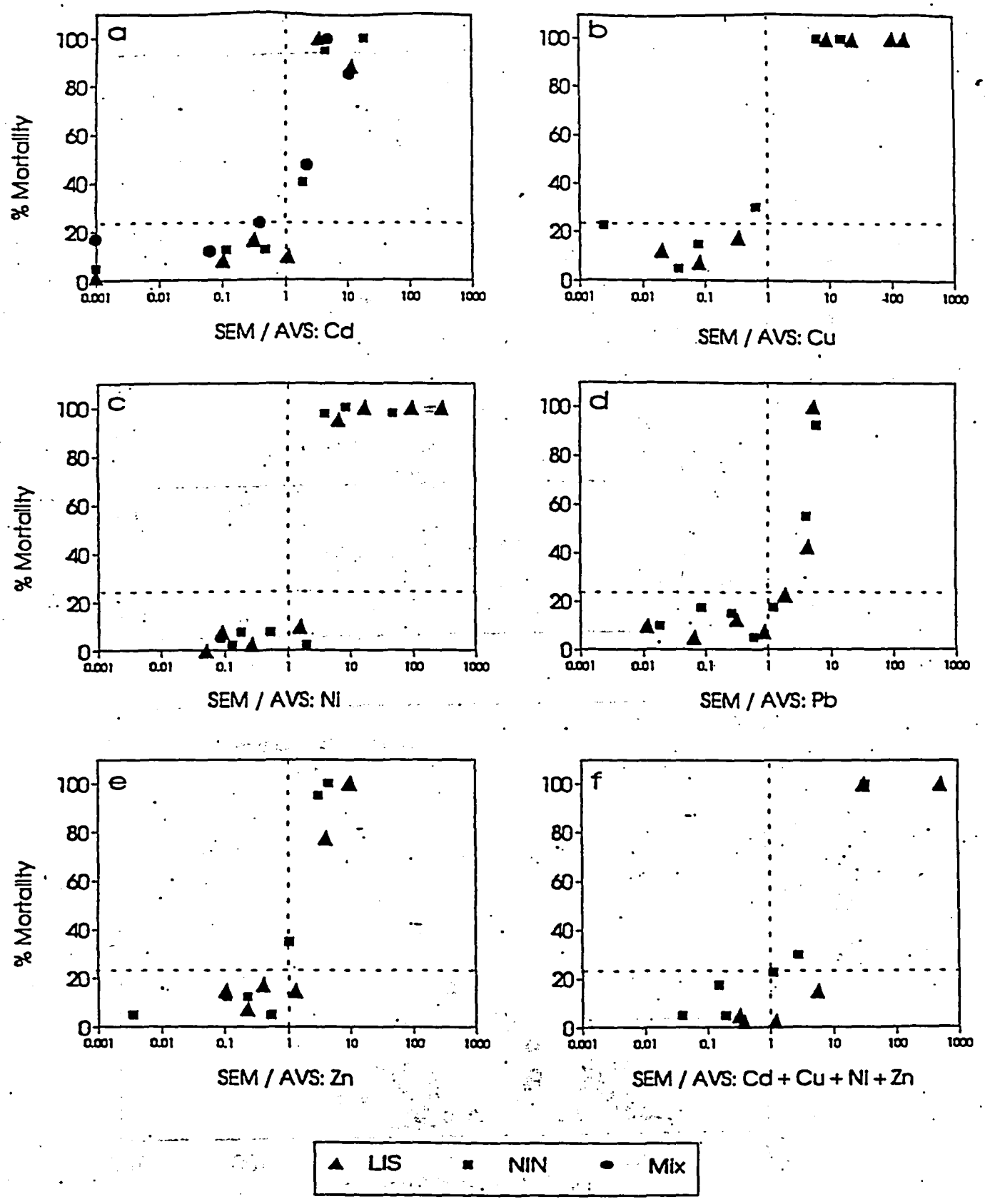


Figure 5-6. Percentage mortality of the amphipod, Ampelisca abdita as a function of the ratio of the sum of the molar concentrations of cadmium, copper, lead, nickel, and zinc simultaneously extracted (SEM) with acid volatile sulfide (AVS) to the molar concentration of AVS (SEM/AVS) in three sediments: Long Island Sound (LIS), Ninigret Pond (NIN), and a 50/50 mixture of these two sediments (Mix). Each panel represents data from a separate experiment. Data below the SEM detection limit are plotted at SEM/AVS = 0.001.

not cause significant mortality. This indicates that there are other binding phases in the sediment. Thus, it is possible to predict with accuracy which sediments will not be toxic, and, with less accuracy, which sediments will be toxic. When the results of all of the experiments are plotted together the mortality of amphipods as a function of SEM/AVS appears metal and sediment independent for the five individual metals, and for a mixture of metals (Figure 5-7).

Mortality was not sediment specific when it was plotted against interstitial water toxic units (IWTU). Sediments with IWTUs of less than 0.5 were not toxic (Figure 5-8). Sediments with IWTUs of greater than 0.5 were increasingly toxic with increasing IWTU value. As was the case when mortality is plotted against SEM/AVS and ratios exceeded 1.0, there were usually sediments with IWTU values greater than 0.5 which did not cause mortality. This was especially true in the range of IWTU values greater than 0.5 but less than 10.0 (Table 5-2). This indicates that not all of the interstitial water metal is bioavailable. Thus for both SEM/AVS ratios and IWTUs, sediments likely to be non-toxic can be predicted with near certainty, but predicting which sediments are likely to be toxic is less accurate.

As was the case with SEM/AVS ratios, the generality of the relationship between mortality and IWTU can be seen when the results from all of the experiments are coplotted (Figure 5-9). This relationship was not metal-specific. Thus the sum of the IWTUs can be used to make predictions about the toxicity (or lack thereof) of any combination of the metals tested in these experiments.

When the results of the individual metals and the mixed metals test are taken together, 98 percent of the 43 sediments with SEM/AVS ratios ≤ 1.0 were not toxic (i.e., caused mortality less than 24 percent). Of the 45 sediments with SEM/AVS ratios > 1.0, 80 percent were toxic. Ninety-four percent of the 52 sediments with IWTU < 0.5 were not toxic, while 92 percent of the 37 sediments with IWTU ≥ 0.5 were toxic. When both SEM/AVS ratio and IWTU are combined the predictive ability is improved. Ninety-eight percent of 43 sediments with SEM/AVS ratios ≤ 1.0 and IWTU < 0.5 were not toxic,

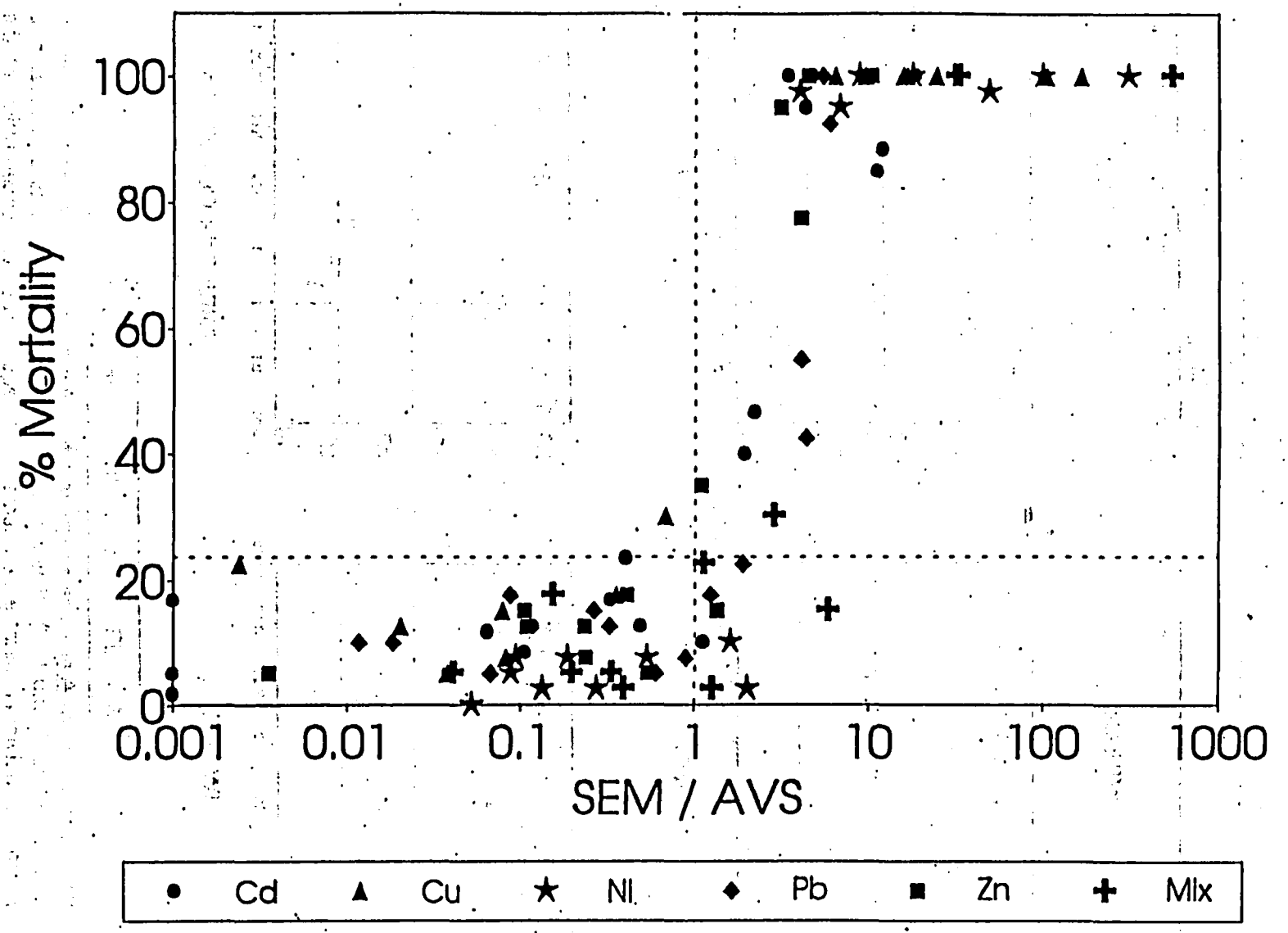


Figure 5-7. Percentage mortality of Ampelisca abdita as a function of the ratio of the sum of the molar concentrations of cadmium, copper, lead, nickel, and zinc simultaneously extracted (SEM) with acid volatile sulfide (AVS) to the molar concentration of AVS (SEM/AVS). All experiments combined. Data below the SEM detection limit are plotted at SEM/AVS = 0.001.

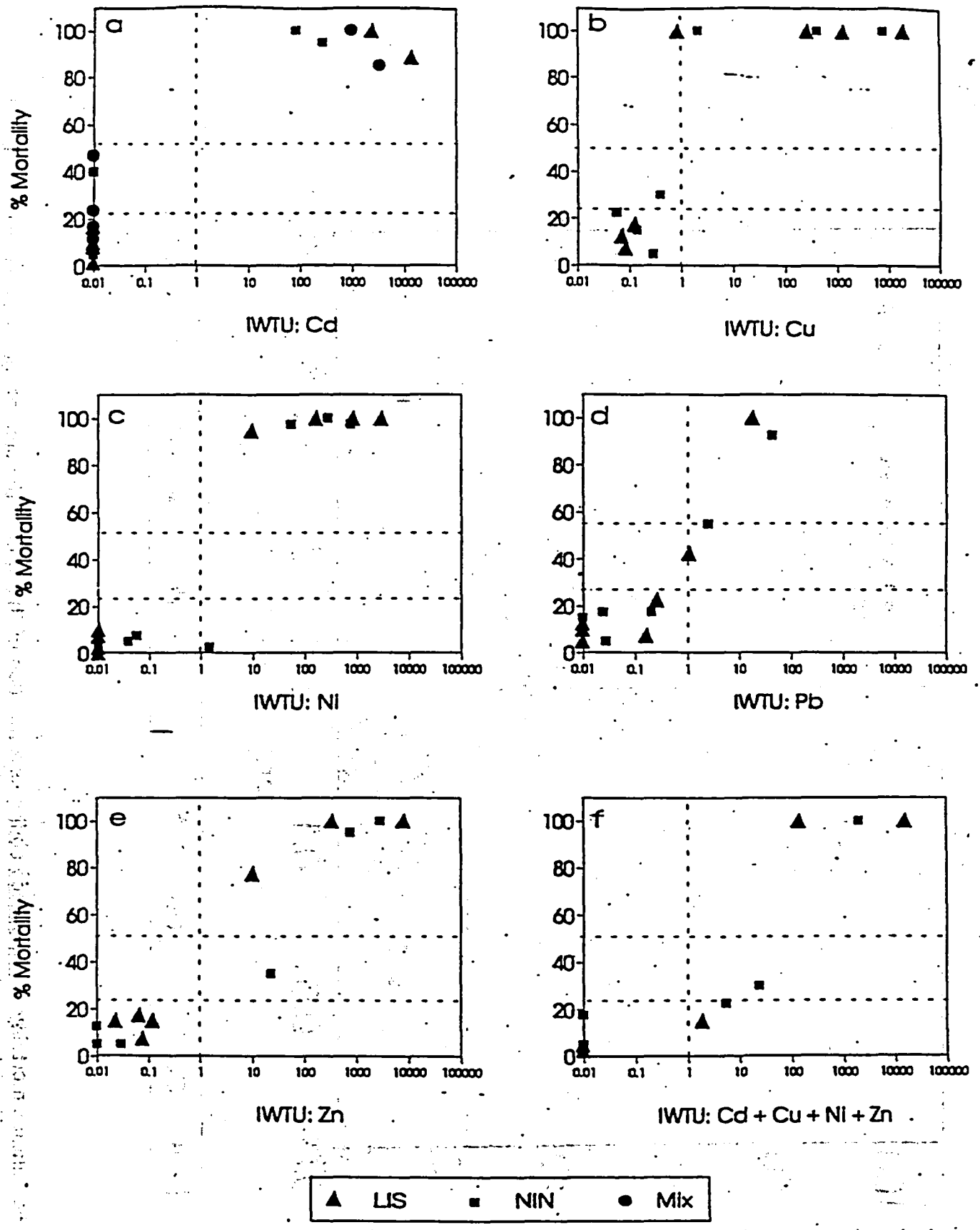


Figure 5-8. Percentage mortality of Ampelisca abdita as a function of interstitial water toxic units in three sediments: Long Island Sound (LIS), Ninigret Pond (NIN), and a 50/50 mixture of these two sediments (Mix). In the individual metal experiments IWTU equals the IW concentration of the individual metal/A. abdita LC50 for that metal. Interstitial water toxic unit (IWTU) for the mixed metals experiment is the sum of the IW Cd concentration/Cd LC50 for A. abdita + IW Cu concentration/Cu LC50 + IW Ni concentration/Ni LC50 + IW Zn concentration/Zn LC50. Each panel represents data from a separate experiment.

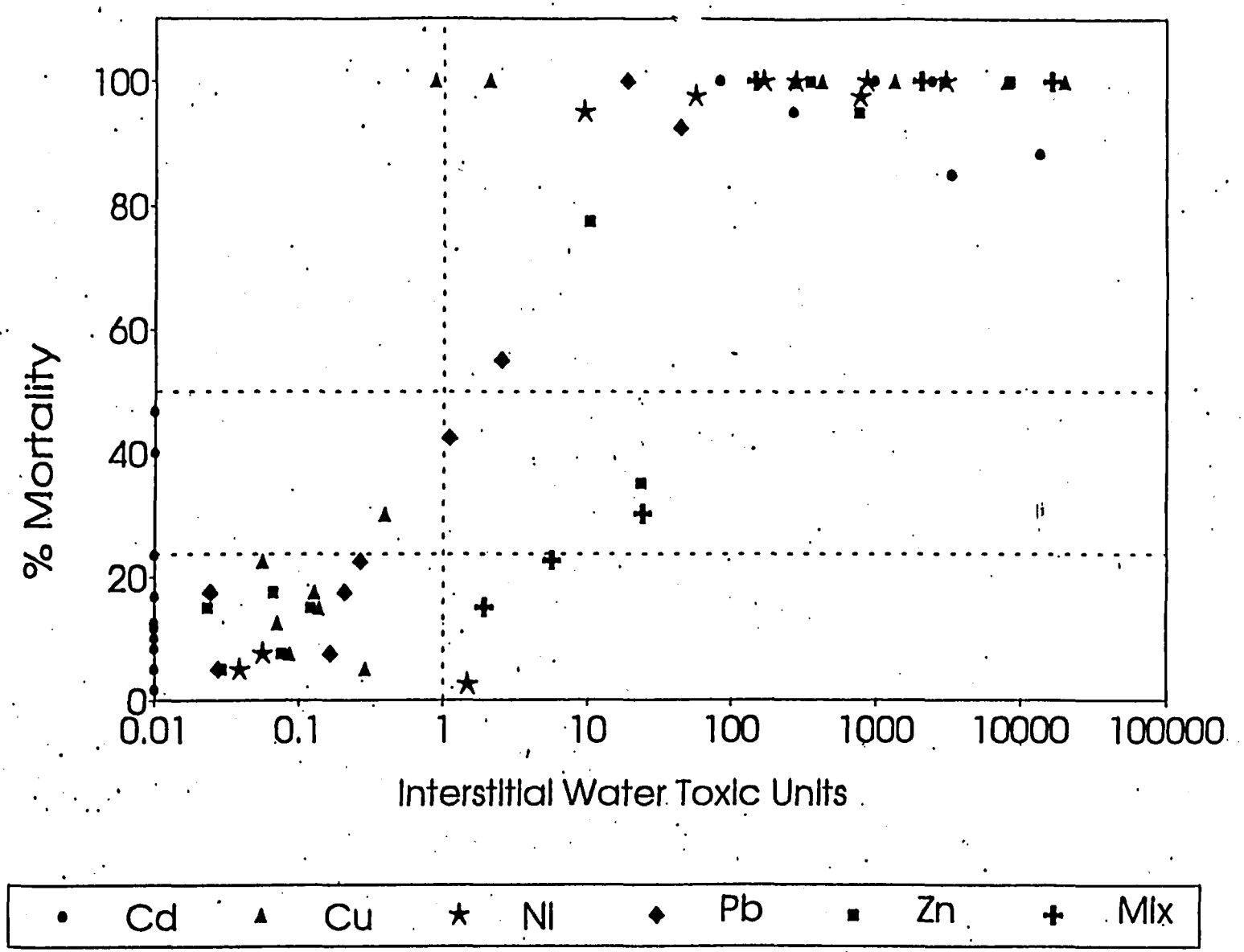


Figure 5-9. Percentage mortality of Ampelisca abdita as a function of interstitial water toxic units. In the individual metal experiments IWTU equals the IW concentration of the individual metal/A. abdita LC50 for that metal. Interstitial water toxic unit (IWTU) for the mixed metals experiment is the sum of the IW Cd concentration/Cd LC50 for A. abdita + IW Cu concentration/Cu LC50 + IW Ni concentration/Ni LC50 + IW Zn concentration/Zn LC50. All experiments combined. Data below the detection limit are plotted at IWTU = 0.01.

while 94 percent of 36 sediments with SEM/AVS ratios > 1.0 and IWTU ≥ 0.5 were toxic (Table 5-3).

TABLE 5-3. ACCURACY OF PREDICTIONS OF THE TOXICITY OF SEDIMENTS FROM A. ABDITA SPIKED-SEDIMENT TESTS AND COMBINED FRESHWATER AND SALTWATER SPIKED-SEDIMENT TESTS AS A FUNCTION OF SEM/AVS RATIOS, INTERSTITIAL WATER TOXIC UNITS (IWTUs) AND BOTH SEM/AVS AND IWTUs.

				% of Sediment	
Study Type	Parameter	Value	n	Nontoxic[1]	Toxic[1]
A. abdita	SEM/AVS	≤ 1.0	43	97.7	2.3
		> 1.0	45	20.0	80.0
	IWTU	< 0.5	52	94.2	3.8
		≥ 0.5	37	8.1	91.9
	SEM/AVS,IWTU	≤ 1.0, < 0.5	43	97.9	2.1
		> 1.0, ≥ 0.5	36	5.6	94.4
Lab-Spike, (FW & SW)	SEM/AVS	≤ 1.0	92	95.7	4.3
		> 1.0	83	26.5	73.5
	IWTU	< 0.5	107	93.5	6.5
		≥ 0.5	77	22.1	77.9
	SEM/AVS,IWTU	≤ 1.0, < 0.5	85	96.5	3.5
		> 1.0, ≤ 0.5	65	12.3	87.7

[1]Nontoxic sediments <24 percent mortality. Toxic sediments >24 percent mortality.

Discussion

The results of the amphipod toxicity tests with sediments spiked with metals indicate that it is not possible to causally predict the toxicity of a sediment using the concentration of metal on a dry weight basis because the relationship between mortality and dry weight metals concentration in our tests was sediment specific. In contrast, the relationships between mortality and SEM/AVS ratio and mortality and interstitial water concentration or toxicants were demonstrated to be sediment independent. This suggests that they are the most useful expressions of bioavailable metal for causally predicting organism response.

Most of the sediments either caused little or no mortality, or nearly complete mortality (Figures 5-9 and 5-10). This is a result of the dynamics of metals and AVS in the sediment, leading to a sharp increase in interstitial water metals concentration when SEM/AVS ratio exceeds 1.0 and sulfide no longer is a significant binding phase (Figures 5-1 and 5-2). When sufficient sulfide is present in the sediment to bind the metal, little or no metal is present in the interstitial water [15]. The divalent metals should appear in the interstitial water in reverse order of the solubilities of their sulfides [12]. Thus we observed that nickel appeared first in the interstitial water in sediments with SEM/AVS ratios slightly greater than one, followed by zinc, cadmium, lead, and copper as the concentration of metals increases relative to that of AVS. When the binding capacity of the sulfide is exhausted the interstitial water concentrations of metal increase sharply enough that nearly 100 percent mortality results in most of our test sediments. The effect is similar to the "throwing of a switch" at SEM/AVS = 1.0. This overwhelming increase in the interstitial water concentration explains why the chemistry of the anaerobic sediments controls the toxicity of metals to organisms living in aerobic sediment microhabitats (e.g., the amphipods living in their burrows in our experiments). It also explains why the toxicity of different metals in sediments is the same on an SEM/AVS basis (Figure 5-7) even though their toxicities differs markedly in water-only toxicity tests (Table 5-1). This sharp increase in interstitial water concentration with increasing sediment concentration is in contrast to the situation with nonionic organic contaminants, which are released from the sediment more gradually, primarily as a function, of the K_{OC} of the compound [16].

When our data are combined with the data available from spiked sediment experiments in the literature, all data demonstrate that SEM/AVS ratios and interstitial IWTU's can be used to predict toxicity. Data from freshwater tests using oligochaetes and snails exposed to sediments spiked with cadmium [7]; and saltwater tests using polychaetes exposed to sediments spiked with cadmium, copper, lead, nickel, or zinc [4], using polychaetes exposed to sediments spiked with cadmium or nickel [5], and copepods exposed to sediments spiked with cadmium [6] all follow the same patterns as our amphipod results when mortality is plotted against SEM/AVS ratio (Figure 5-10). These

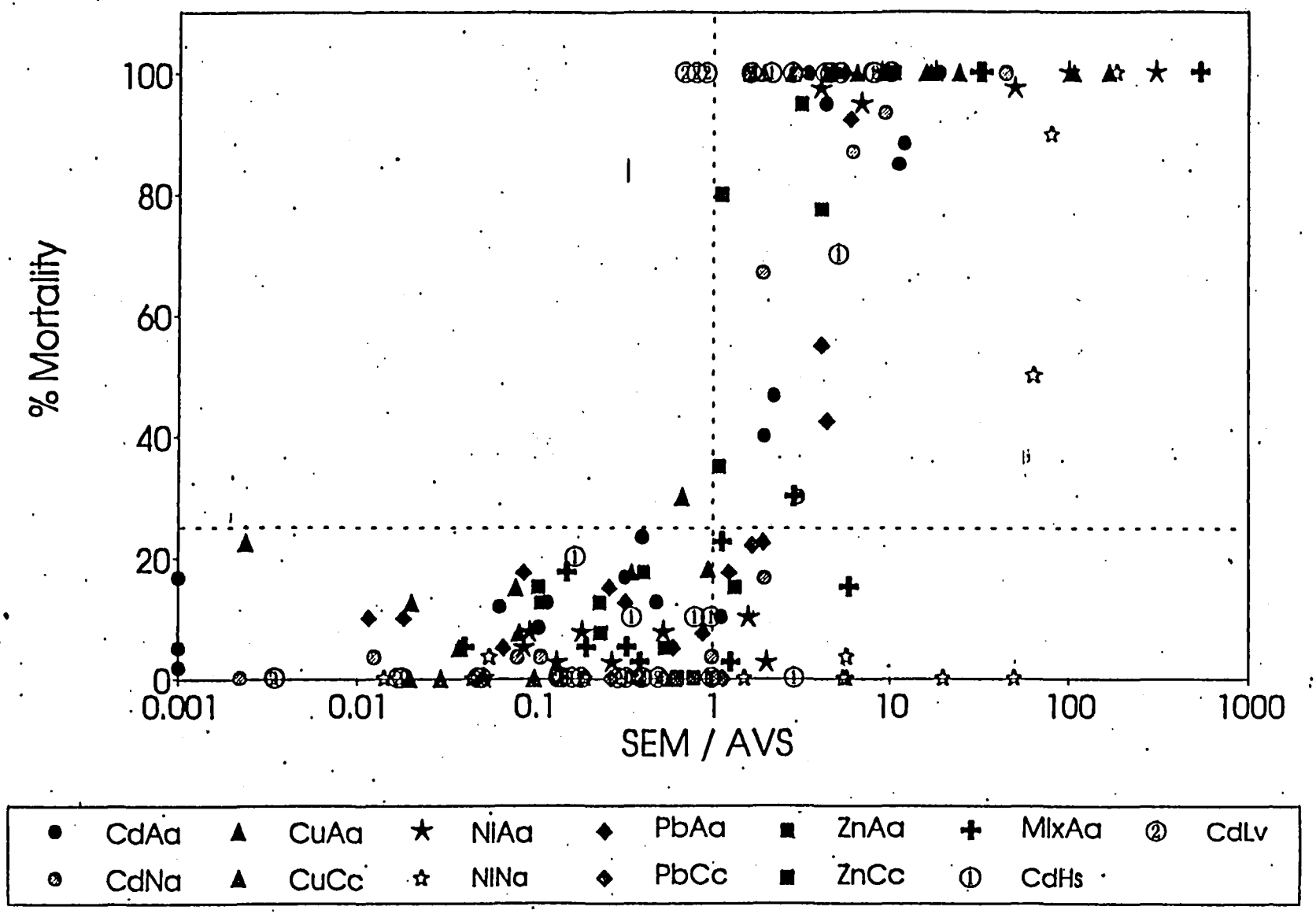


Figure 5-10. Percentage mortality of saltwater and freshwater benthic species including oligochaetes (Lv), polychaetes (Cc, Lv, Na), amphipods (Aa) and snails (Hs) exposed to sediments spiked with cadmium, copper, lead, nickel, and/or zinc as a function of the SEM/AVS ratio. Data below the SEM detection limit are plotted at SEM/AVS = 0.001.

combined data describe tests with six freshwater and saltwater species and sediments from seven sites having AVS concentrations ranging from 1.9 to 65.7 μmol/g dry wt and TOC ranging from 0.15 to 10.6 percent. Mortality in the individual and mixed metals experiments was sediment independent when plotted on an SEM/AVS basis. Sediments with an SEM/AVS ratio of less than 1.0 were not toxic. In sediments with SEM/AVS greater than 1.0, mortality increased with increasing SEM/AVS ratio, but not all sediments with SEM/AVS ratios of > 1.0 were toxic. This is due, in part, to the presence of other binding factors.

In addition, organism behavior in a toxicity test can control exposure and limit the impact of metals in sediments. Many of the sediments which had SEM/AVS ratios > 1.0 but were not toxic were from experiments using the polychaete, Neanthes araneceodentata, exposed to sediments spiked with cadmium or nickel [5]. This is especially true of the nontoxic sediments with the highest SEM/AVS ratios. The polychaetes did not burrow in most of these sediments, and presumably were not fully exposed to the metals in the sediment (Figure 5-11) and therefore survived in sediments that would likely otherwise have been toxic (Figure 5-10).

The combined data from all available freshwater and saltwater tests also follow the same pattern as our saltwater amphipod data when plotted on an IWTU basis (Figure 5-12). Mortality was not sediment specific when it was plotted against IWTU. Sediments with IWTUs of less than 0.5 were generally not toxic. Sediments with IWTUs of greater than 0.5 were increasingly toxic with increasing IWTU value. Here again, as with SEM/AVS ratios > 1.0 vs mortality, many of the sediments having IWTUs > 0.5 which were not toxic are likely the result of interstitial water ligands which may reduce the bioavailability and toxicity of dissolved metals. Polychaete avoidance of otherwise toxic sediments is also a factor.

With the combined data 96 percent of the 92 of sediments with SEM/AVS ratios $\leq$ 1.0 were not toxic, while 74 percent of the 83 sediments with SEM/AVS ratios > 1.0 were toxic. Ninety-four percent of the 107 sediments with IWTU < 0.5 were not toxic,

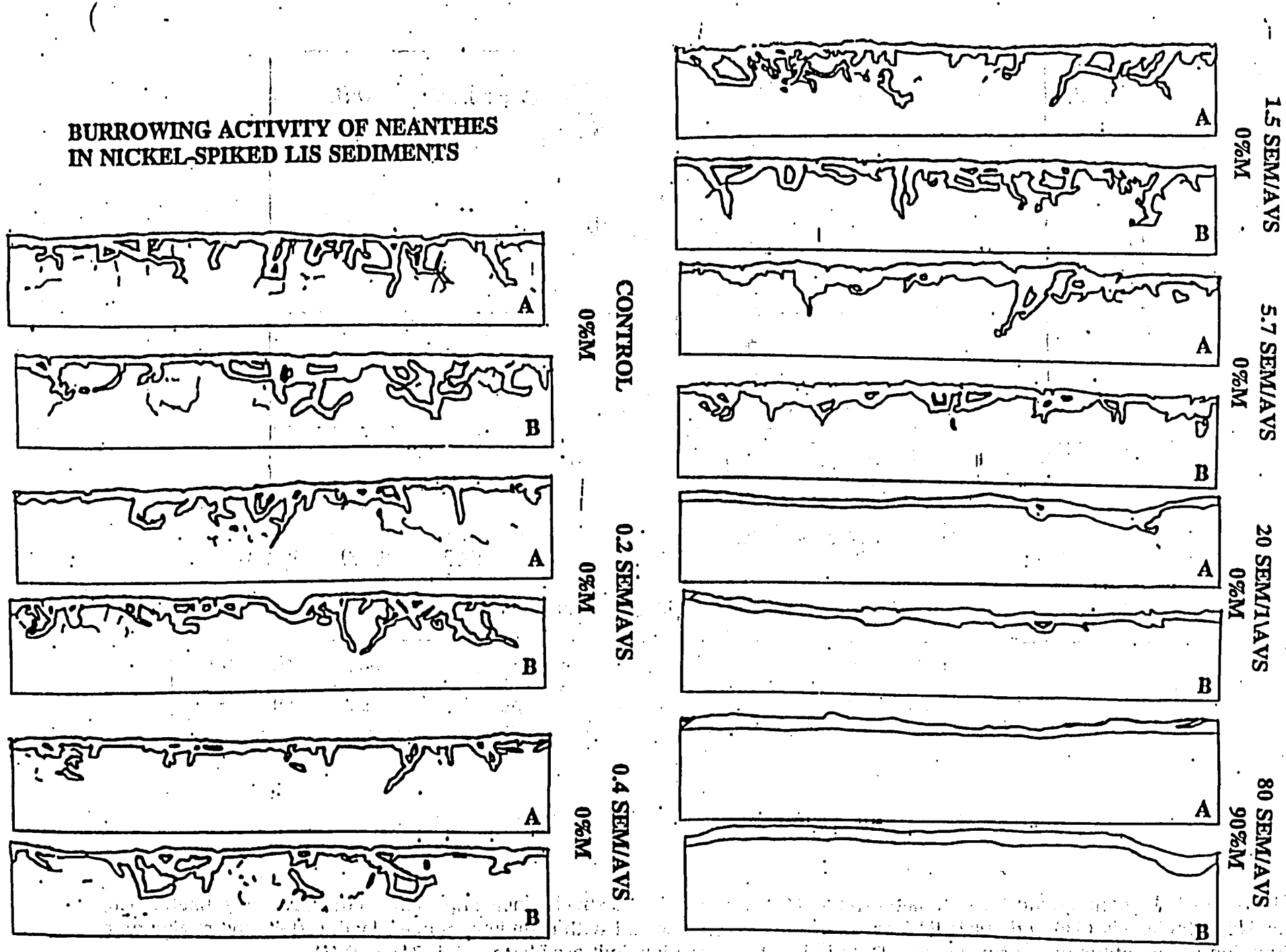


Figure 5-11. Burrowing patterns of Neanthes arenaceodentata in Ni-spiked sediments. Two replicates (A and B) are shown. Treatments were 1) control; 2) SEM/AVS = 0.1; 3) SEM/AVS = 0.28; 4) SEM/AVS = 1.3; 5) SEM/AVS = 4.9; 6) SEM/AVS = 16.9; 7) SEM/AVS = 125. From [5]

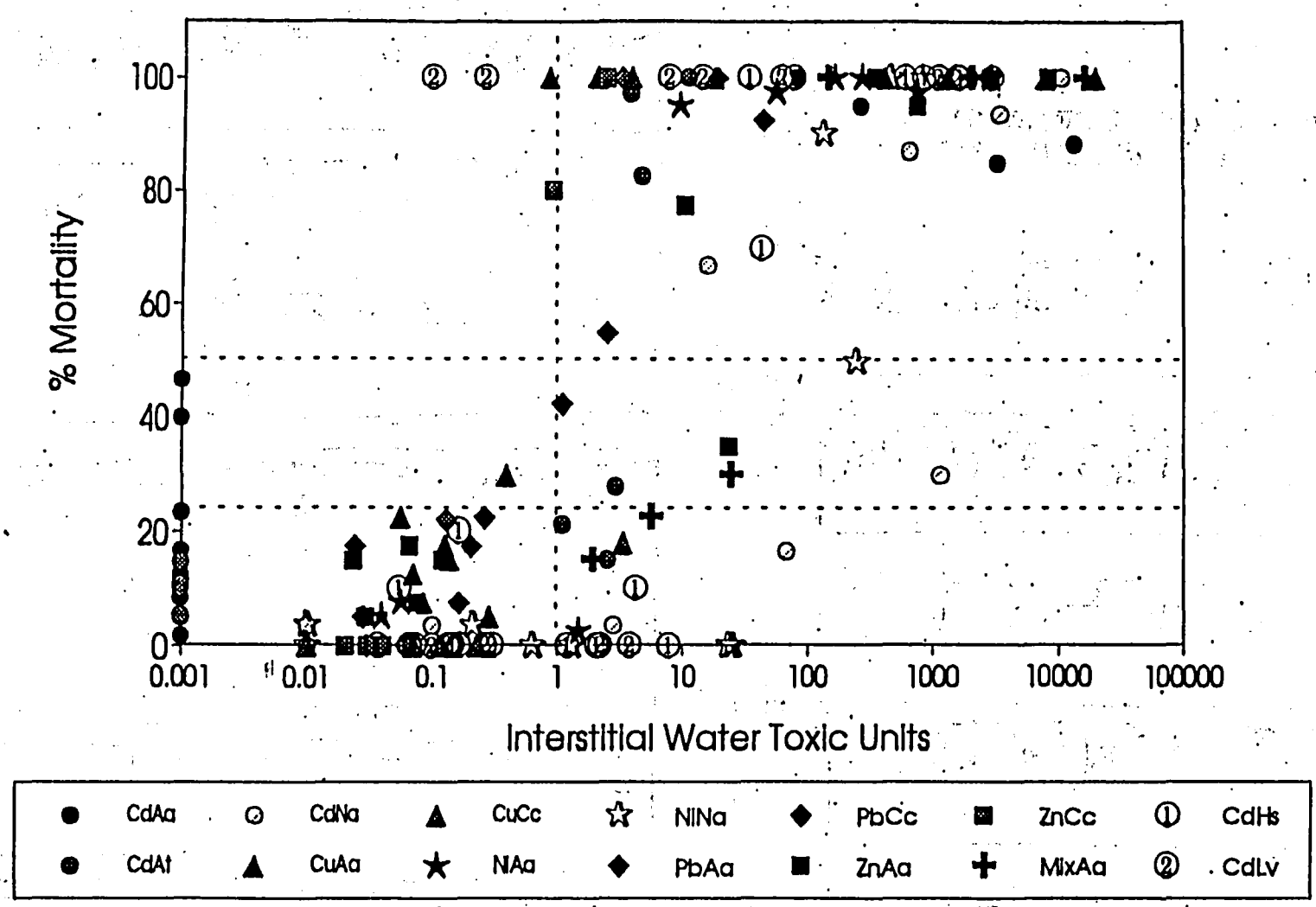


Figure 5-12. Percentage mortality of saltwater and freshwater benthic species including oligochaetes (Lv), polychaetes (Cc, Lv, Na), amphipods (Aa) and snails (Hs) exposed to sediments spiked with cadmium, copper, lead, nickel, and/or zinc as a function of interstitial water toxic units. Data below the detection limit are plotted at IWTU = 0.01.

while 78 percent of the 77 sediments with IWTU $\geq$ 0.5 were toxic. When both SEM/AVS ratio and IWTU are combined predictive ability is improved. Ninety-six percent of the 85 sediments with SEM/AVS ratios $\leq$ 1.0 and IWTU < 0.5 were not toxic, while 88 percent of the 65 sediments with SEM/AVS ratios > 1.0 and IWTU $\geq$ 0.5 were toxic (Table 5-3). More IWTU data are available than SEM/AVS data because Green et al. [6] did not measure AVS in the 10 sediments which they tested. The predictions would be even more accurate (especially in the elimination of "false positives" (non-toxic sediments with SEM/AVS > 1.0 and IWTU > 0.5) if data from exposures in which polychaetes avoided the sediment were not considered [5]. This close relationship between IWTU and sediment toxicity has been found in an earlier study with cadmium in field sediments [17] as well as studies with nonionic organic chemicals both in the field [18,19] and in the laboratory [20,16].

One limitation to the data cited above is that all tests were acute exposures and these results may not be applicable to chronic exposures. Also metals bioaccumulation was not measured, except in one case [7]. The applicability of AVS and interstitial water normalizations to chronic exposures and bioaccumulation in benthic organisms are discussed elsewhere in this document. Another important limitation to the use of AVS is that it is only a factor in anaerobic sediments. It did, however, seem to be a controlling factor in our experiments, with organisms living in aerobic microenvironments. This anaerobic limitation does not apply to IWTU, of course. The advantages and disadvantages of each of these prediction methods will be discussed in detail in Chapter 10.

Our results also show that although SEM/AVS and IWTU are useful predictors of toxicity, there are other important factors as well. The fact that a significant number of sediments (20 percent) had SEM/AVS ratios of greater than 1.0 but were not toxic indicates that other binding phases in anaerobic sediments, in addition to AVS, are also controlling bioavailability. Organic carbon appears to be one of these [21]. While the SEM/AVS model of bioavailability accurately predicts which sediments will not be toxic,

a model which utilizes SEM/AVS ratios but incorporates these other variables might more accurately predict which sediments will be toxic [16].

Similarly, a significant number of sediments with greater than 0.5 IWTUs were not toxic. Ankley et al. [22] suggested that differences between the hardness of the interstitial water and that of the water in the water-only tests might effect the accuracy of prediction of sediment toxicity using IWTUs in fresh water, unless the IWTUs are hardness-corrected. Further, Green et al. [6] and Ankley et al. [22] hypothesized that increased DOC in the interstitial water reduced the bioavailability of cadmium in their sediment exposures, relative to the water-only exposures. Green et al. [6] found that the LC50 value for cadmium in a water-only exposure was less than 1/2 that of a pore-water-only exposure, and less than 1/3 that in pore-water associated with sediments. A significant improvement in the accuracy of toxicity predictions using IWTUs might be achieved if DOC binding in the interstitial water is taken into account.

APPENDIX 5A

MATERIALS AND METHODS: AMPHIPOD TESTS

Organism collection and acclimation -

Ampelisca abdita were collected from tidal flats in the Pettaquamscutt (Narrow) River, a small estuary flowing into Narragansett Bay, Rhode Island. Surface sediment containing the amphipods was either sieved in the field or transferred to the laboratory within one half hour and then sieved through a 0.5 mm mesh screen. In the laboratory, amphipods and amphipod tubes were vigorously sieved in a tub of seawater, then the sieve was quickly lowered into the water and the amphipods were collected from the water surface. The amphipods were maintained for three to seven days in the laboratory in presieved uncontaminated collection site sediment and flowing filtered seawater in 4-liter glass jars, and acclimated to the test temperature at the rate of 2 to 4°C per day. During acclimation, amphipods were fed the laboratory-cultured diatom, Phaeodactylum tricornutum, ad libitum.

One sediment, Ninigret Pond in the cadmium experiment, was tested using the amphipod Rhepoxynius hudsoni. R. hudsoni was collected at Ninigret Pond, Rhode Island, using collection and acclimation methods similar to those for A. ampelisca, except that R. hudsoni was washed directly from the sieve into sorting dishes after collection.

Water-only tests -

Ten-day static renewal tests were conducted with A. abdita to determine their water-only LC50s for Cd, Cu, Ni, Pb, and Zn in seawater. Animals were exposed, unfed, to five concentrations of metal and a control, with two replicates per concentration.

Amphipods were exposed in 900 mL glass canning jars that contained 800 mL of water. Acclimated amphipods were sieved from the holding jars, sequentially distributed to 100 mL plastic cups (10 amphipods per cup), then randomly added to the exposure chambers. Seventy-five to 100 percent of the water in each replicate was renewed every

other day, depending on the experiment. Water was sampled at least once during the test (usually twice, once near the beginning and once near the end of the test) to determine the concentration of metal. In some experiments aliquots from the two replicates were pooled prior to analysis. Exposure chambers were covered with black plastic. The exposure chambers were checked daily and amphipods which appeared dead were removed and examined under a dissecting microscope. Live animals were returned to the test and dead animals were recorded and discarded.

Spiked sediment tests -

Amphipods were exposed to control and metal-spiked sediments in 10-day tests with continuous renewal of overlying water. In all experiments two sediments of different AVS concentrations were used: Ninigret Pond (AVS = 1.18 to 2.25 μM/g) and Long Island Sound (AVS = 9.72 to 19.9 μM/g). In the cadmium test a mixture of these two sediments was also used (AVS = 4.34 μM/g). The nominal treatments used in most experiments, expressed as the molar ratio of metal to AVS were 0.0 (control), 0.1, 0.3, 1, 3, 10, and 30 (Table 1). There were four replicates per treatment in each test: two "biological" replicates were used to assess mortality, and two "chemical" replicates were used for metal and AVS analyses of the sediment at test initiation and termination. Twenty (30 in the cadmium test) amphipods were added to each "biological" and the day 10 "chemical" replicate at the start of the test. Interstitial water samples were collected in diffusion samplers (peepers) from each of these three replicates at the termination of the experiments.

The Long Island Sound (LIS) sediment was collected from an uncontaminated site in central Long Island Sound (40°7.95'N and 72°52.7'W) with a Smith-McIntyre grab sampler, returned to the laboratory, press sieved wet through a 2 mm mesh stainless steel screen, homogenized and stored at 4°C. There were two separate collections of LIS (LIS1 and LIS2) sediment. The percent total organic carbon for LIS1 was 0.88, for LIS2 it was 0.99. The grain size composition of LIS1 was 5 percent sand, 71 percent silt, and 24 percent clay. Grain size data are not available for LIS2, but it was of similar composition.

Sediment was also collected in Ninigret Pond (NIN), Charlestown, Rhode Island. The upper few inches of sediment were collected with a shovel, returned to the laboratory, sieved wet through a 2 mm stainless steel screen, rinsed several times to remove high-organic fine particles, homogenized and stored at 4°C. There were two collections made in Ninigret Pond, from two different sites (NIN1 and NIN2). Both sediments had TOC values of 0.15 percent and were 100 percent sand (Table 1). NIN2 was made up of slightly finer sand, most of which would pass through a 0.5 mm sieve. Most of the NIN1 sediment was retained on a 0.5 mm sieve.

Sediments were spiked with metal chloride or nitrate salts in glass, 1 gallon jars. Methods differed slightly from experiment to experiment but typically we added 1200 mL of wet sediment to 2000 mL of 20°C seawater that contained the desired weight of metal chloride. The spiked sediments were stirred with a nylon stirrer attached to an electric drill until homogeneous, then the overlying air in each jar was replaced with nitrogen and the jars were capped and rolled for 1 hour. Jars of sediment were held at 20°C for 8 to 10 days before the start of the test. We siphoned the water and any precipitate off the sediment surface and rehomogenized the sediment before adding it to the exposure chambers.

The exposure chambers were 900 mL glass canning jars, each with a 1.3 cm diameter overflow hole (covered with 400-micron Nitex® mesh) 11.7 cm from the bottom of the jar. Each jar contained 200 mL of sediment and held about 600 mL of sea water over the sediment. Each jar was covered with a 8 cm diameter glass Carolina dish with a 17 mm diameter hole for the seawater delivery tube and air line consisting of a 2 mL glass pipette. We positioned the water delivery and air lines so that the sediment was not disturbed.

Diffusion samplers [23,24] "peepers", were constructed from polyethylene vials (21 mm high, 20 mm diameter, 5 mL capacity). A 1.6 cm hole was cut in the cap, polycarbonate membrane (1 micron) was placed over the open end of the vial and the cap replaced under water so that the sampler was filled with 20°C, 30 ppt salinity water at

the start of the test. A 21.5 cm long nylon strap was attached to the vial to serve as a handle to facilitate handling and removal of the diffusion sampler from the exposure chamber. For the mixed metals experiment each diffusion sampler consisted of two vials attached back-to-back to double the volume of interstitial water collected. (The peeper design used in the cadmium experiment was different and is described in Di Toro et al., [12].

Sand-filtered Narragansett Bay water, heated to 20°C ± 1°C, with a mean salinity of 30 ppt (28 to 34 ppt) was used in the experiments. Seawater flowed into each exposure chamber from a distribution system consisting of chambers with self-priming siphons and splitter chambers. Flow rate for each exposure chamber was approximately 28 to 35 volume additions per day (except in the cadmium experiment in which it was approximately 10 volume additions per day). Exposure chambers were placed in 20°C water baths to maintain temperature. The exposure chambers were kept under constant light to help keep the amphipods burrowed into the sediment.

The test was started by placing a diffusion sampler in each exposure chamber and adding 200 mL of sediment, to just cover the diffusion sampler. Seawater was allowed to flow through the chambers for 1 day. Amphipods were removed from the holding containers as described above, distributed sequentially to 100 mL plastic cups until there were 20 amphipods per cup (30 in the cadmium experiment), then one cup of amphipods was added randomly to each exposure chamber. The seawater delivery system was turned off for 1 hour and any amphipods that had not burrowed into the sediment in that time were replaced, except in those replicates where there was an obvious dose response (i.e. where there were a greater than average number of unburrowed individuals in both replicates). Samples of sediment were taken from the day zero chemistry replicates for metals and AVS analyses. All but about 1 cm of overlying water was removed from each day zero chemistry replicate with a vacuum pump and pipette tip. The sediment and a small amount of remaining seawater was homogenized with a stainless steel spatula. Approximately half the sediment was placed in an acid-stripped polyethylene jar for acid-extractable metals analysis, while the remainder was poured into a 100 mL polyethylene

specimen cup for AVS and SEM analysis. Each jar was capped and the samples held in the dark at 4°C until analysis.

The experimental chambers were checked daily and amphipods which appeared dead were removed and examined under a dissecting microscope. Live animals were returned to the test, dead animals were recorded and discarded. The volume of water delivered to each exposure container was measured before each test and the total flow rate to the system was measured and adjusted daily. Temperature of the water bath and salinity of the incoming seawater was measured daily. The overlying water in each biological replicate was sampled for metal concentration at least once near the beginning and near the end of each test. In some tests the samples from the two replicates were pooled. Each overlying water sample was placed in an acid-stripped 7 mL polyethylene vial and acidified with 50 μl of concentrated nitric acid (pH$\leq$1).

At the end of the test the diffusion samplers were carefully removed from each replicate. Any sediment remaining on the cap or membrane portion of the sampler was rinsed off using clean seawater. The membrane was then punctured with an acid-stripped 5 mL disposable pipette tip and the contents of the sampler removed by pipette. The interstitial water collected from each diffusion sampler was added to an acid-stripped 7 mL polyethylene vial, acidified with 50 μl of concentrated nitric acid (pH$\leq$1) and stored for metals analysis. The sediment from the "chemical" replicates was sampled for metals and AVS content as described for the day zero chemistry replicates. The contents of each amphipod "biological" replicate were sieved through a 0.5 mm screen. Material retained on the sieve was examined immediately or preserved with Rose Bengal stain for later sorting. Amphipods were counted and any missing animals were assumed to have died and decomposed. Any replicates in which 10 percent or more amphipods were not found were recounted by another investigator as a QA check.

Chemical analyses -

Sediment samples were analyzed for AVS by a cold-acid purge- and-trap technique described by Di Toro et al. [12,2]. SEM analyses for the copper, nickel and zinc experiments were performed using the graphite furnace AA. SEM analyses for the lead and the mixed metals experiments were performed using inductively coupled plasma emission spectrometry (ICP). SEM was not measured in the cadmium experiment because the importance of SEM vs total metal was not understood at that time. However, cadmium does not form sulfides which are insoluble in the AVS procedure [2] so acid-extractable and SEM cadmium concentrations are interchangeable. SEM for only the metal under study was measured in the individual chemical experiments. However, the sum of the SEM for all of the cationic metals is only 3.2 μM/g for LIS, and 0.081 μM/g for NIN and thus of little importance in the SEM/AVS ratio for the level of metal spiking used.

To allow for comparisons with other metals toxicity studies, acid-extractable metals analyses were also performed. For this analysis, metals were extracted from freeze-dried sediments by ultrasonic agitation with 2 M cold nitric acid (50 mL to 5 g wet sediment) and the extracted metals separated from the sediment residue by centrifugation. The resultant solution was analyzed by ICP.

The acidified interstitial and overlying waters were analyzed for trace metals by ICP. The interstitial water samples from the mixed metals experiment were diluted fivefold with 2 M HNO_3^- in order to provide sufficient solution for analysis. The interstitial water samples from the copper experiment were also analyzed using the graphite furnace. The interstitial waters from the cadmium experiment were analyzed using a cadmium ion-specific electrode. Total cadmium was estimated by multiplying the Cd^{2+} measured by the electrode by 20 (Di Toro et al., 1990), which is the ratio of total Cd to Cd_{2+} in seawater.

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CHAPTER 6

FIELD COLLECTED SAMPLES

The objective of this chapter is to further demonstrate the utility of interstitial water concentrations of metals and sediment concentrations normalized based on SEM/AVS ratios to explain the bioavailability of sediment-associated metals to benthic organisms. The sediments examined in this chapter are all field collected from locations with high metals concentrations. The first part of this chapter presents previously unpublished data on the relationship between total metal concentrations, interstitial metal concentrations and SEM/AVS ratios, and toxicity to the saltwater amphipod (Ampelisca abdita) exposed to sediments from five marine sites located in Maryland; Massachusetts; New York; New Brunswick, Canada and Liaoning Province, China together with previously published results using New York sediments with a saltwater polychaete (Neanthes arenaceodentata) [1]. Next, data are presented on these relationships with a freshwater amphipod (Hyalella azteca) and an oligochete (Lumbriculus variegatus) exposed to sediments from four field locations. Data from locations in New York, Michigan, and Washington have been published previously [2,3] while those from Missouri are new. All are herein analyzed collectively. Finally, this chapter combines results from all experiments using field-collected saltwater and freshwater sediments with those from all available laboratory spiked-sediment tests using a variety of saltwater and freshwater species [4].

Methods for sediment collection, storage and handling, chemical analyses, and toxicity testing for the saltwater amphopod (A. abdita) exposed to five saltwater sediments can be found in Appendix 6A. Methods used to collect, store, and handle freshwater sediments and test sediments with the amphipod, H. azteca, have been described for samples from Steilacoom Lake, Washington, and Keweenaw Waterway, Michigan, by Ankley et al. [5] and for H. azteca and the oligochaete worm, L. variegatus, with sediments from Foundry Cove, New York by Ankley et al. [2]. These same procedures were also used with sediments from Turkey Creek, Missouri. General biological and chemical procedures, as well as the conceptual experimental design, were essentially the same for saltwater and freshwater tests, except that for freshwater tests bulk metals

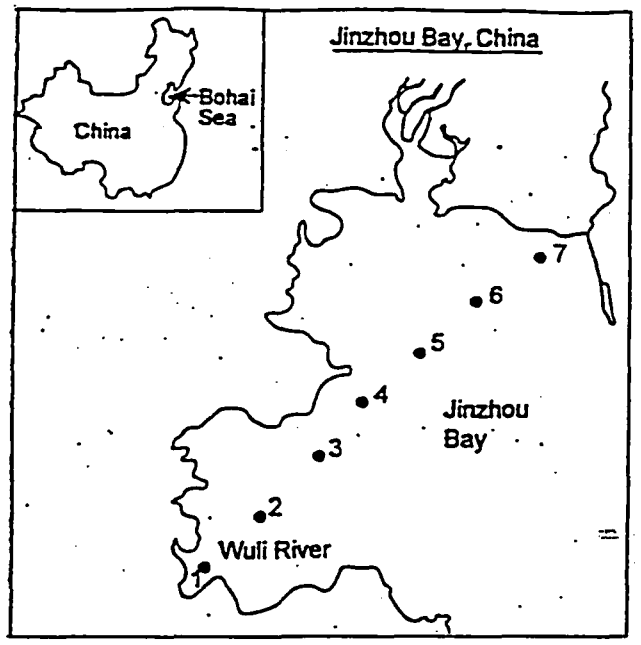
analyses were not performed and interstitial water was extracted by centrifugation instead of diffusional samplers.

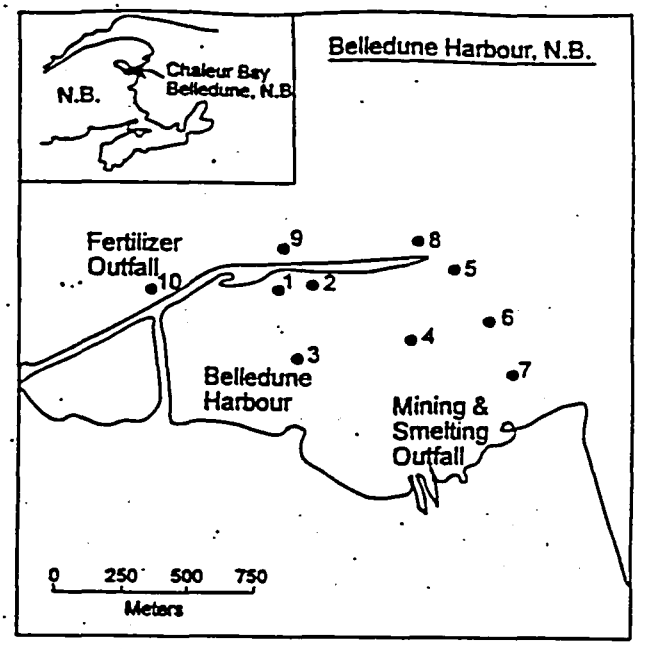
Results Saltwater Field Sites

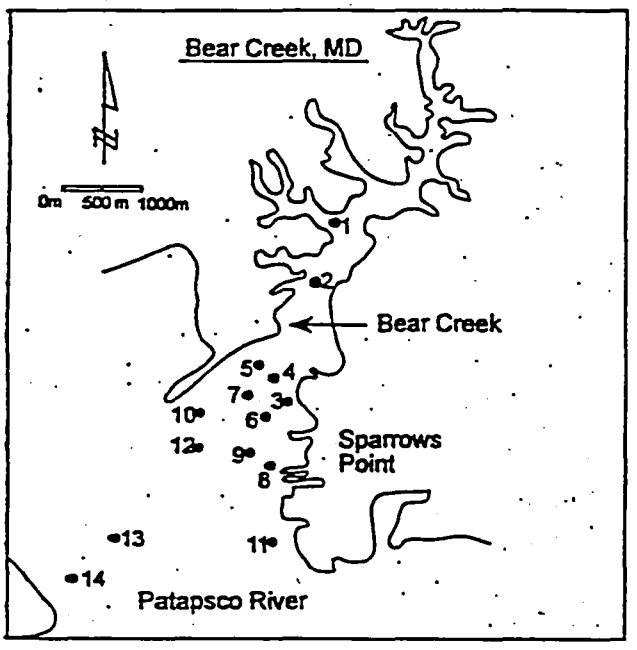
Description of Field Sites and Toxicity Test Results

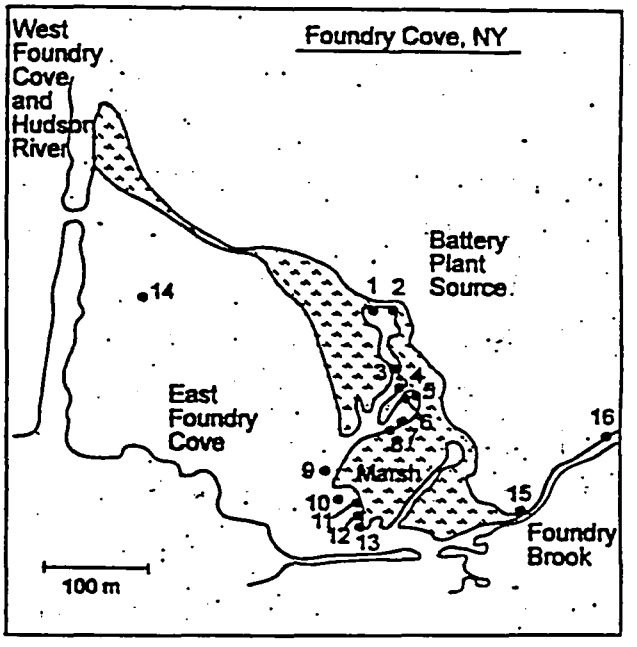
Jinzhou Bay is located in the northeastern quadrant of the Bohai Sea, China (Figure 6-1). It has an area of about 150 km^2, including 62 km^2 of tideflats, with an average depth of 3.5m [6]. A zinc smelter located near the mouth of the Wuli River is the largest source of metals to the bay, although other industrial discharges are contributors. Sediments for this study were collected from seven locations along a 30 km transect from the river to the northeastern portion of the bay. Total concentrations of divalent metals in sediments collected ranged from 261 to 36,200 μg/g dry weight (Table 6-1). Zinc constituted between 78.5 and 86.5 percent of the total. Sediments also contained low concentrations of PAHs (< 12 μg/g for individual PAHs), PCBs (< 0.03 μg/g for individual congeners) and chlorinated pesticides (< 0.03 μg/g for any individual pesticide). Concentrations of TOC ranged from 0.11 to 11.5 percent, AVS 3.0 to 126 μmol/g, SEM 2.9 to 374 μmol/g and SEM/AVS ratios from 0.51 to 8.36. The sum of the interstitial water toxic units (IWTU) for the five divalent metals ranged from no metal detected (<0.01) to 0.58. The four sediments with the highest metals concentrations were toxic (> 24 percent mortality) to A. abdita. However, only the most contaminated sediment contained greater than 0.5 IWTU and had an SEM/AVS ratio > 1.0, which suggests that metals may not be principal cause of the toxicity observed in the other three sediments (Figures 6-2 and 6-3).

Belledune Harbor, which receives outfalls from a lead smelter and fertilizer plant, is located in the southwestern portion of Chaleur Bay, New Brunswick, Canada (Figure 6-1). Harbor sediments are particularly enriched, relative to adjacent areas, in concentrations of cadmium, lead, and zinc; other metals are somewhat elevated [7]. The closure of the lobster fishery due to the elevation of cadmium concentrations in algae, snails, mussels,









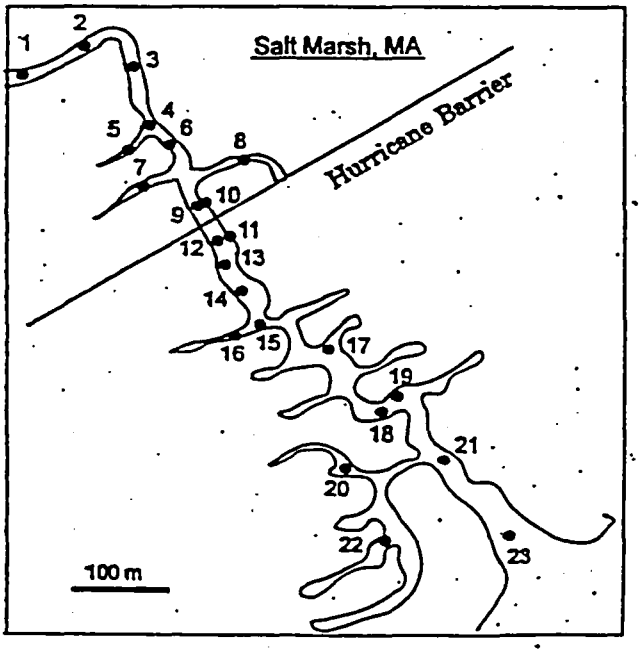


Figure 6-1. Location of field sites and stations sampled in Jinzhou Bay, China; Belledune Harbor, New Brunswick, Canada; Bear Creek, Maryland; Foundry Cove, New York and a salt marsh in Massachusetts.

TABLE 6-1. SUMMARY OF SEDIMENT CHARACTERISTICS, METAL CONCENTRATIONS AND AMPHIPOD MORTALITY IN SEDIMENTS FROM JINZHOU BAY, CHINA; BELLEDUNE HARBOR, NEW BRUNSWICK, CANADA; FOUNDRY COVE, NEW YORK; BEAR CREEK, MARYLAND; A SALT MARSH IN MASSACHUSETTS

Station	Percent TOC	Percent Silt/Clay	Bulk Divalent Metals (µg/g) Cd	Cu	Ni	Pb	Zn	Sum µmol	SEM µmol/g	AVS µmol/g	SEM/AVS	IWTU	Percent Mortality
Jinzhou Bay, China													
NJAM*	*	***	0.10	13.0	2.30	32.0	67.0	1.40	1.42	12.2	0.11	ND	2.0
1	11.5	***	303	2010	31.0	5410	28400	496	374	44.7	8.36	0.58	100
2	2.00	***	151	295	24.2	608	4440	80.5	63.5	126	0.51	ND	90.0
3	0.37	***	9.13	39.4	10.2	113	737	81.1	10.8	17.8	0.61	ND	37.5
4	0.50	***	41.4	46.8	17.4	142	1320	84.2	18.5	36.6	0.51	0.17	30.0
5	0.26	***	2.60	6.40	8.60	22.2	221	84.7	2.99	3.02	0.99	0.03	2.5
6	0.11	***	8.40	11.8	9.40	17.0	300	86.5	3.85	5.42	0.71	ND	7.5
7	0.17	***	4.80	13.0	7.40	17.6	239	84.8	2.92	3.56	0.82	ND	2.5
Belledune Harbor, N.B.													
LIS*	0.99	94	0.90	45.8	20.9	31.7	122	3.09	2.70	16.8	0.16	ND	10.0
1	0.98	**	9.68	50.8	33.2	498	401	90.6	6.65	27.2	0.24	0.04	7.5
2	1.29	**	11.5	101	38.0	955	784	92.1	17.3	80.3	0.22	0.06	12.5
3	1.08	**	15.0	104	39.7	1140.0	897	92.8	18.2	102	0.18	0.18	12.5
4	1.62	**	12.7	85.5	38.8	906	874	92.8	16.3	96.6	0.17	0.07	12.5
5	1.20	**	8.01	57.6	37.3	539	581	91.6	11.1	47.4	0.23	0.02	15.0
6	1.12	**	6.76	49.3	31.7	463	503	91.7	10.2	38.5	0.26	0.05	12.5
7	1.10	**	7.37	68.5	31.2	689	843	93.5	16.8	56.1	0.30	0.62	12.5
8	0.73	**	1.22	15.5	28.6	94.5	137	83.7	1.96	5.54	0.35	ND	7.5
9	0.87	**	1.94	19.5	27.7	131	178	86.3	3.16	16.7	0.19	0.06	17.5
10	0.92	**	2.04	21.9	33.3	149	192	74.7	1.87	11.3	0.17	ND	5.0
Foundry Cove, NY													
LIS*	0.88	94	0.40	56.3	26.5	35.1	160	3.95	0.24	12.0	0.02	ND	10.0
1	10.2	***	38900	143	31500.0	194	403	885	778	5.60	139	43.5	82.5
2	5.20	***	5920	87.3	5180.0	157	297	146	93.4	18.0	5.17	9.21	32.5
3	13.1	***	5950	81.4	4160.0	92.9	278	129	105	12.2	8.65	3.33	52.5
4	8.73	***	9520	106	3700.0	135	313	154	136	26.8	5.10	2.16	20.0
5	9.37	***	13100	116	7670.0	156	356	254	168	64.6	2.59	1.81	80.0
6	5.03	***	5500	101	2340.0	357	303	96.3	52.2	12.5	4.19	1.07	35.0
7	0.79	***	66.1	28.4	60.6	10.0	79.5	3.32	0.67	0.44	1.55	0.42	17.5
8	13.6	***	522	66.9	386	98.3	219	16.0	8.64	20.2	0.43	0.45	17.5
9	5.82	***	6320	74.3	3500.0	113	246	120	86.4	24.7	3.50	1.48	15.0
10	10.9	***	18.6	31.3	38.5	27.2	101	2.99	1.27	2.62	0.48	0.30	7.5
11	0.55	***	35.2	18.1	45.4	6.2	65.4	2.39	0.42	0.41	1.03	0.30	17.5
12	16.4	***	163	57.6	137	87.7	231	8.62	1.91	0.40	4.83	1.42	12.5
13	14.6	***	88.5	44.5	92.1	47.9	142	5.44	1.94	0.69	2.80	0.44	15.0
14	7.18	***	363	104	227	127	317	14.1	5.36	37.1	0.14	1.11	12.5
15	4.76	***	20.6	92.7	28.9	177	234	6.57	0.56	13.1	0.04	1.60	17.5
16	1.45	***	10.1	26.2	17.8	48.2	124	2.93	0.20	1.38	0.15	ND	20.0
Bear Creek, MD													
LIS*	3.89	87	0.77	52.6	27.6	12.9	141	3.52	2.82	9.75	0.29	0.03	0.0
1	7.10	99	8.79	206	53.7	195	1580	29.3	28.3	269	0.11	0.03	82.5
2	7.38	97	10.0	228	62.6	212	1700	31.7	30.6	304	0.10	0.03	95.0
3	5.75	97	5.36	266	60.0	209	1140	23.7	20.2	76.1	0.27	0.03	85.0
4	5.47	96	4.84	207	55.7	175	958	19.7	17.4	70.1	0.25	0.03	85.0
5	6.15	80	3.45	151	38.5	162	567	12.5	17.1	45.3	0.38	0.03	67.5
6	3.32	58	4.82	191	49.9	173	1000	20.0	16.5	46.6	0.35	0.03	40.0
7	0.13	7	0.00	3.18	2.01	3.0	35.6	0.64	0.63	0.40	1.58	0.04	5.0
8	5.19	97	5.82	254	48.8	250	1110	23.1	22.9	147	0.16	0.02	92.5
9	4.40	93	4.19	241	52.8	274	978	21.0	19.1	89.3	0.21	0.03	12.5
10	0.17	5	0.17	9.40	4.87	9.4	69.3	1.34	1.25	0.45	2.78	0.03	5.0
11	4.61	98	2.61	140	50.7	162	617	13.3	11.8	50.0	0.24	0.03	2.5
12	0.16	4	0.17	41.4	2.84	7.4	42.7	1.39	0.74	0.40	1.85	0.02	5.0
13	4.19	94	1.71	139	46.7	128	459	10.6	9.84	7.20	1.37	0.03	17.5
14	3.14	91	1.34	96.9	39.0	88.5	346	7.90	6.71	0.40	16.8	0.03	2.5
Salt Marsh, MA													
LIS*	0.99	94	0.00	55.7	25.2	35.1	142	3.63	2.82	15.5	0.18	ND	5.0

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Station	Percent TOC	Percent Silt/Clay	Bulk Divalent Metals (µg/g) Cd	Cu	Ni	Pb	Zn	Sum µmol	SEM µmol/g	AVS µmol/g	SEM/AVS	IWTU	Percent Mortality
LIS*	0.99	94	0.00	61.5	27.5	38.8	164	4.12	2.52	16.1	0.16	ND	0.0
REF*	1.24	17	0.42	9.93	4.49	9.5	28.1	0.71	0.41	13.8	0.03	ND	12.5
REF*	1.24	17	0.34	6.62	3.11	6.8	22.8	0.54	0.38	11.0	0.03	0.06	7.5
REF*	1.47	11	0.46	15.2	3.99	8.3	28.4	0.79	0.50	4.00	0.13	ND	2.5
1	3.22	17	2.07	147	25.0	410	517	12.6	8.39	86.4	0.10	0.30	12.5
2	1.56	4	0.56	144	48.6	66.9	398	9.50	6.36	1.42	4.49	1.00	40.0
3	0.36	2	0.00	128	9.18	87.6	65.6	3.59	1.30	0.44	3.00	0.14	12.5
4	0.48	3	0.00	32.4	5.94	28.1	32.9	1.25	0.95	0.59	1.60	0.22	7.5
5	2.00	62	2.02	300	36.5	95.7	463	12.9	9.60	419	0.02	ND	17.5
6	2.28	21	5.77	155	108	61.0	1100	21.4	17.8	12.4	1.44	0.19	0.0
7	2.49	24	1.60	823	113	143	930	29.8	25.0	16.6	1.51	ND	10.0
8	2.55	49	1.03	1420	72.1	304	1480	47.8	31.7	69.1	0.46	ND	22.5
9	0.61	4	0.06	152	12.0	63.4	236	6.51	3.00	0.50	6.00	0.12	5.0
10	1.98	8	0.44	359	29.0	137	455	13.7	7.05	11.5	0.61	ND	15.0
11	3.54	61	7.74	851	31.1	128	2310	49.9	23.0	14.1	1.63	0.64	7.5
12		2	0.00	111	14.8	65.6	239	5.97	1.41	1.32	1.07	0.10	5.0
13		16	1.67	523	43.2	151	545	18.0	11.4	85.5	0.13	0.09	17.5
14	4.39	26	2.34	572	42.9	192	629	20.3	13.9	19.1	0.73	0.25	10.0
15	1.13	11	0.68	236	20.0	62.6	272	8.52	6.08	18.6	0.33	0.11	5.0
16	2.74	33	0.00	639	28.0	226	685	22.1	16.2	2.35	6.90	0.11	7.5
17	2.45	12	2.58	348	28.1	97.5	410	12.7	7.20	21.8	0.33	0.10	5.0
18	0.51	5	0.60	184	11.6	38.7	172	5.91	4.57	5.86	0.8	0.07	12.5
19	1.18	13	0.81	179	12.5	52.4	188	6.16	3.72	38.9	0.10	ND	10.0
20	3.13	28	0.37	47.5	11.5	28.4	86.0	2.39	1.71	11.7	0.15	ND	7.5
21	0.63	5	0.47	93.2	7.79	19.9	103	3.27	2.08	18.0	0.12	ND	5.0
22	2.03	17	0.54	88.7	9.51	29.4	152	4.03	2.52	18.0	0.14	ND	2.5
23	0.13	2	0.26	29.8	4.26	6.2	41.9	1.21	0.73	3.24	0.23	0.07	2.5

* Reference sediments from Long Island Sound (LIS), lower Narragansett Bay (NJAM) or a clean site nearby (REF).
** ND = No detectable metal.

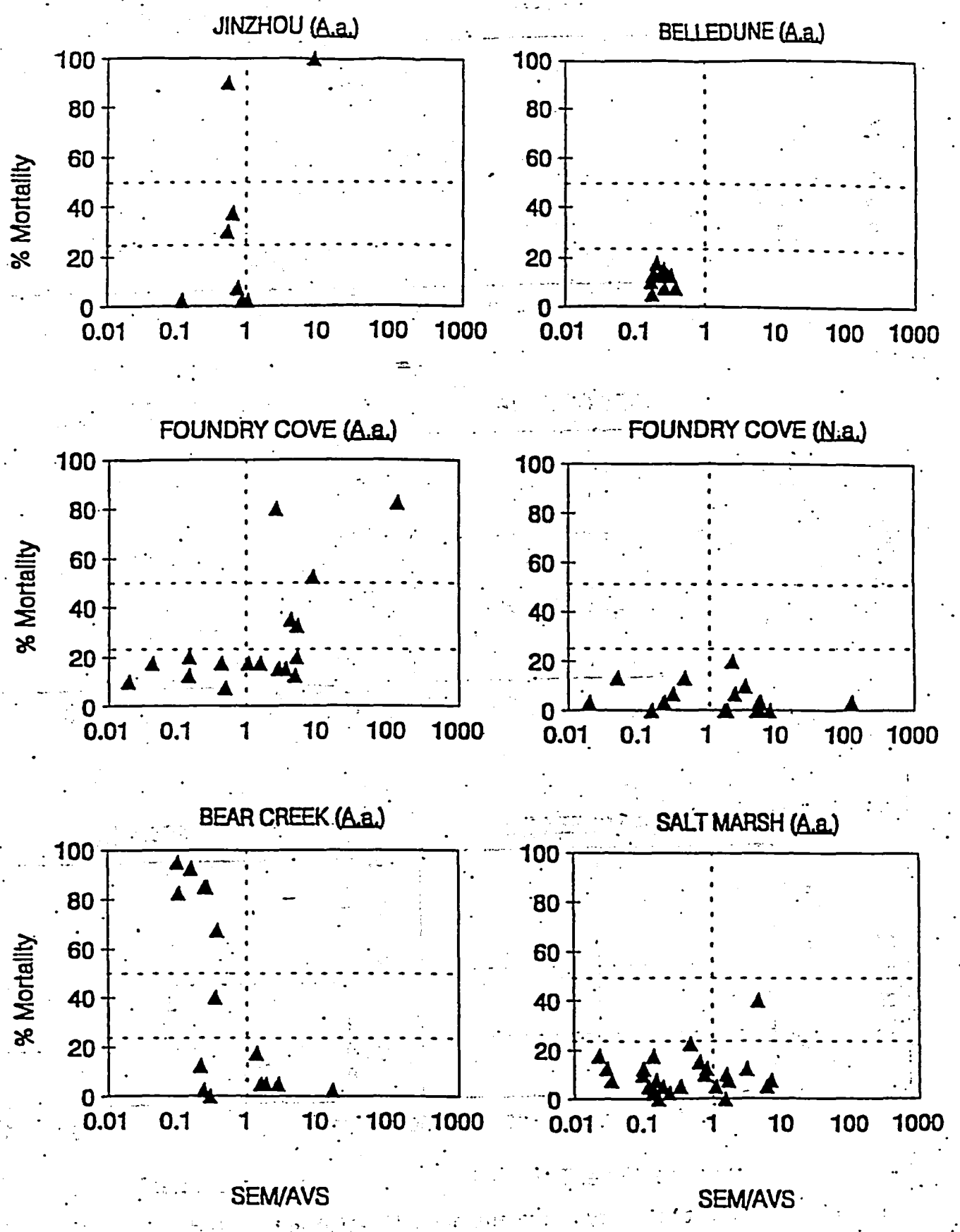

Figure 6-2. - Percent mortality of the amphipod (Ampelisca abdita, A.a.) and polychaete (Neanthes arenaceodentata, N.a.) as a function of SEM/AVS ratios in sediments from Jinzhou Bay, China; Belledune Harbor, New Brunswick, Canada; Foundry Cove, New York; Bear Creek, Maryland and a salt marsh in Massachusetts.

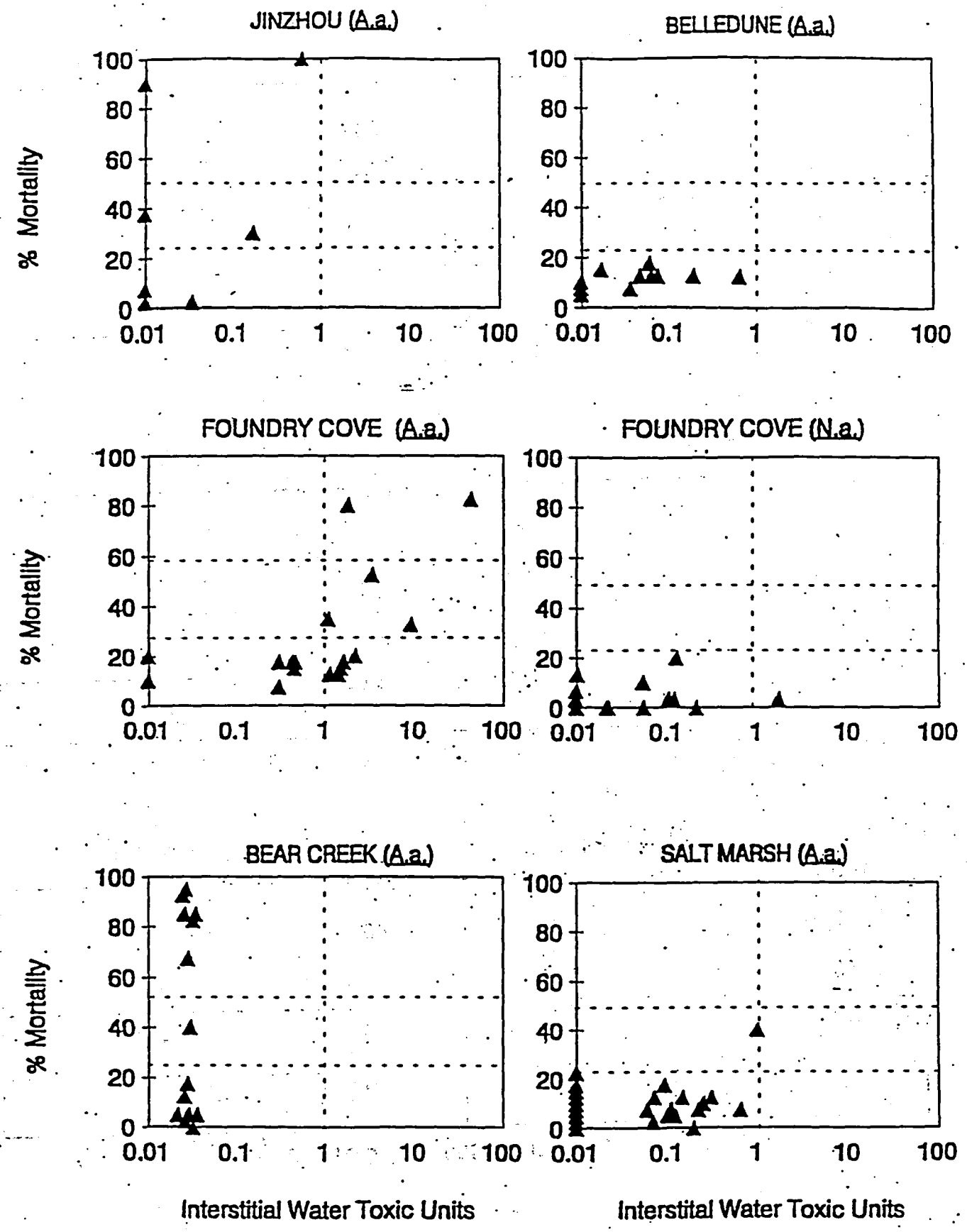

Figure 6-3. - Percent mortality of the amphipod (Ampelisca abdita, A.a.) and polychaete (Neanthes arenaceodentata, N.a.) as a function of interstitial water toxic units (IWTU) of cadmium, copper, nickel, and zinc in sediments from Jinzhou Bay, China; Belledune Harbor, New Brunswick, Canada; Foundry Cove, New York; Bear Creek, Maryland and a salt marsh in Massachusetts.

scallops, barnacles, crabs, and lobsters has been of particular concern [8,9]. Sediments for our study were collected by Ponar grab from 10 stations; 7 inside and 3 outside the harbor. Total concentrations of divalent metal in these sediments ranged from 277 to 2,200 μg/g dry weight, with 74.7 to 93.5 percent of the total consisting of lead and zinc (Table 6-1). Concentrations of TOC ranged from 0.73 to 1.62 percent, AVS 5.5 to 102 μmol/g, and SEM 1.9 to 18.2 μmol/g with SEM/AVS ratios of 0.17 to 0.35. The sum of the interstitial water toxic units ranged from <0.01 to 0.62. None of the sediments were toxic (≤ 24 percent mortality) to A. abdita as would be predicted based upon SEM/AVS ratios and IWTUs (Figures 6-2 and 6-3).

Foundry Cove, New York is located on the upper tidal reach (salinities 0 to 6 mg/kg) of the Hudson River immediately south of Cold Spring, New York (Figure 6-1). A battery plant was the principal source of the approximately equimolar concentrations of cadmium and nickel in the sediments; smaller amounts of cobalt were also discharged [10]. Sediments for our study were collected by shovel or Ponar grab from 16 stations in East Foundry Cove. Total concentrations of divalent metal in our sediments ranged from 170 to 71,200 μg/g dry weight with cadmium plus nickel accounting for up to 99.0 percent of the metal measured in the most contaminated sediments (Table 6-1). Concentrations of TOC ranged from 0.55 to 16.4 percent, with many sediments consisting principally of partially decayed marsh vegetation. Concentrations of AVS ranged from 0.40 to 64.6 μmol/g, SEM 0.20 to 778 μmol/g and SEM/AVS ratios 0.04 to 139. The sum of the interstitial water toxic units (IWTU) for cadmium and nickel ranged from <0.01 to 43.4. Molar concentrations of cadmium and nickel in the interstitial water were similar. However, cadmium contributed over 95 percent to the sum of the toxic units because the 10-day LC50 for nickel to A. abdita (2400 μg/L) is 67 times that of cadmium (36.0 μg/L). Sediments with the highest dry weight metals concentrations (8,600 to 71,200 μg/g) were generally toxic (> 24 percent mortality) to A. abdita. In contrast, others with similar concentrations (≤ 13,800 μg/g) were not toxic (≤ 24 percent mortality). Sediments with SEM/AVS ratios ≤ 1.0 were always nontoxic, whereas only 5 of 11 sediments with SEM/AVS ratios >1.0 were toxic (Figure 6-2). Sediments with ≤ 0.50 IWTUs were always nontoxic, those with >2.2 IWTUs were always toxic and two of seven sediments

with intermediate IWTUs ($\geq$ 0.5 to $\leq$ 2.2) were toxic (Figure 6-3). Data on chemical concentrations and polychaete (N. arenaceodentata) mortality in tests with Foundry Cove sediments are not included in Table 6-1 because they have been presented elsewhere by Pesch et al. [1]. Six of 17 sediments tested with this polychaete had SEM/AVS ratios <1.0, 16 of 17 sediments had interstitial water toxic units <1.0 and none of the 17 sediments were toxic (Figures 6-2 and 6-3).

Bear Creek is a tributary of the Patapsco River just east of Baltimore, Maryland (Figure 6-1). Sediments from this portion of Baltimore Harbor are known to be toxic and contain high concentrations of metals, PAHs, PCBs, and other substances [11,12] from many municipal and industrial sources. Sediments used in our study were collected from 14 stations using a modified Van Veen grab. Total concentrations of divalent metals in sediments ranged from 43.8 to 2210 μg/g dry weight, with zinc accounting for approximately 75 percent of the total concentration (Table 6-1). Concentrations of TOC ranged from 0.13 to 7.38 percent, silt and clay 4 to 99 percent, AVS 0.40 to 304 μmol/g, SEM 0.63 to 30.6 μmol/g, and SEM/AVS ratios 0.10 to 16.8. Seven of the 14 sediments from Bear Creek were toxic to A. abdita these included 7 of the 9 sediments with the highest dry weight metals concentrations (11.8 to 30.6 μmol/g). Sediments that were nontoxic contained metals concentrations from 0.6 to 21.0 μmol/g. Both toxic and nontoxic sediments had $\leq$ 0.03 interstitial water toxic units of metal (Figure 6-3). Given the absence of interstitial water metal, it is not surprising that SEM/AVS ratios for sediments from Bear Creek were not related to sediment toxicity; ie., five sediments having SEM/AVS ratios > 1.0 were not toxic and seven of the sediments having SEM/AVS ratios < 1.0 were toxic (Figure 6-2). Most toxic sediments released visible oil sheens when stirred suggesting that PAHs may ultimately prove to be a source of the observed sediment toxicity. These observations support the conclusion that toxicity observed in Bear Creek sediments was not metal-associated.

The salt marsh containing a small tidal creek less than 500 m long (Figure 6-1) is near Fairhaven, Massachusetts on the western side of Buzzards Bay. The creek is divided by a hurricane barrier into an upper section of low salinity and a lower section with higher

salinity. A metal products manufacturer was the principal source for metals in the sediments. Sediments were collected by plastic scoops from 23 locations; 10 from the upper side of the hurricane barrier and 13 from the lower section. Total concentrations of divalent metals in these sediments ranged from 82.6 to 3320 μg/g dry weight (Table 6-1). Zinc and copper were the principal metals on a dry weight basis in these sediments. Concentrations of TOC ranged from 0.13 to 4.39 percent, silt and clay 1.5 to 61.5 percent, AVS 0.44 to 419 μmol/g, SEM 0.73 to 31.7 μmol/g, and SEM/AVS ratios 0.10 to 6.90. Only 1 of 23 sediments from the salt marsh was toxic to A. abdita (Figures 6-2 and 6-3). The SEM/AVS ratio for the toxic sediment was 4.49 and IWTUs were 1.00. All other sediments were nontoxic, had SEM/AVS ratios from 0.03 to 6.90 and IWTUs from 0.03 to 0.64 (21 of 22 contained < 0.3 IWTUs).

Freshwater Field Sites

Description of Field Sites and Toxicity Test Results

High concentrations of copper in sediments from Steilacoom Lake, Washington originated principally from attempts to control aquatic vegetation using copper sulfate. Copper SEM concentrations in sediments from eleven locations tested ranged from 0.60 to 3.91 μmol/g (38 to 248 μg/g), AVS from < 0.02 to 5.65 μmol/g, and SEM/AVS ratios from 0.23 to 67.5 (Table 6-2) [5]. Eight of the 11 sediments tested had SEM/AVS ratios > 1.0. No copper was detected in interstitial water (IWTU < 0.22) and no sediments were toxic to H. azteca (Figures 6-4 and 6-5). Absence of toxicity in sediments having SEM/AVS ratios > 1.0 (Figure 6-5) and the lack of detectable copper in the interstitial water is likely a consequence of the presence of other sediment binding phases [5].

In contrast, 10 of 11 sediments from Keweenaw Watershed, Michigan, were lethal to H. azteca [5]. Mining-derived copper concentrations in sediments ranged from 0.36 to 174 μmol/g (22.9 to 11,000 μg/g), AVS < 0.006 to 11.6 μmol/g, and SEM/AVS ratios 0.4 to > 17,500 (Table 6-2). The one sediment not toxic to amphipods had 0.41 toxic units of copper in interstitial water and an SEM/AVS ratio of 0.40 (Figures 6-4 and 6-5).

TABLE 6-2. SUMMARY OF SEDIMENT CHARACTERISTICS, METAL CONCENTRATIONS AND AMPHIPOD (HYALELLA AZTECA = H.A.) OR OLIGOCHAETE (LUMBRICULUS VARIEGATUS = L.V.) MORTALITY IN FRESHWATER SEDIMENTS FROM STEILACOOM LAKE, WASHINGTON; KEWEENAW WATERSHED, MICHIGAN, TURKEY CREEK, MISSOURI AND FOUNDRY COVE, NEW YORK.

Station	SEM, umol/g[1] Day 0/10	AVS, umol/g Day 0/10	Average SEM/AVS	IWTU[2] H.a. (L.v.)	Percent Mortality H.a. (L.v.)
		Steilacoom Lake, Washington			
1	0.89/1.36	4.01/5.65	0.23	<0.22	0
2	3.05/2.00	2.89/1.02	1.51	<0.22	5
3	1.93/1.85	0.30/<0.02	>49.5	<0.22	0
4	2.84/3.78	1.94/0.92	2.79	<0.22	10
5	1.25/3.56	2.06/0.29	6.45	<0.22	5
6	0.60/2.02	4.16/0.81	1.32	<0.22	15
7	0.66/1.11	1.48/1.44	0.61	<0.22	0
8	1.33/2.68	1.60/<0.05	>27.2	<0.22	0
9	1.95/3.91	0.39/<0.03	>67.5	<0.22	10
10	1.27/2.01	2.17/1.60	0.93	<0.22	5
11	2.90/2.05	0.65/0.41	4.11	<0.22	0
*					0
		Keweenaw Watershed, Michigan			
1	-/4.68	-/11.6	0.40	0.41	20
2	-/26.4	-/<0.006	>4,440	1.19	55
3	-/62.6	-/0.03	2,090	9.97	100
4	-/15.1	-/0.08	189	4.52	100
5	-/19.6	-/0.06	332	2.81	85
6	-/5.65	-/0.01	565	1.71	75
7	-/8.49	-/0.12	70.7	5.45	95
8	-/0.74	-/0.01	17,500	19.6	100
9	-/28.1	-/0.46	61.1	3.19	95
10	-/0.36	-/0.09	4.0	0.52	35
11	-/10.8	-/0.02	674	3.10	90
*					10
		Turkey Creek, Missouri			
1	-/67.2	-/28.1	2.39	0.73	20
2	-/51.5	-/52.2	0.99	0.44	15
3	-/85.4	-/30.1	2.84	1.11	45
4	-/47.6	-/48.4	0.98	0.38	0
5	-/50.1	-/44.2	1.13	1.83	5
6	-/82.1	-/38.2	2.15	1.31	20
7	-/94.5	-/78.2	1.21	0.49	45
*	-	-	-	-	5

TABLE 6-2. SUMMARY OF SEDIMENT CHARACTERISTICS, METAL CONCENTRATIONS AND AMPHIPOD (HYALELLA AZTECA = H.A.) OR OLIGOCHAETE (LUMBRICULUS VARIEGATUS = L.V.) MORTALITY IN FRESHWATER SEDIMENTS FROM STEILACOOM LAKE, WASHINGTON, KEWEENAW WATERSHED, MICHIGAN, TURKEY CREEK, MISSOURI AND FOUNDRY COVE, NEW YORK.

(continued)

Station	SEM, umol/g[1] Day 0/10	AVS, umol/g Day 0/10	Average SEM/AVS	IWTU[2] H.a. (L.v.)	Percent Mortality H.a. (L.v.)
		Foundry Cove, New York			
1	789/703	3.12/5.65	189	18.8 (0.50)	100 (87)
2	66.4/115	9.39/13.8	7.69	11.5 (1.54)	100 (0)
3	43.8/915	15.3/13.6	4.78	94.6 (2.44)	100 (0)
4	92.2/106	10.4/19.0	7.24	7.29 (0.61)	100 (0)
5	50.1/74.8	7.59/9.83	7.11	4.58 (0.18)	80 (0)
6	176/210	46.9/31.2	5.25	11.93 (0.55)	100 (0)
7	0.29/0.50	0.09/0.10	4.11	- (3.291)	100 (0)
8	9.23/14.0	5.12/5.20	2.25	77.3 (6.49)	40 (0)
9	92.9/58.5	6.73/14.7	8.90	3.16 (1.53)	100 (24)
10	0.31/0.31	0.92/1.17	0.32	2.43 (0.27)	0 (0)
11	0.38/0.52	0.39/0.16	2.11	- (0.54)	100 (0)
12	3.02/2.20	1.92/6.15	0.97	32.7 (1.35)	60 (-)
13	2.02/1.79	1.18/0.64	2.25	110 (1.13)	80 (0)
14	3.34/7.86	20.0/10.0	0.31	2.03 (3.02)	20 (0)
15	1.78/0.44	9.07/9.92	0.12	0.40 (0.32)	0 (0)
16	0.00/0.05	0.94/0.49	0.05	- - (0.38)	0 (0)

* Reference sediments were from uncontaminated West Bearskin Lake, Minnesota

[1]Simultaneously extracted metal (SEM) is SEM copper for Steilecoom Lake and Keweenaw Watershed, SEM zinc for Turkey Creek and SEM cadmium plus nickel for Foundry Cove.

[2]Interstitial Water Toxic Units (IWTU) are calculated using 10-day water only LC50s for Hyallella azteca of 2.8 µg/L for cadmium, 31 µg/L for copper, 780 µg/L for nickel and 436 µg/L (hardness 330 mg/L) for zinc and for Lumbriculus variegatus 158 µg/L for cadmium and 12,200 µg/L for nickel.

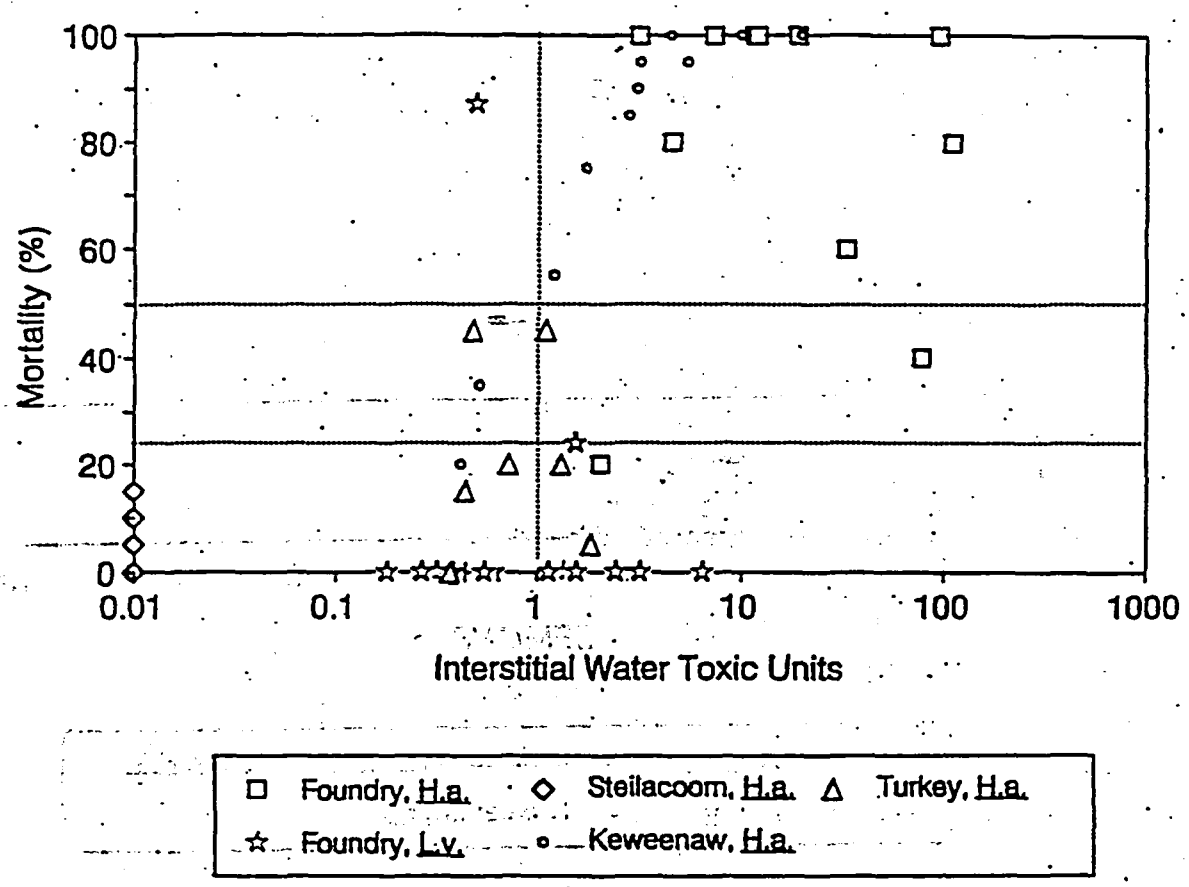

Figure 6-4. Percent mortality of the amphipod Hyalella azteca (H.a.), and the oligochaete, Lumbriculus variegatus (L.v.), as a function of interstitial water toxic units (IWTU) of metals in sediments from four freshwater field locations. The lower horizontal dashed line at 24 percent indicates the boundary between toxic and nontoxic sediments. The higher horizontal dashed line at 50 percent mortality and the vertical dashed line at 1.0 IWTU indicate the hypothetical boundary between sediments expected to be toxic to less than 50 percent of the organisms (IWTU < 1.0) and those expected to be toxic to greater than 50 percent (IWTU > 1.0). Interstitial water concentrations with nondetectable metal are plotted at 0.01 IWTU.

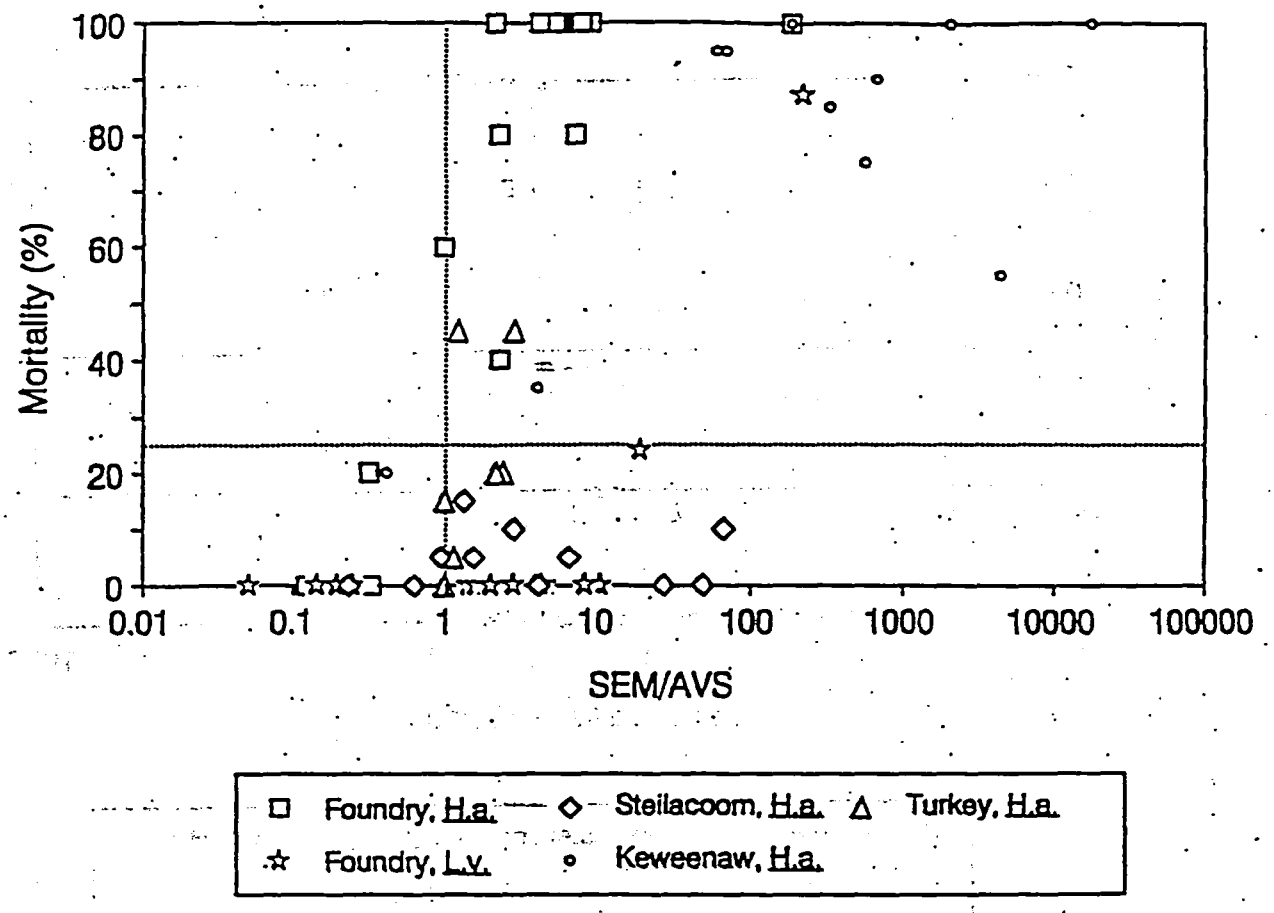

Figure 6-5. Percent mortality of the amphipod, Hyalella azteca (H.a.), and the oligochaete, Lumbriculus variegatus (L.v.), in sediments from four freshwater locations as a function of the SEM/AVS ratio. The horizontal dashed line at 24 percent mortality indicates the boundary between toxic and nontoxic sediments. The vertical dashed line at SEM/AVS = 1.0 indicates the boundary between sulfide bound unavailable metal and potentially available metal.

Toxic sediments had 0.52 to 19.6 IWTUs of copper and SEM/AVS ratios $\geq$ 4.0. AVS concentrations in the 10 toxic sediments were extremely low (< 0.01 to 0.46 μmol/g) with comparatively high copper concentrations (0.36 to 1.74 μmol/g); nine SEM/AVS ratios were $\geq$ 61. Amphipod mortality in response to copper concentrations in water-only tests (Figure 6-6) was almost identical to amphipod mortality as a function of interstitial water copper concentration in sediment tests (Figure 6-3) [5]. The 10 day LC50 for amphipods exposed to copper in water-only tests did not differ from the LC50 based on interstitial dissolved copper concentrations and amphipod mortality from tests with Keweenaw sediments; 31(28 to 35)μg/L versus 28(21 to 38)μg/L.

Sediments from Turkey Creek, Missouri contained high and relatively uniform concentrations of zinc (47.6 to 94.5 μmol/g; 3,110 to 6,180 μg/g) and AVS (28.1 to 78.2 μmol/g; Table 6-2) originating from strip mine tailings. Therefore, SEM/AVS ratios (0.98 to 2.84) and IWTUs (0.44 to 1.83) varied little in the seven sediments tested. The two sediments having SEM/AVS ratios $\leq$ 1.0 were nontoxic and had $\leq$ 0.44 interstitial water toxic units of zinc (Figures 6-4 and 6-5) SEM/AVS ratios of the five remaining sediments ranged from 1.13 to 2.84, IWTUs from 0.49 to 1.83. Two of these sediments were toxic.

Sediments from Foundry Cove, New York tested with saltwater A. abdita and N. arenaceodentata were also tested using the freshwater amphipod H. azteca and the oligochaete L. variegatus by Ankley et al. [2]. Sediments contained approximately equimolar concentrations of cadmium and nickel with the sum of the SEM concentrations of these metals from freshwater tests ranging from < 0.01 to 789 μmol/g, AVS 0.39 to 31.2 μmol/g, and SEM/AVS ratios from 0.05 to 189 (Table 6-2). Four of five sediments with SEM/AVS ratios $\leq$ 1.0 were not toxic to amphipods while all sediments having SEM/AVS ratios > 1.0 were toxic (Figures 6-4 and 6-5). Only the 2 sediments with the highest SEM/AVS ratios (8.90 and 189) were toxic to the oligochaete; 14 of 16 sediments were not toxic. Sediments with interstitial water toxic units $\geq$ 3.16 were toxic to amphipods; when 0.40 to 2.43 toxic units were present, no toxicity was observed. Interstitial molar concentrations of nickel almost always exceeded those of cadmium by one to three orders of magnitude [5]. However, cadmium was most likely the cause of

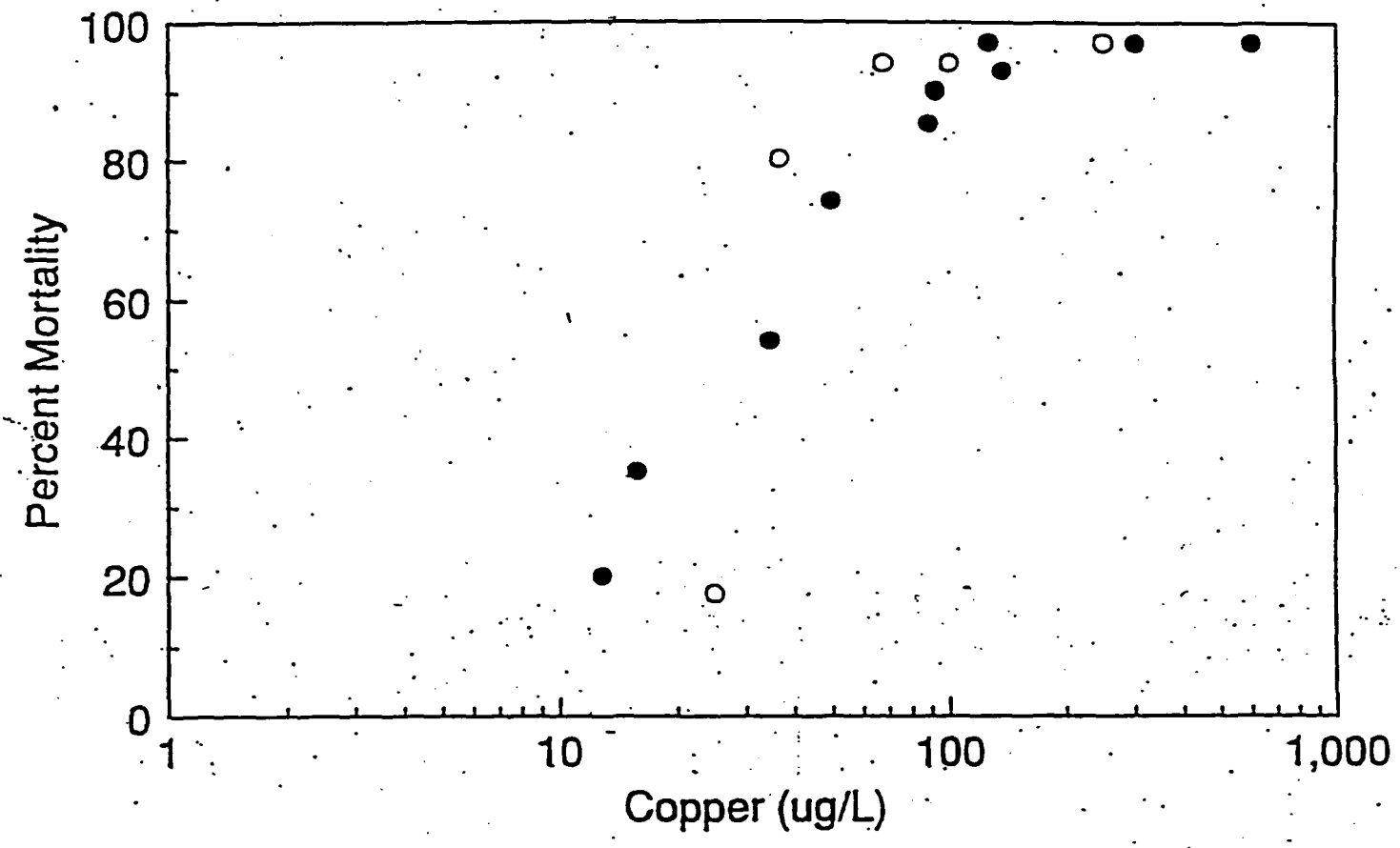

Figure 6-6. Toxicity of copper to Hyalella azteca versus copper concentrations in a water-only exposure (open symbols) and interstitial water in sediment exposures using Keweenaw Waterway sediments (closed symbols) (Ankley et al., 1993).

both amphipod and oligochaete mortalities because cadmium is over 250 times more toxic than nickel to H. azteca; 10 day water-only LC50 for cadmium 2.8 μg/L, and nickel 780 μg/L. Similarly, cadmium is about 80 times more toxic to L. variegatus than nickel; 10 day water-only LC50 158 μg/L for cadmium and 12,200 μg/L for nickel. Cadmium contributed from 88.6 to 99.9 percent of the total interstitial toxic units of metals.

Discussion

Saltwater Field Sites

Bulk metals concentrations in saltwater sediments can not be used to causally relate metal concentrations to the acute response of amphipods and polychaetes (Figure 6-7). Mortality of amphipods in 70 sediments from five saltwater locations, or polychaetes in 16 sediments from Foundry Cove, was not related to the sum of the molar concentrations of cadmium, copper, lead, nickel, and zinc on a dry weight of sediment basis. Sediments having dry weight metals concentrations from 9.50 to 885 μmol/g from 17 stations in Jinzhou Bay, Bear Creek, Foundry Cove, and the marsh in Massachusetts were toxic (mortality > 24 percent). In contrast dry weight metals concentrations from 0.20 to 885 μmol/g were nontoxic (mortality ≤ 24 percent); an overlap of 2 to 3 orders of magnitude in metals concentration.

Normalizing metals concentrations in these sediments using SEM/AVS ratios, without insight into mortality caused by co-occurring toxic substances, also does not permit accurate causal predictions of metal toxicity in sediments from the field (Figure 6-8). Of the 59 sediments with SEM/AVS ratios ≤ 1.0 (Table 6-1), 49 (83 percent) were not toxic and 10 (17 percent) were toxic. These 10 toxic sediments were from Jinzhou Bay and Bear Creek. Of the 37 sediments with SEM/AVS ratios > 1.0, only 7 were toxic. Absence of toxicity when SEM/AVS ratios are > 1.0 has commonly been observed. However, when SEM/AVS ratios are ≤ 1.0, toxicity has been observed in only 4 of 92 sediments spiked with metals [4] and 1 of 15 sediments from freshwater field sites [2,5] (Table 6-3). For all five of these sediments, the true SEM/AVS ratios may have been >

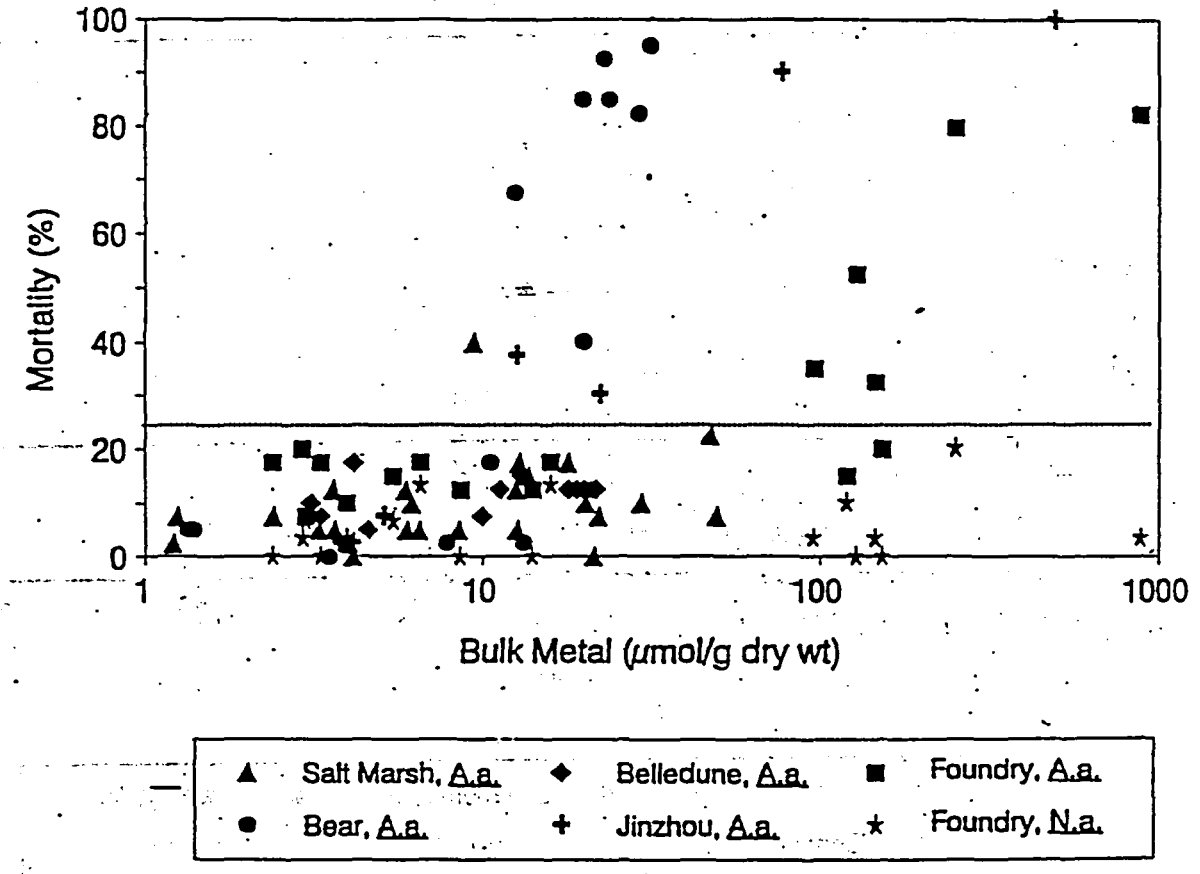

Figure 6-7. Percent mortality of the amphipod, Ampelisca abdita (A.a.), and the polychaete, Neanthes arenaceodentata (N.a.), in sediments from five saltwater locations in the United States, Canada, and China as a function of the sum of the concentrations of cadmium, copper, lead, nickel, and zinc in μmoles divalent metal per gram dry weight sediment. The dashed horizontal line at 24 percent mortality indicates the boundary between toxic and nontoxic sediments.

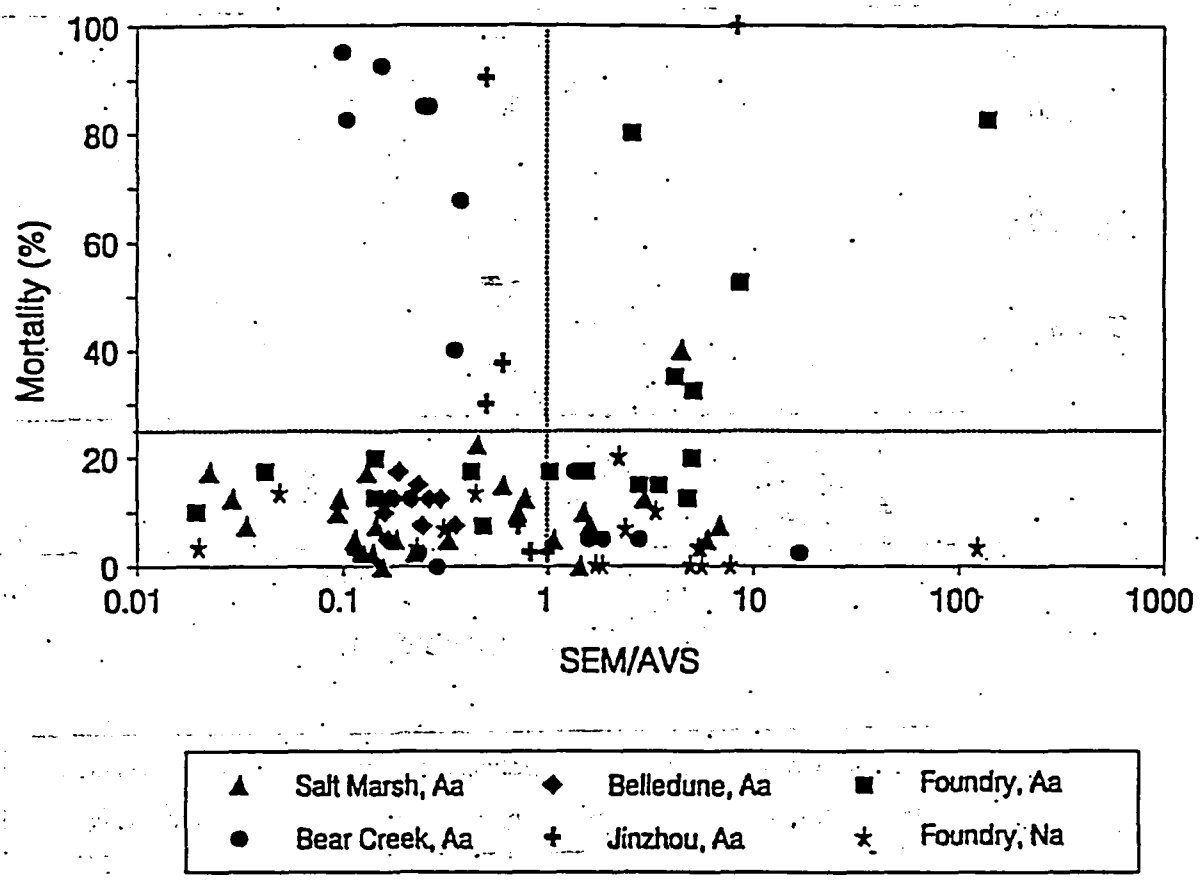

Figure 6-8. Percent mortality of the amphipod, Ampelisca abdita (A.a.), and the polychaete, Neanthes arenaceodentata (N.a.), in sediments from five saltwater field locations as a function of the ratio of the sum of the molar concentrations of cadmium, copper, lead, nickel, and zinc simultaneously extracted (SEM) with acid volatile sulfide (AVS) to the molar concentration of AVS (SEM/AVS ratio). The horizontal dashed line at 24 percent mortality indicates the boundary between toxic and nontoxic sediments. The vertical dashed line at SEM/AVS = 1.0 indicates the boundary between sulfide-bound unavailable metal and potentially available metal.

TABLE 6-3. ACCURACY OF PREDICTION OF THE TOXICITY OF SEDIMENTS FROM SALTWATER (SW) AND FRESHWATER (FW) FIELD LOCATIONS, SPIKED-SEDIMENT TESTS AND COMBINED FIELD AND SPIKED-SEDIMENT TESTS AS A FUNCTION OF SEM/AVS RATIOS, INTERSTITIAL WATER TOXIC UNITS (IWTUs) AND BOTH SEM/AVS AND IWTUs.

				% of Sediments	
Study Type	Parameter	Value	n	Nontoxic[1]	Toxic[1]
SW Field	SEM/AVS[2]	≤1.0	42	100.0	0.0
		>1.0	31	80.6	19.4
	IWTU	<0.5	59	100.0	0.0
		≥0.5	15	53.3	46.7
	SEM/AVS, IWTU	≤1.0, <0.5	39	100.0	0.0
		>1.0, ≥0.5	11	45.5	54.5
FW Field	SEM/AVS	≤1.0	15	93.3	6.7
		>1.0	48	47.9	52.1
	IWTU	<0.5	20	95.0	5.0
		≥0.5	38	42.1	57.9
	SEM/AVS, IWTU	≤1.0, <0.5,	10	100.0	0.0
		>1.0, ≥0.5	34	29.4	70.6
Lab-Spike, (FW & SW)	SEM/AVS	≤1.0	92	95.7	4.3
		>1.0	83	26.5	73.5
	IWTU	<0.5	107	93.5	6.5
		≥0.5	77	22.1	77.9
	SEM,AVS, IWTU	≤1.0, <0.5,	85	96.5	3.5
		>1.0, ≥0.5	65	12.3	87.7
All	SEM/AVS[2]	≤1.0	149	96.6	3.4
		>1.0	162	43.2	56.8
	IWTU	<0.5	187	95.7	4.3
		≥0.5	129	31.0	69.0
	SEM,AVS, IWTU	≤1.0, <0.5,	134	97.8	2.2
		>1.0, ≥0.5	110	20.9	79.1

[1]Nontoxic sediments <24 percent mortality. Toxic sediments >24 percent mortality.
[2]Excludes sediments from Bear Creek, Maryland and Jinzhou Bay, China whose toxicity was not metals-related.

1.0 as concentrations were within the precision expected in AVS and SEM analyses and three had > 0.5 IWTU of metal. Given the fact that field sediments from highly industrialized locations contain many substances other than metals and are often toxic, non-metals associated toxicity should always be suspected. If toxic sediments have SEM/AVS ratios $\leq$ 1.0, we might suspect the cause to not be metals; with SEM/AVS > 1.0, toxicity may be related to metals.

Metals concentrations, when expressed on a sum of the interstitial water toxic unit (IWTU) basis (Figure 6-9), can provide insight that in part may explain apparent anomalies between SEM/AVS ratios and the observed toxicity of these sediments. In spite of the presence of very high dry weight metals concentrations, 56 of 70 sediments had < 0.5 IWTU of metal. Of the 10 toxic sediments having SEM/AVS ratios < 1.0, none had > 0.5 IWTU of metal. This suggests that metals are unlikely the cause of the toxicity. Three of these sediments were from Jinzhou Bay and seven from Bear Creek (most of which released oil when agitated). The absence of toxicity in many sediments having SEM/AVS ratios > 1.0 is understandable because most (66.7 percent; 12 of 18) of these nontoxic sediments had < 0.5 IWTUs of metal. Of the seven toxic sediments having SEM/AVS ratios > 1.0 (one each from Jinzhou Bay and the salt marsh and five from Foundry Cove) all had > 0.5 IWTU of metals. Further, interstitial metal concentrations are likely to overestimate the concentration of available metal because of differences in metal form, greater binding to dissolved organic carbon or ligands in interstitial water [13], release of bound metal in sampling or analytical procedures [14] or organism avoidance of metal exposure [1].

We believe that is inappropriate to further include in this chapter data from locations having sediments whose toxicity is almost certainly not due to metals. This decision is additionally justified because in experiments with metal-spiked sediments [4], only 3 of 85 sediments having IWTU < 0.5 and SEM/AVS ratios < 1.0 were toxic. Therefore, data from Bear Creek, Maryland and Jinzhou Bay, China are not included in the text, figures, and tables that follow. These data were included above to demonstrate the value of both SEM/AVS ratios and IWTUs to discriminate between metals-associated and nonmetals-

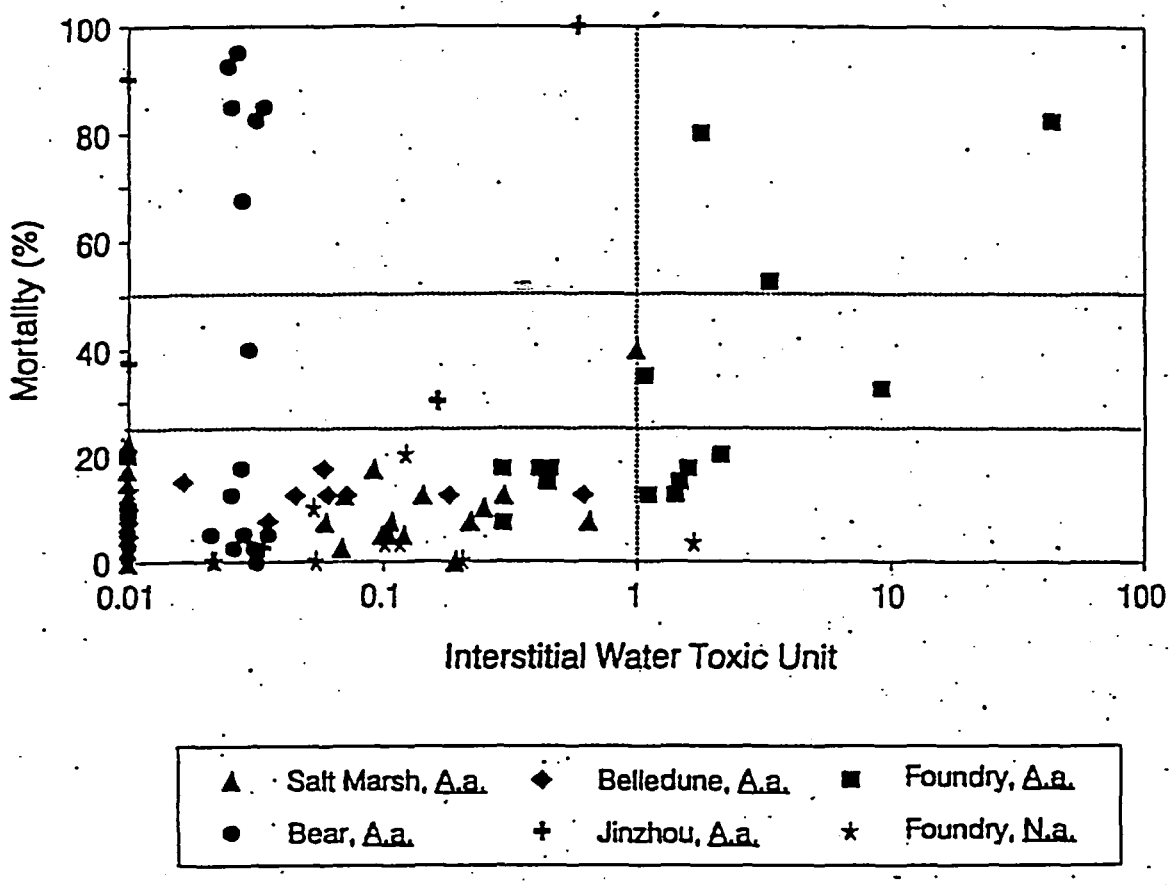

Figure 6-9. Percent mortality of amphipod, Ampelisca abdita (A.a.), and the polychaete, Neanthes arenaceodentata (N.a.), as a function of interstitial water toxic units (IWTUs) of metals in sediments from five saltwater field locations. IWTUs are the sum of metal-specific interstitial water concentrations/10-day LC50 for cadmium, copper, lead, nickel, and zinc. The lower horizontal dashed line at 24 percent indicates the boundary between toxic and nontoxic sediments. The higher horizontal dashed line at 50 percent mortality and the vertical dashed line at 1.0 IWTU indicate the hypothetical boundary between sediments expected to be toxic to less than 50 percent of the organisms (IWTU < 1.0) and those expected to be toxic to greater than 50 percent (IWTU > 1.0). Interstitial water concentrations with nondetectable metal are plotted at 0.01 IWTU.

associated toxicity in sediments. For the data from saltwater field locations in Belledune Harbor, the salt marsh and Foundry Cove, all 42 sediments with SEM/AVS ratios $\leq$ 1.0 were not toxic (Figure 6-10; Table 6-3). Of the 31 sediments that had SEM/AVS ratios > 1.0, only six sediments (from Foundry Cove and the salt marsh) were toxic and all had > 0.50 IWTUs (Table 6-3). Of the 25 nontoxic sediments with SEM/AVS ratios > 1.0, 71.4 percent (10 of 14) of the sediments tested with amphipods and 90.9 percent (10 of 11) of the sediments tested with polychaetes had < 0.5 IWTUs, thus in part explaining the absence of toxicity.

Saltwater and Freshwater Field Sites Combined

Metals concentrations in sediment interstitial water from all freshwater sites suggests that metals contributed to the observed mortalities of amphipods and oligochaetes (Figure 6-4). Therefore, all available freshwater data are included in Figure 6-5 and 6-11 to 6-15. For sediments with IWTUs $\geq$ 0.5, 57.9 percent of 38 sediments were toxic; 20 of 26 for amphipods and 2 of 12 for oligochaetes (Table 6-3).

The pattern of organism response to metals normalized on an SEM/AVS basis is similar for saltwater (Figure 6-10) and freshwater (Figure 6-5) sediments. Therefore, data in both figures were pooled (Figure 6-11) to illustrate the overall utility of the SEM/AVS normalization to explain metals availability in field sediments. The absence of toxicity in all but one sediment having SEM/AVS ratios $\leq$ 1.0 from all field sediments is important given that total divalent metals concentrations (or SEM) for these sediments ranged from 43.8 to 13,800 μg/g for tests with saltwater or freshwater amphipods, 170 to 71,200 μg/g for polychaetes, and 170 to 76,800 for oligochaetes (Tables 6-1 and 6-2). Fifty-six of 57 (98.2 percent) of these freshwater and saltwater sediments having SEM/AVS ratios $\leq$ 1.0 were not toxic to sensitive organisms. In the toxic sediment with SEM/AVS < 1.0, the SEM/AVS ratio was 0.97 (Table 6-3; Figure 6-11). For field sediments having SEM/AVS ratios > 1.0, 31 of 79 (39.2 percent) were toxic (Table 6-3). Therefore, we believe that SEM/AVS ratios of $\leq$ 1.0, can accurately predict field sediments likely to not be acutely toxic due to metals. Use of an SEM/AVS ratio of > 1.0 alone to predict

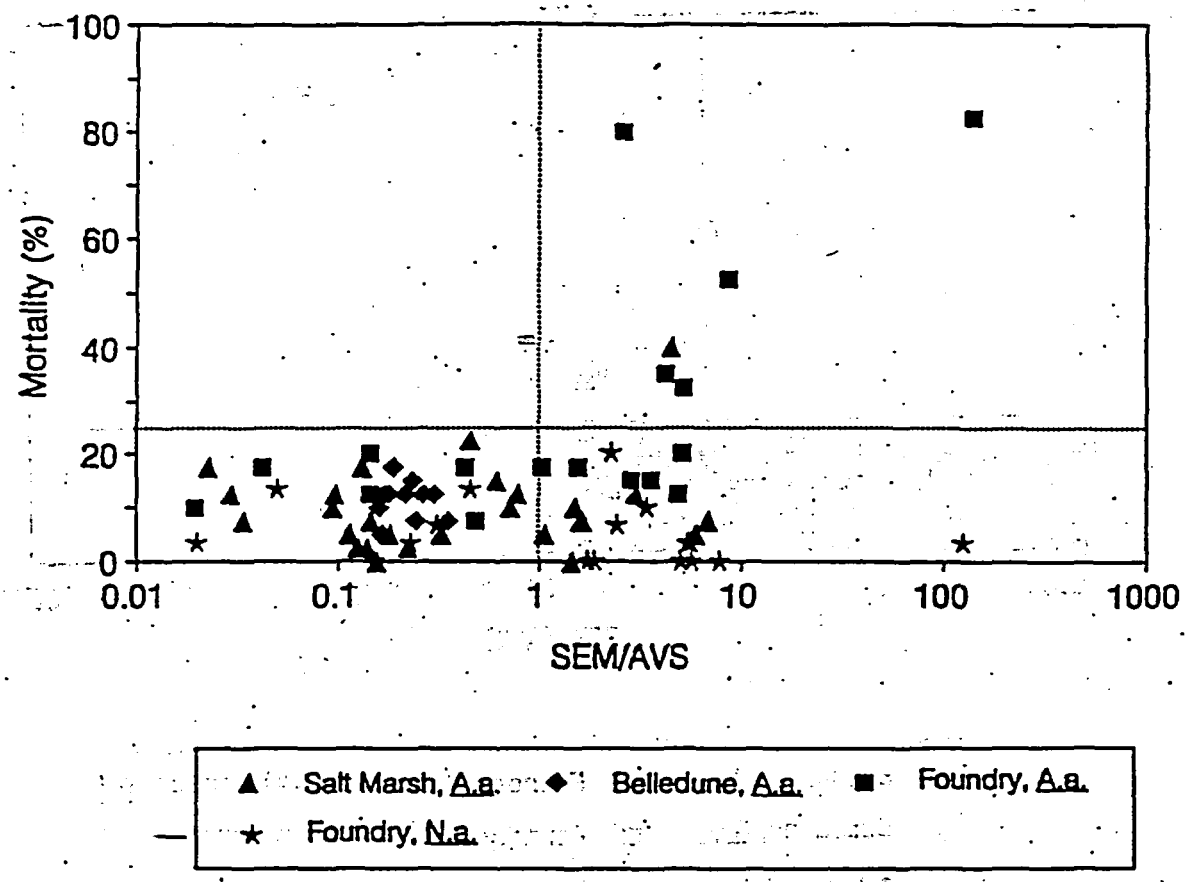

Figure 6-10. Percent mortality of the amphipod, Ampelisca abdita (A.a.), and the polychaete, Neanthes arenaceodentata (N.a.), in sediments from three saltwater field locations as a function of the SEM/AVS ratio. The horizontal dashed line at 24 percent mortality indicates the boundary between toxic and nontoxic sediments. The vertical dashed line at SEM/AVS = 1.0 indicates the boundary between sulfide bound unavailable metal and potentially available metal.

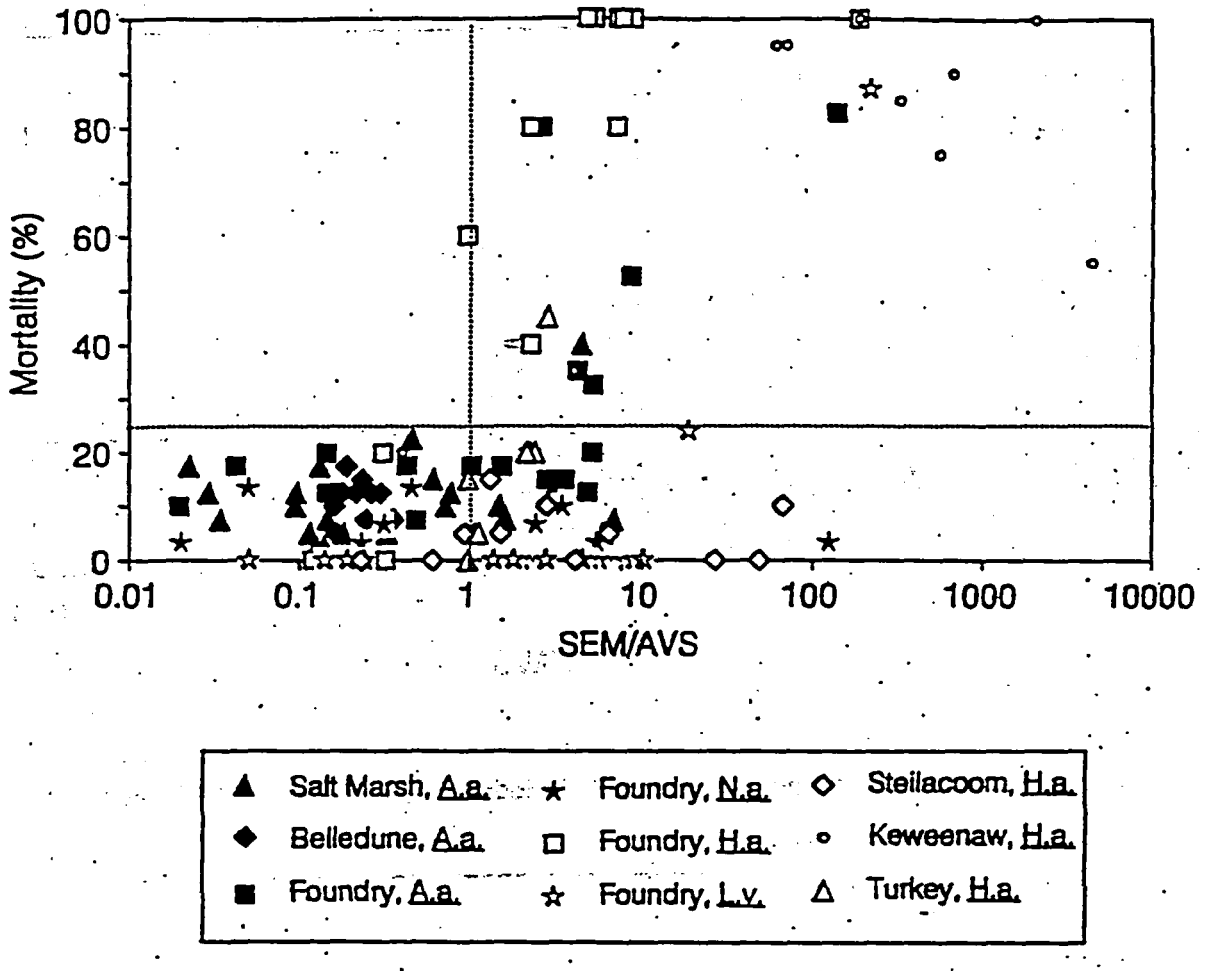

Figure 6-11. Percent mortality of amphipods Ampelisca abdita (A.a.) and Hyalella azteca (H.a.), oligochaetes Lumbriculus variegatus (L.v.) and polychaetes Neanthes arenaceodentata (N.a.) exposed to sediments from three saltwater (solid symbols) and four freshwater (open symbols) field locations as a function of the SEM/AVS ratio. The horizontal dashed line at 24 percent mortality indicates the boundary between toxic and nontoxic sediments. The vertical dashed line at SEM/AVS = 1.0 indicates the boundary between sulfide-bound unavailable metal and potentially available metal.

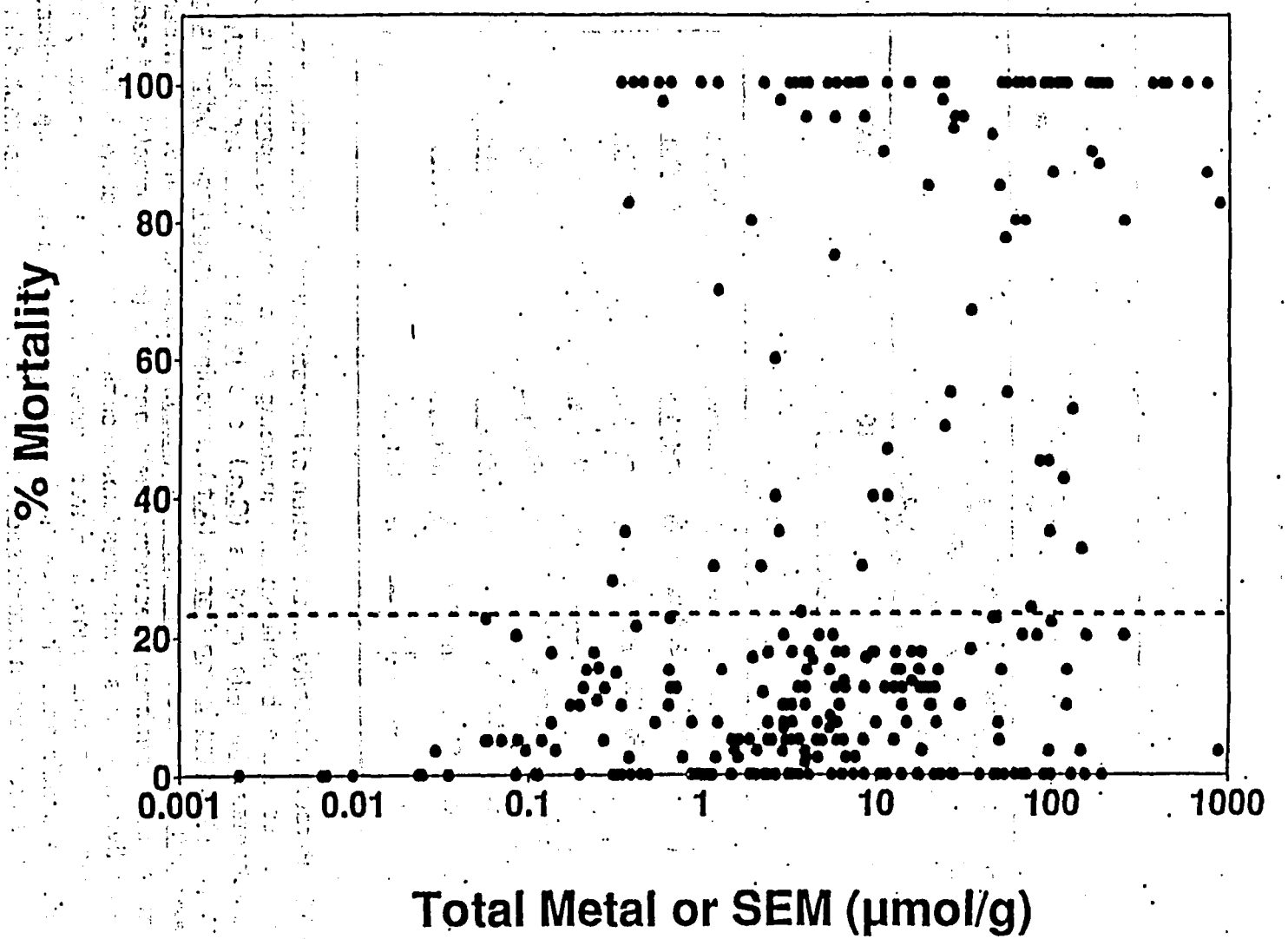

Figure 6-12. Percent mortality as a function of total dry weight metals concentrations including oligochaetes Lumbriculus variegatus (L.v.), polychaetes Capitella capitata (C.c.) and Neanthes arenaceodentata (N.a.), harpacticoids Amphiascus tenuiremis (A.t.), amphipods Ampelisca abdita (A.a.) and Hyalella azteca (H.a.) and snails Helisoma sp. (H.sp.) exposed to sediments from saltwater field locations, freshwater field locations and sediments spiked with individual metals or mixtures.The dashed horizontal line at 24 percent mortality indicates the boundary between toxic and nontoxic sediments.

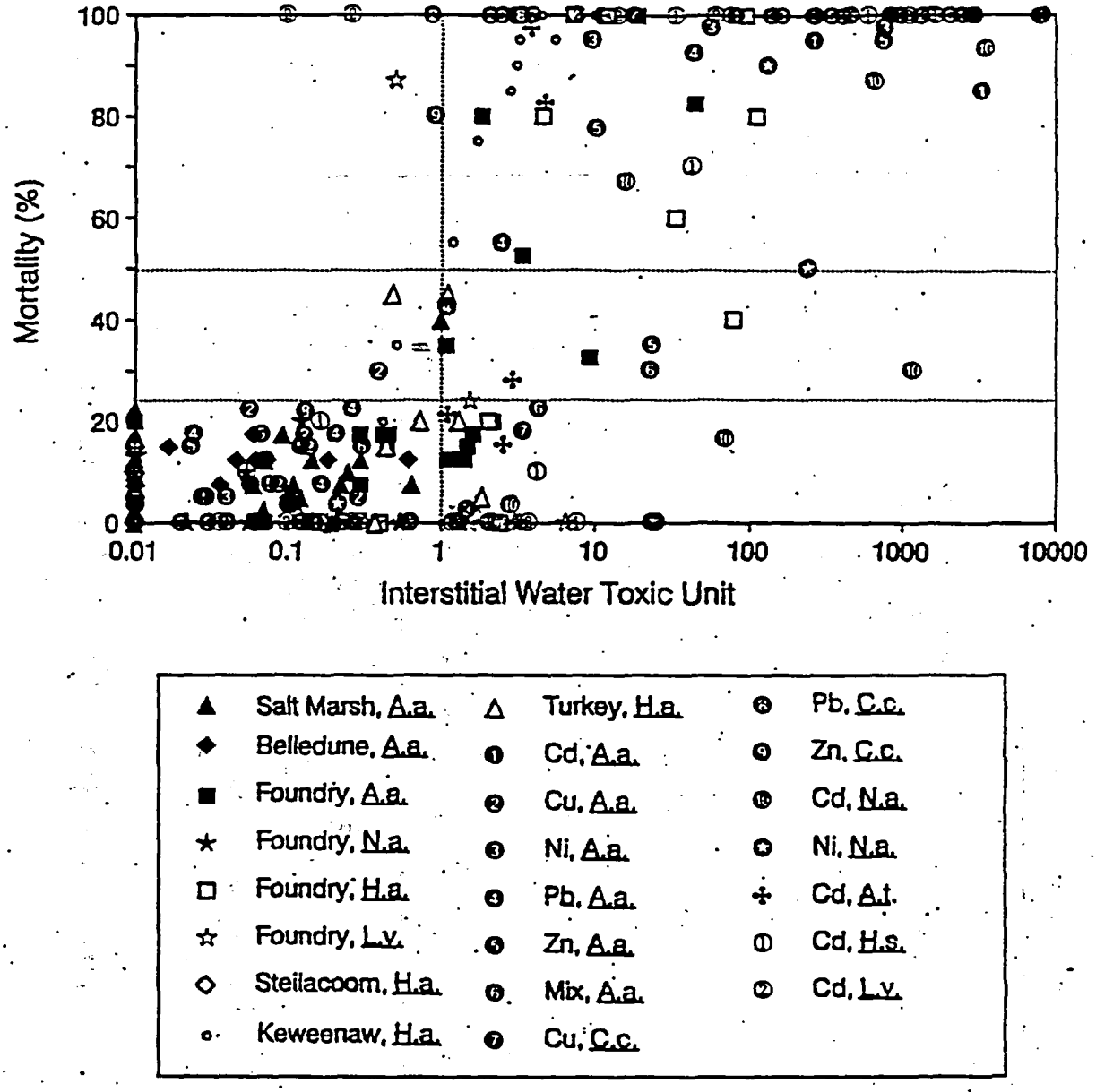

Figure 6-13. Percent mortality as a function of interstitial water toxic units of metals for saltwater and freshwater benthic species including oligochaetes Lumbriculus variegatus (L.v.), polychaetes Capitella capitata (C.c.), and Neanthes arenaceodentata (N.a.), harpacticoids Amphiascus tenuiremis (A.t.), amphipods Ampelisca abdita (A.a.) and Hyalella azteca (H.a.), and snails Helisoma sp. (H.sp.) exposed to sediments from saltwater field locations (solid symbols), freshwater field locations (open symbols) and sediments spiked with individual metals or mixtures (closed circles with internal symbol = saltwater, or open circles with internal number = freshwater). Field locations, metal spiked and species tested are indicated. The lower horizontal dashed line at 24 percent indicates the boundary between toxic and nontoxic sediments. The higher horizontal dashed line at 50 percent mortality and the vertical dashed line at 1.0 IWTU indicate the hypothetical boundary between sediments expected to be toxic to less than 50 percent of the organisms (IWTU < 1.0) and those expected to be toxic to greater than 50 percent (IWTU > 1.0). Interstitial water concentrations with nondetectable metal are plotted at 0.01 IWTU.

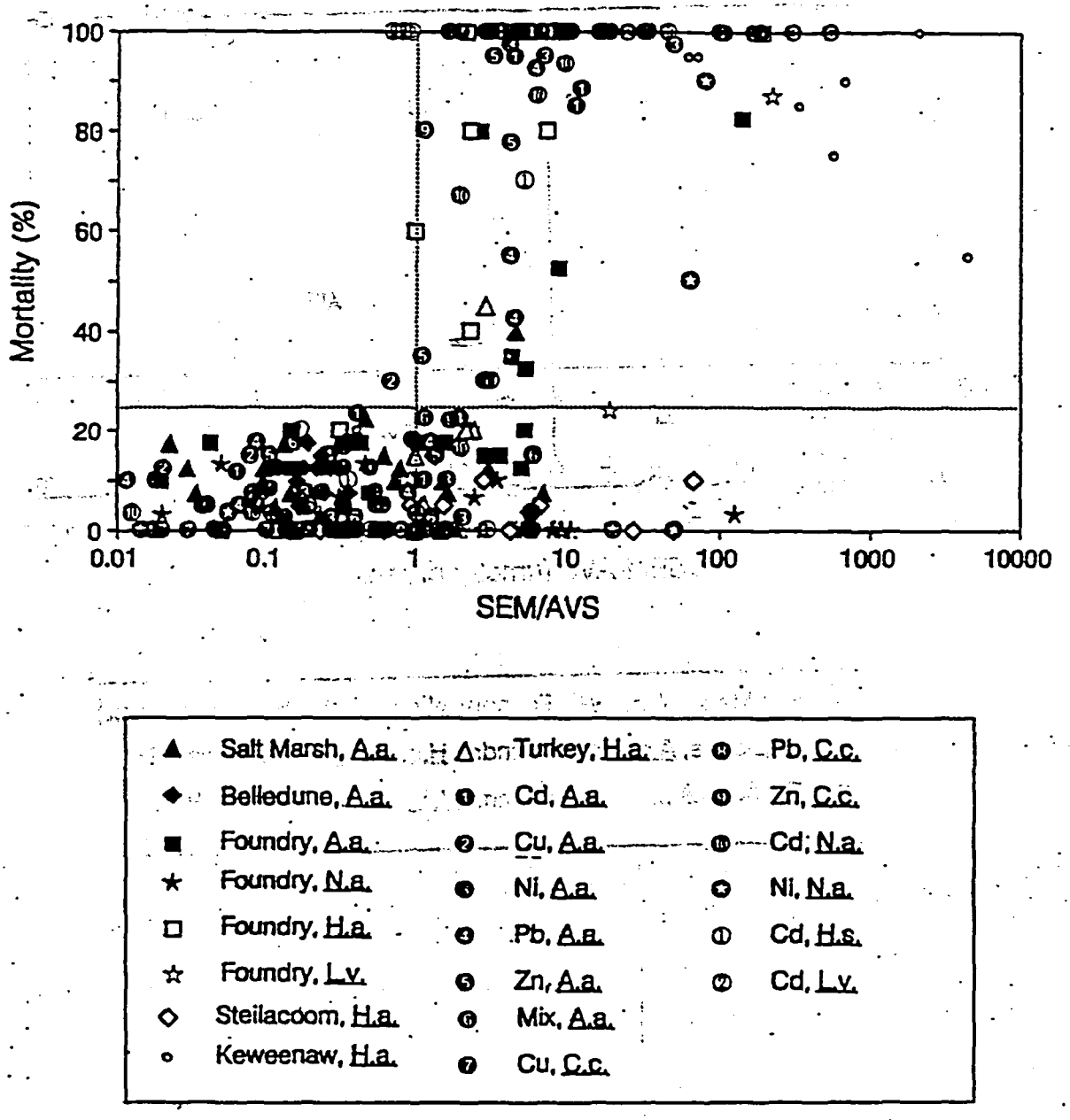

Figure 6-14. Percent mortality as a function of SEM/AVS ratio for saltwater and freshwater benthic species including oligochaetes Lumbriculus variegatus (L.v.), polychaetes Capitella capitata (C.c.), and Neanthes arenaceodentata (N.a.), amphipods Ampelisca abdita (A.a.) and Hyalella azteca (H.a.), and snails Helisoma sp. (H.s.) exposed to sediments from saltwater field locations (solid symbols), freshwater field locations (open symbols) and sediments spiked with individual metals or mixtures (closed circles with internal symbols = saltwater, or open circles with internal symbol = freshwater). Field locations, metal spiked and species tested are indicated. The horizontal dashed line at 24 percent mortality indicates the boundary between toxic and nontoxic sediments. The vertical dashed line at SEM/AVS = 1.0 indicates the boundary between sulfide-bound unavailable metal and potentially available metal.

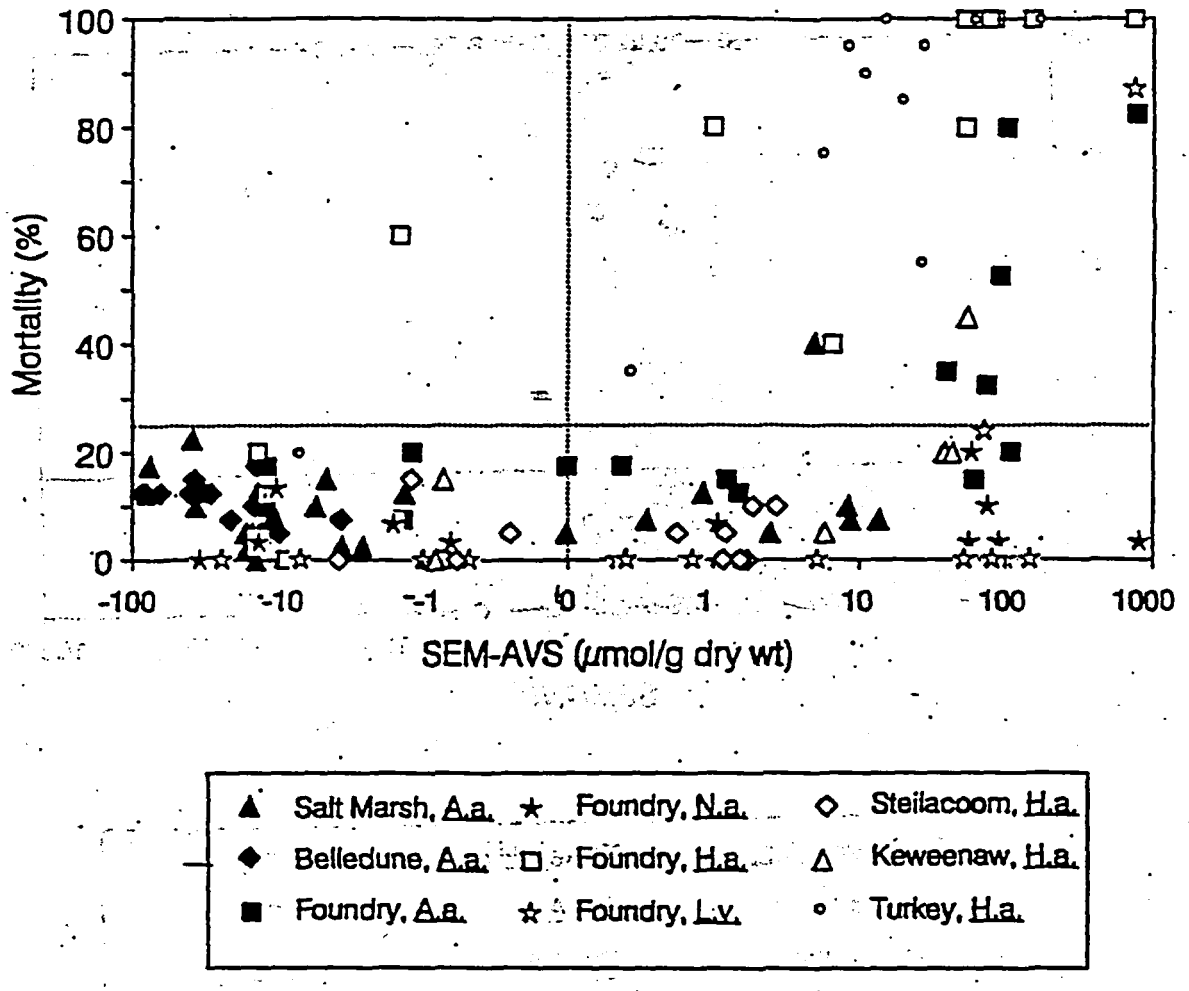

Figure 6-15. Percent mortality of amphipods Ampelisca abdita (A.a.) and Hyalella azteca (H.a.), oligochaetes Lumbriculus variegatus (L.v.) and polychaetes Capitella capitata (C.c.) and Neanthes arenaceodentata (N.a.) exposed to sediments from three saltwater and four freshwater field locations as a function of the sum of the molar concentratons of SEM minus the molar concentration of AVS (SEM-AVS). The dashed horizontal line at 24 percent mortality indicates the boundary between toxic and nontoxic sediments. The vertical dashed line at SEM-AVS = 0.0 indicates the boundary between sulfide-bound unavailable metal and potentially available metal.

sediment toxicity is useful but less accurate than predicting absence of toxicity (Table 6-3) as would be expected based on partitioning theory and organism-sediment interactions. In both oxic and anoxic transition zones occupied by organisms, other sediment binding phases, metal form, and avoidance behavior of organisms can limit metal availability, exposure, and toxicity.

Field Sites and Spiked Sediments Combined

The utility of metals concentrations normalized by dry weight, interstitial water toxic units (IWTUs), or SEM/AVS ratios to explain the bioavailability of divalent metals and permit prediction of sediment toxicity is summarized in Figures 6-12, 6-13, 6-14, and Table 6-3. The figures and table are compilations of all available data from 10-day lethality tests where mortality, IWTUs and SEM/AVS ratios are known from experiments with sediments most certainly toxic only because of metals. They include sediments from saltwater field sites, freshwater field sites, or sediments spiked with individual metals or metal mixtures. The relationship between benthic organism mortality in 10-day sediment lethality tests and bulk metals concentrations in spiked and field sediments is not useful to causally relate metal concentrations to organism response (Figure 6-12). The overlap among bulk metals concentrations which cause no toxicity and those which are 100 percent lethal is almost four orders of magnitude. Sediments having less than 0.01 μmol of metal/g dry weight are all reference or control sediments.

The toxicities observed when sediment concentrations are normalized on an IWTU basis are typically consistent with the toxic unit concept; that is if IWTUs are $\leq$ 1.0 sediments should be lethal to $\leq$ 50 percent of the organisms exposed; significant mortality probably should be absent at < 0.5 IWTU (Figure 6-13). The exceptions to the expectation that sediments with IWTUs < 0.5 should not be toxic are the two cadmium-spiked freshwater sediments where pore water sampling procedures were a likely problem. Of the spiked and field sediments evaluated which had IWTUs < 0.5, 95.7 percent of 187 sediments were nontoxic (Table 6-3). For all sediments having IWTUs > 0.5, 69.0 percent of 129 sediments were toxic (Table 6-3). Given the effect on toxicity or

bioavailability of the presence of DOC or ligand-associated metal in interstitial water, water quality (hardness or salinity), and organism behavior, it is not surprising that many sediments having IWTUs > 0.5 are not toxic.

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. [15], and recommendations for assessing the bioavailability of metals proposed by Ankley et al. [16]. Sediments spiked with metals and field sediments from saltwater and freshwater locations with SEM/AVS ratios $\leq$ 1.0 were uniformly (96.6 percent of 149 sediments) nontoxic (Figure 6-14; Table 6-3). The majority (56.8 percent) of 162 sediments having SEM/AVS ratios > 1.0 were toxic. Use of both IWTUs and SEM/AVS ratios did not improve the accuracy of predictions of sediment that were nontoxic (97.8 percent; Table 6-3). However, it is noteworthy that toxic sediments were predicted with 79.1 percent accuracy in 110 sediments when both SEM/AVS > 1.0 and IWTUs $\geq$ 0.5 were used jointly as decision parameters (Table 6-3). This approach is, therefore, very useful in identifying sediments of concern.

Because AVS can bind divalent metals and presumably some other metals on a mole to mole basis, normalizing metals concentrations in sediments from the field as the difference of SEM-AVS, instead of the conventional SEM/AVS ratio, can provide important insight into the extent of available additional sulfide binding capacity, or the extent to which AVS binding has been exceeded (Figure 6-15). Further, absence of organism response when AVS binding is exceeded can indicate the potential magnitude of importance that other binding phases may have in controlling bioavailability. This insight into additional binding capacity of AVS and other sediment phases and the magnitude of exceedance of binding are important advantages for normalization of the concentration of metals in sediments on an AVS basis over that of interstitial water concentration. For most nontoxic saltwater and freshwater field sediments we have tested, 1 to 100 μmoles of additional metal would be required to exceed the sulfide binding capacity; i.e., SEM-AVS = -1 to -100 μmol/g. In contrast, most toxic field sediments contained 1.0 to 1,000 μmoles of metal beyond the binding capacity of sulfide alone. Data on nontoxic field

sediments whose sulfide binding capacity is exceeded (SEM-AVS is > 0.0 μmoles/g) provides the best indication of magnitude and importance of non-sulfidic binding phases. This is particularly true for some sediments from locations such as Steilacoom Lake and the Keweenaw Watershed where AVS concentrations were low resulting in high SEM/AVS ratios with little difference between SEM concentrations and sulfide binding potentials (SEM-AVS is numerically low, whereas SEM/AVS ratios are high). The field sediments we tested frequently contain 1.0 to 1,000 μmoles of metal over that bound by sulfide yet they remain nontoxic. This indicates that the role of other sediment phases in metal bioavailability has great significance. Therefore, further refinement on the prediction of sediments likely to cause toxicity will require estimates of partition coefficients and binding strengths of these sediment phases.

Summary

We believe that results from tests using sediments spiked with metals and sediments from the field in locations where toxicity is metals-associated demonstrate the value of normalizing sediment concentrations by SEM/AVS ratio and IWTUs, instead of dry weight metals concentrations, in expressing biological availability of metals. Importantly, data from spiked sediment tests strongly indicate that metals are not the cause of the toxicity observed in field sediments when both SEM/AVS ratios are < 1.0 and IWTU are < 0.5. Concentrations of metals in sediments on an SEM-AVS basis provides important insight into available additional binding capacity by sulfides and other phases of sediments and the extent to which sulfide binding has been exceeded. Predictions of sediments not likely to be toxic because of metals based on SEM/AVS ratios and IWTUs for all data from spiked and field sediment tests are extremely accurate ($\geq$ 95.7 to 97.8 percent) using either or both parameters. While predictions of sediments likely to be toxic are less accurate (56.8 to 79.1 percent), this approach is extremely useful in identifying sediments of potential concern. Several sources of uncertainty related to sediment geochemistry, the kinetics of binding and release, and organism-sediment interaction need further research.

APPENDIX 6A

METHODS

Saltwater Field Sites

Sediment Collection, Storage and Handling -

Sediments were collected by plastic scoop, shovel, Ponar grab, or modified Van Veen grab from Jinzhou Bay, China (September, 1992); Belledune Harbor, New Brunswick, Canada (August, 1990); Bear Creek, Maryland (February, 1992); a tidal marsh near Fairhaven, Massachusetts (March 1991) and Foundry Cove, New York (August 1989) (Figure 6-1). Samples consisting of approximately 5 to 10 cm of surficial sediment were homogenized and aliquots removed for total metal, total organic carbon and grain size analyses. Sediments were transported under ice and stored at 4°C in sealed glass jars with limited headspace containing nitrogen until use. Prior to conducting toxicity tests, sediments were rehomogenized, taking care to limit oxidation of metal sulfides.

At all stations at the salt marsh in Massachusetts, interstitial water diffusion samplers (peepers) were placed immediately below the sediment surface 13 days prior to sediment collection to permit comparisons between in situ interstitial metals concentrations and interstitial metals concentrations quantified during toxicity tests. Peepers consisted of 5 ml polyethylene vials (21 mm high, 20 mm diameter), covered with a 1 micron polycarbonate membrane and filled with 30 mg/kg salinity water [4]. A plastic strap around the peeper extended above the sediment to facilitate recovery. Immediately prior to sediment sampling, peepers were removed and rinsed to remove sediments. The water contained within the peepers was removed by pipette and placed in a 7 ml polyethylene vial and acidified with 50 μl of concentrated (pH $\leq$ 1.0) nitric acid.

Toxicity Tests -

The 10-day lethality tests with the amphipod, Ampelisca abdita, generally followed methodologies described by ASTM [17], Di Toro et al. [15] and Berry et al. [4]. Those

with the polychaete Neanthes arenaceodentata are described by Pesch et al. [1]. Amphipod exposure chambers consisted of 900 ml glass canning jars, with a 1.3 cm diameter overflow hole covered with 400 micron Nitex® mesh. Each chamber contained 200 ml of sediment and 600 ml of seawater. Polychaete chambers consisted of 600 ml beakers containing 200 ml of sediment. One day before the start of the test, sediment from each station was placed into each of four [two chemistry (day 0 and 10), and two biology] replicate exposure chambers. For each experiment with sediments from the five saltwater locations, one or more treatments consisted of four replicate chambers containing sediment from an uncontaminated reference station in central Long Island Sound, Narragansett Bay or an uncontaminated sediment from a location near the study site. Sediments from all stations at Foundry Cove and stations 1 to 10 at the Massachusetts salt marsh site had interstitial salinities less than those tolerated by Ampelisca or Neanthes, therefore, sediments were mixed with brine to obtain 26 to 32 mg/kg interstitial salinities prior to testing. Peepers were placed in both biology replicates and the day 10 chemistry replicate. To provide continuous renewal of overlying water, filtered seawater (20°C; 28 to 34 mg/kg salinity) flowed through each replicate chamber at approximately 30 volume additions per day.

Each exposure began with random placement of 20 amphipods or 15 polychaetes in the day 10 chemistry replicate and in the two biology replicates for each treatment. Sediment from the day 0 chemistry replicate was homogenized, and aliquots removed and frozen for AVS, SEM, and bulk metal analyses. Experimental chambers were checked daily for dead animals and water flow. Overlying water was sampled at the beginning of every test and at least once thereafter, with samples acidified and stored in vials as described above. On day 10, peepers were removed from each sediment and the water sample acidified and stored. Sediment from the day 10 chemistry replicate was homogenized, and aliquots removed for AVS and SEM analyses. Sediments from the biology replicates were sieved through a 0.5 mm mesh screen to quantify dead and surviving organisms. Samples with more than 10 percent of the amphipods missing were recounted by a second person. Missing amphipods were assumed to be dead. For illustrative purposes, sediments were classified as toxic if mortality was greater than 24 percent as proposed by Mearns et al.

[18] from results of sediment tests with the amphipod Rhepoxynius abronius. Sediments having less than or equal to 24 percent mortality were considered as nontoxic.

Chemical Analyses -

Sediment samples were analyzed for AVS by the cold-acid purge and trap technique described by Allen et al. [14], Cornwell and Morse [19] and Boothman and Helmstetter [20]. SEM and bulk metals analyses were performed using inductively coupled plasma emission spectrometry (ICP). For analyses of bulk (dry weight) metals, the metals were extracted from freeze-dried sediments by ultrasonic agitation with 2 M cold nitric acid (50 ml/5 g wet sediment) at 60°C overnight followed by centrifugation. Results of sample blanks and recoveries of known metal additions demonstrated 85 to 100 percent recoveries from sediments, 85 to 115 percent recoveries from sample extracts and an absence of contamination in our analytical procedures. The SEM concentration reported is the sum of cadmium, copper, lead, nickel, and zinc on a micromole per gram dry sediment basis. Concentrations of all metals in sediments exceeded analytical detection limits.

Interstitial water from peepers and overlying water were analyzed using ICP or graphite furnace atomic absorption spectroscopy. Detection limits varied as a function of sample size and methods of analysis. Concentrations in water are reported as the sum of the interstitial water toxic units (IWTU) of detectable metal. IWTUs are the sum of μg metal/L in interstitial water ÷ 10 day LC50 in water-only tests in μg/L for all five metals, where the 10 day LC50 for A. abdita is 36.0 μg Cd/L, 20.5 μg Cu/L, 3020 μg Pb/L, 2400 μg Ni/L, and 343 μg Zn/L [4] and for N. arenaceodentata is 3,670 μg Cd/L and 16,090 μg Ni/L [1]. Thus, if interstitial water is the principal source of metals toxicity, and availability of metals is the same in water of water-only tests and interstitial water in sediment tests, 50 percent mortality would be expected with sediments having 1.0 IWTUs. In this section, we use 0.5 IWTUs to indicate sediments unlikely to cause significant mortality because on the average water-only LC0 and LC50 values differ approximately by a factor of two. This factor is reasonable because mortality was always absent in spiked-sediment

saltwater tests at 0.5 IWTU [4]. For illustration, a concentration of 0.01 IWTU is used to indicate interstitial water samples that contain no detectable metal.

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CHAPTER 7

COLONIZATION EXPERIMENTS

All experiments presented thus far demonstrating that AVS is important in controlling the toxicity of sediment-associated metal have relied on 10-day laboratory lethality tests using individual benthic species exposed to homogenized sediments from field sites or sediments spiked with divalent metals [1,2]. Chronic exposures of individual species or benthic communities have not only recently been completed using sediments whose metal and AVS concentrations have been measured and have varied with depth as is normal in the field [3,4,5].

The benthic colonization test [6] is particularly useful in evaluating the effects of substances on developing benthic communities in the laboratory and field. In this test, the most sensitive early life stages of benthic organisms found in unfiltered seawater are chronically exposed to chemicals as they settle and grow in replicated control and treated sediment-filled aquaria. Resultant communities are diverse, consisting of thousands of individuals, represented by 40 or more species and several phyla. Results from early colonization experiments where chemicals were continuously added to incoming seawater revealed test sensitivities predicted by water quality criteria (WQC); i.e., generally, observed effect concentrations were greater than WQC and no observed effect concentrations were less than WQC [7]. More recently, organic chemicals have been spiked into sediments [8,9] and comparisons between results of these tests and chemical-specific sediment quality criteria indicate SQC are protective [7].

This chapter presents the results of a 118 day benthic colonization experiment in which sediments were spiked with cadmium to obtain nominal SEM/AVS ratios of 0.0 (control), 0.1, 0.8, and 3.0. Numbers and kinds of organisms that colonized the sediment are compared to total cadmium, interstitial water cadmium, and SEM/AVS ratios as exposure conditions changed temporally and spatially as a function of sediment depth to evaluate if these measurements can be used to determine sediments which are not chronically toxic to benthic organisms. The methods used are presented in Appendix 7A.

Results

Exposure

At the beginning of the experiment the average AVS concentration of the sediments for the four treatments was 17.2 μmol/g dry weight and measured SEM/AVS ratios, 0.00, 0.10, 0.60, and 2.63, approximated nominal values; control, 0.1, 0.8, and 3.0, respectively (Table 7-1). The average AVS concentration in all samples of homogenized sediment analyzed throughout the experiment was 17.2 μmol/g (range 12.2 to 22.7 μmol/g), a concentration the same as that at test initiation. The average SEM/AVS ratios in cadmium-spiked sediments over the length of the experiment also differed little from that at test initiation for nominal SEM/AVS = 0.1 (0.09 for day 0 versus 0.10 overall) and SEM/AVS = 0.08 (0.66 for day 0 versus 0.60 overall). The apparent 25.3 percent decrease in SEM/AVS ratio in the 3.0 SEM/AVS treatment (3.52 for day 0 versus 2.63 overall) probably results from an unusually low analysis of AVS of 13.0 μmol/g at test initiation. If the mean AVS for all treatments on day 0 is more representative of the true value in this treatment, then a more accurate SEM/AVS ratio would be 2.66 for day 0 and 2.57 overall. Therefore, chemical analyses of homogenized sediments indicate that the exposure was constant throughout the experiment.

However, chemical analysis of horizons from sediment cores demonstrate that SEM and AVS concentrations and SEM/AVS ratios varied with sediment depth. Data from two cores sampled on day 14 from a control treatment show AVS concentrations <1.0 μmol/g in the surface 1.0 cm, from about 1.0 to 8.0 μmol/g at 1.0 to 3.0 cm depth, and greater than 15.0 μmol/g below 3.0 cm depth (Figure 7-1). At day 28, AVS concentrations in the surface 3.0 cm of sediment in the control, 0.1 and 0.8 SEM/AVS treatments were lower, with those in the surficial 0.6 cm being 20 percent of those on day 0 (Figures 7-1 and 7-2). By contrast, AVS concentrations below 3.0 cm in depth remained similar to those at

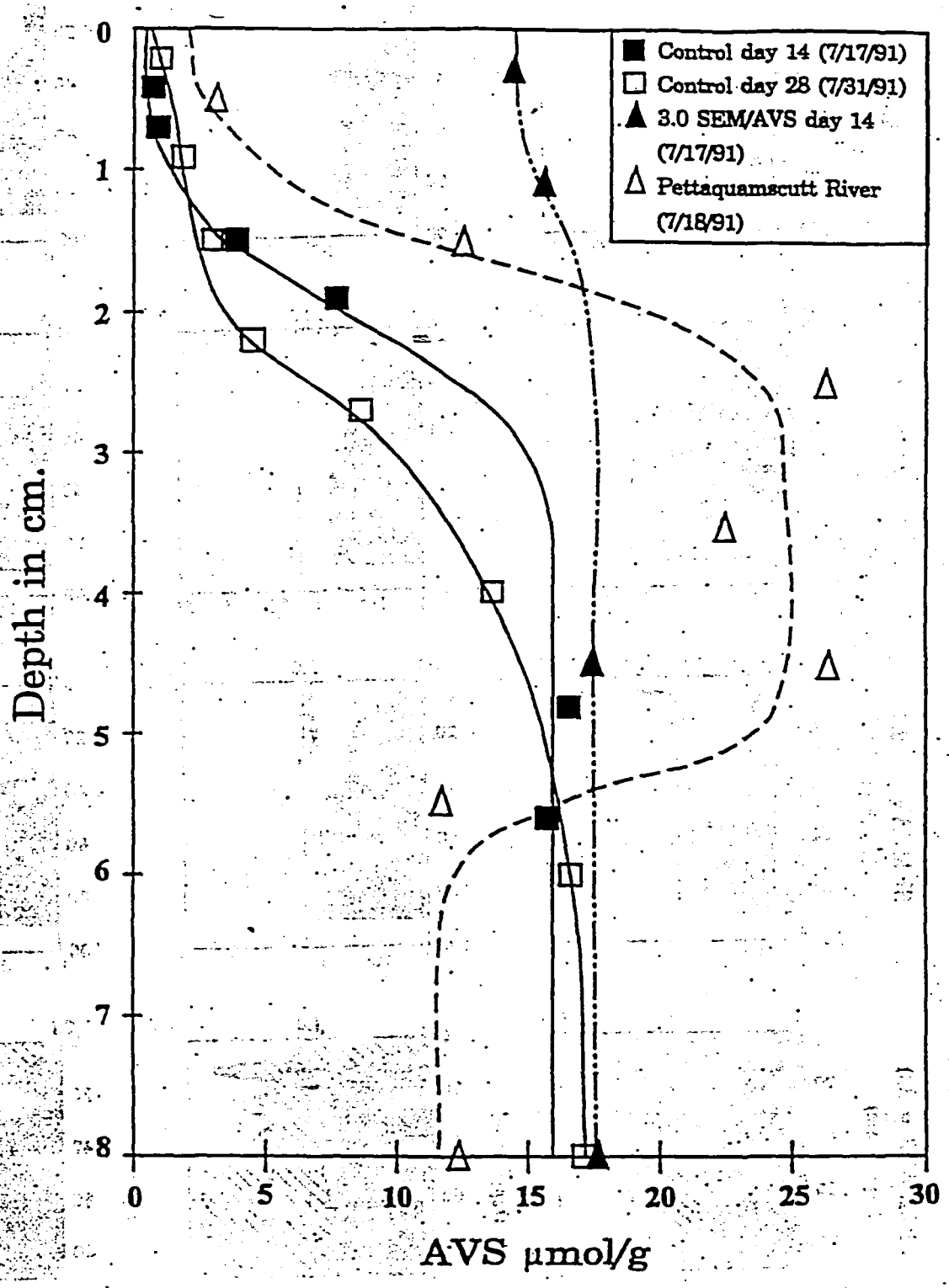


Figure 7-1. Comparison between the AVS concentrations by sediment depth in the cadmium colonization experiment on day 14 (July 17, 1991), day 28 (July 31, 1991), and in Pettaquamscutt River, Rhode Island (July 18, 1991).

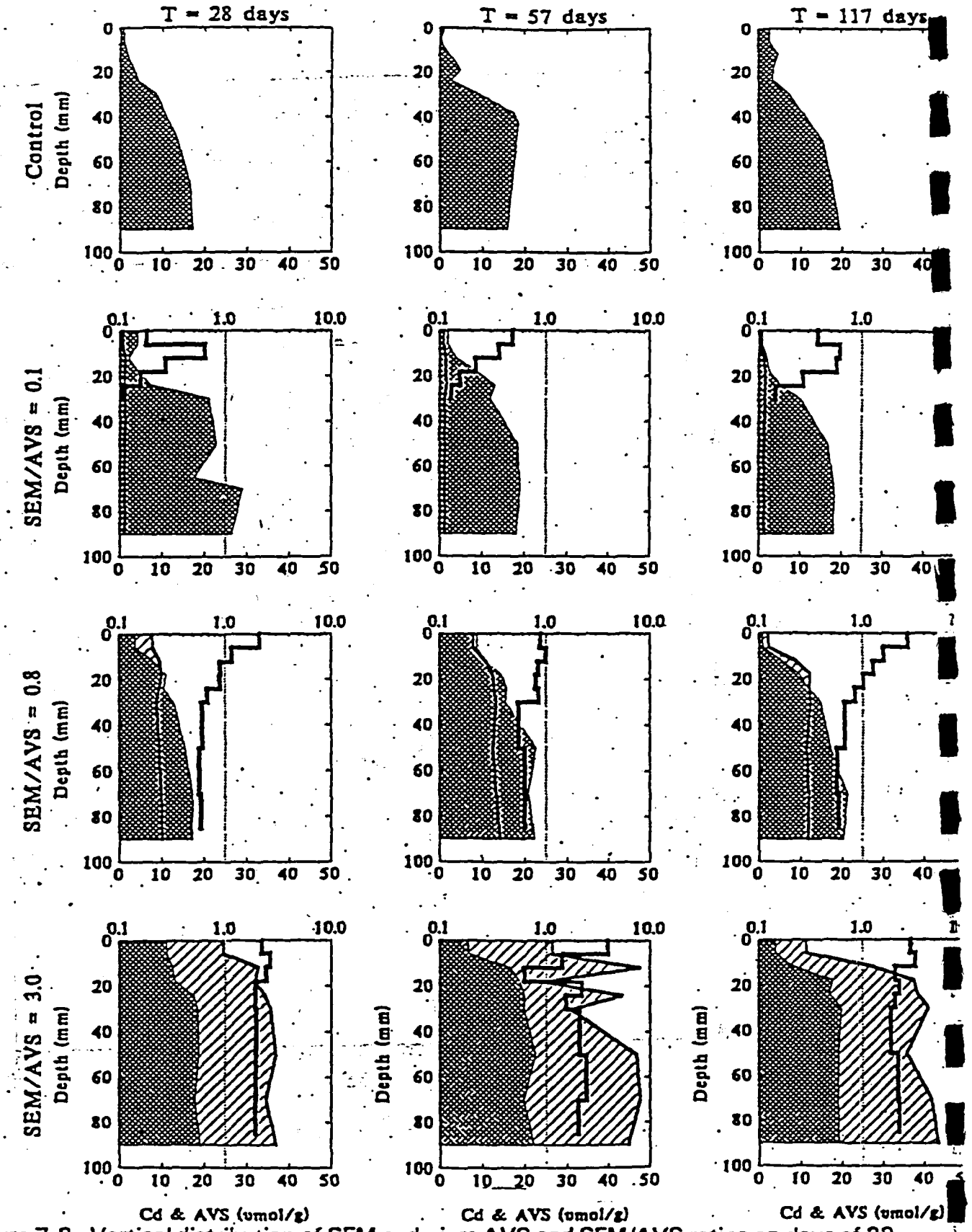


Figure 7-2. Vertical distribution of SEM cadmium AVS and SEM/AVS ratios on days of 28, 57, and 117 of the cadmium colonization experiment. The four treatments are control and nominal SEM/AVS ratios of 0.1, 0.8, and 3.0. Measured SEM cadmium concentrations in μmol/g are plotted as a thin line, AVS concentrations in μmol/g as a cross hatched area and SEM/AVS ratios as a thick line. The striped area indicates where SEM exceeds AVS.

test initiation. Vertical distribution of AVS in the 0.1 and 0.8 SEM/AVS treatments were generally similar to the control on days 24, 56, and 117. Loss of AVS in surficial sediments in these treatments was due to oxidation, most likely of principally iron sulfide.

TABLE 7-1. MEASURED CONCENTRATIONS OF ACID VOLATILE SULFIDE (AVS, μMOL/G), CADMIUM SIMULTANEOUSLY EXTRACTED WITH AVS (SEM, μMOL/G) AND SEM/AVS RATIOS IN HOMOGENIZED SEDIMENTS FROM DAY 0 TO 117 OF THE BENTHIC COLONIZATION TEST.

		Day of Measurement					
Nominal Cd/AVS	Measure	0	14	28	56	117	Mean
Control	SEM	0.0	0.0	0.0	0.0	0.0	0.0
	AVS	20.4	13.7	15.8	12.2	21.6	16.7
	SEM/AVS	0.0	0.0	0.0	0.0	0.0	0.0
0.1	SEM	1.5	1.6	1.5	1.4	1.3	1.5
	AVS	16.1	13.6	12.4	19.0	13.6	14.9
	SEM/AVS	0.09	0.12	0.12	0.07	0.10	0.10
.8	SEM	12.9	12.9	11.5	11.6	11.8	12.1
	AVS	19.5	22.3	17.2	21.1	20.5	20.1
	SEM/AVS	0.66	0.58	0.67	0.55	0.58	0.60
3.0	SEM	45.8	38.3	49.1	47.2	40.5	44.2
	AVS	13.0	13.5	19.6	22.7	15.4	16.8
	SEM/AVS	3.52	2.84	2.50	2.08	2.63	2.63
Mean	AVS	17.2	15.8	16.2	18.8	17.8	17.2

However, in the 3.0 SEM/AVS treatment from day 14 throughout the experiment, profiles of AVS concentration with depth were different from profiles in lower treatments. On day 14, concentrations of AVS in sediments from the 3.0 SEM/AVS treatment were essentially constant at all depths (Figure 7-1). In this sediment, concentration of AVS ranged from 13.8 to 16.2 μmol/g (mean = 15.1 μmol/g) in individual horizons in the surface 2.4 cm, and from 10.7 to 21.7 μmol/g (mean = 17.5 μmol/g) below 2.4 cm. At later sampling days, AVS was only slightly oxidized in the 3.0 SEM/AVS treatment compared to the other treatments (Figure 7-2). Lesser oxidation in this treatment was likely due to lower oxidation rates of cadmium sulfide [10]. Little oxidation of AVS below

2.4 cm is evident during the experiment in the control, 0.1 and 0.8 SEM/AVS treatments and below 1.2 cm in the 3.0 SEM/AVS treatment.

Vertical profiles of AVS in sediments from the cadmium colonization experiment on day 14 (July 17, 1991) and day 28 (July 31, 1991) were qualitatively and, to a lesser extent, quantitatively similar to those observed in sediment cores from the nearby Pettaquamscutt River, Rhode Island (July 18, 1991) [11] (Figure 7-1). Relative to AVS concentrations with depth in the experiment, AVS concentrations in Pettaquamscutt River sediment were only slightly higher from the surface to about 5.0 cm, proportional increase in concentrations from the surface to about 2.5 cm were similar and AVS concentrations were stable in both the field and our laboratory sediments from about 2.5 to 5.0 cm. Sediments from Pettaquamscutt River consisted of approximately 39.5 percent sand, 58.0 percent silt, 2.5 percent clay, and 1.3 percent TOC. The granulometry of sediments used in our experiment was markedly different; 5.6 percent sand, 70.7 percent silt, 23.7 percent clay, and 1.0 percent TOC.

Loss of cadmium from spiked sediments was essentially confined to the surface 1.2 cm (Figure 7-2). Decreases of cadmium in surface sediments were less than decreases in AVS in the control, 0.1 and 0.8 SEM/AVS treatments. Decreases in cadmium with depth were similar for all three cadmium-spiked treatments. In the surface 0.6 cm, cadmium concentrations for all treatments averaged 65.4, 67.0, and 22.7 percent of those below 3.0 cm on day 28, 56, and 117, respectively. Cadmium concentrations in the 0.6 to 1.2 cm horizon were 95.4, 86.8, and 79.0 percent of those below 3.0 cm on day 28, 56, and 117, respectively. Cadmium concentrations below 1.2 cm remained unchanged throughout the experiment.

Vertical profiles of measured SEM/AVS ratios were consistent with the observed oxidation of AVS in surficial sediments as tempered by losses of cadmium (Figure 7-2). At sediment depths greater than about 2.4 cm, there was little or no oxidation of AVS, no loss of cadmium and SEM/AVS ratios remained stable near the nominal values. In surficial sediments, losses of AVS exceeded those of cadmium causing SEM/AVS ratios to increase

dramatically, which could potentially release previously bound metal to affect benthic organisms. While SEM/AVS ratios increased to as much as 0.75 in individual 0.6 cm horizons in the nominal 0.1 SEM/AVS treatment, the molar concentration of AVS was always in excess of that for cadmium, therefore, metals toxicity was unlikely. In the nominal 0.8 SEM/AVS treatment, loss of AVS exceeded that of cadmium and measured SEM/AVS ratios exceeded 1.0 in from one to all five (22 of the 40 samples) 0.6-cm sediment horizons down to 3.0 cm in all cores sampled on days 28, 56, and 117. SEM/AVS ratios in the surface 1.8 cm of sediment averaged 1.45 on day 28, 1.01 on day 56, and 1.94 on day 117. Measured SEM/AVS ratios in individual horizons from the nominal 3.0 SEM/AVS treatment always exceeded a ratio of 1.0, hence, were always potentially toxic.

Concentrations of cadmium measured in interstitial water collected by peepers were consistent with sulfide binding (Table 7-2). Cadmium concentrations in interstitial water were below the limit of analytical detection (< 3 μg/L) in 70.8 percent of 24 samples from control replicates and 50 percent of 24 sample from the 0.1 SEM/AVS treatment. In the 0.1 SEM/AVS treatment, average concentrations in surface (6.4 μg/L) and bottom (3.6 μg/L) peepers were less than the saltwater acute (42 μg/L) and chronic (9.3 μg/L) water quality criteria [12]. Therefore, neither acute lethality nor chronic effects would be expected in sediments where the nominal SEM/AVS ratio was 0.1. Interstitial water concentrations in the nominal 0.8 SEM/AVS treatment are elevated over that in the control as might be expected given that measured SEM/AVS ratios frequently exceeded 1.0. Cadmium concentrations in interstitial water in the 0.8 SEM/AVS treatment averaged 58 μg/L in surface peepers and 48 μg/L in bottom peepers. These average concentrations were sufficiently high to be acutely toxic to the most sensitive saltwater species and chronically toxic to many sensitive arthropods and polychaete species [12]. Interstitial concentrations in the 3.0 SEM/AVS treatment always exceeded acute and chronic water quality criteria concentrations and were sufficiently great to result in acute lethality for most saltwater species tested in water-only tests [12]. Therefore, both SEM/AVS ratios and interstitial water concentrations indicate effects on benthic taxa should occur in this

treatment. Given the above exposure conditions and speculation on organism response, the following section describes observed organism responses.

TABLE 7-2. MEAN CADMIUM CONCENTRATION (μG/L) IN INTERSTITIAL WATER COLLECTED IN THREE DIFFUSION SAMPLERS (PEEPERS) PLACED IMMEDIATELY BELOW THE SEDIMENT SURFACE AND THREE PEEPERS 2.0 CM ABOVE THE BOTTOM OF TEST AQUARIA. TREATMENTS WERE CONTROL AND NOMINAL MOLAR RATIOS OF CADMIUM TO ACID VOLATILE SULFIDE (AVS) OF 0.1, 0.8, and 3.0

Nominal Cd/AVS	Peeper Location	Day of Measurement 14	28	56	117	Treatment Mean
Control	Surface	ND[a]	ND	ND	ND	ND
	Bottom	4	7	ND	ND	3.5
0.1	Surface	8	8	8	ND	6.4
	Bottom	ND	ND	10	ND	3.6
0.8	Surface	28	48	157	ND	58
	Bottom	38	85	48	20	48
3.0	Surface	138,000	76,000	66,000	28,000	77,000
	Bottom	174,000	135,000	154,000	88,000	138,000

ND[a] = Less than detection limit 3.0 μg/L. Mean concentrations derived using one-half the detection limit for samples below the detection limit.

Effects

Sediment-associated cadmium had an effect on both the timing of organism appearance on and in the sediment and the abundance and species composition of organisms found in each treatment. In the control, 0.1 and 0.8 SEM/AVS treatment, a reddish brown microfloral layer appeared on the sediment surface after about week three; however, this layer did not appear until after about week 9 in the 3.0 SEM/AVS treatment. Animals including snails, polychaetes and tonicities began to appear in the control. 0.1 and 0.8 SEM/AVS treatments shortly after the appearance of diatoms at about week three, whereas in the 3.0 SEM/AVS treatment they did not appear until after about 9 to 11 weeks.

The microfloral layer, sampled on day 80 contained the pennate diatoms Entomonies, Nitzschia, Plagiotropis, Bacillaria, Amphora, Thalassiosira, Navicula, Rhzicoshpenia, Licmophora, Lithodesmium, Cyclotella, Rhabdonema, Skeletonema, Diploneis, and Chaetoceros, in approximate order of decreasing abundance. The density of pennate diatoms measured on day 80 corroborated visual observations of periphyton abundance on the sediment surface (Table 7-3). The mean diatom density in control aquaria, 1.92×10^6 cells/cm^2 of sediment surface, was not different from the 1.32×10^6 cells/cm^2 in the 0.1 SEM/AVS aquaria or the 1.00×10^6 cells/cm^2 in the 0.8 SEM/AVS aquaria. Diatom densities were significantly lower (0.16×10^6 cells/cm^2 of sediment surface) in the 3.0 SEM/AVS aquaria. The density of diatoms in five of eight aquaria for this treatment were less than the lowest density (0.17×10^6 cells/cm^2) in any aquarium from other treatments.

TABLE 7-3. NUMBER OF DIATOMS $\times 10^6$ PER SQUARE CENTIMETER OF SEDIMENT SURFACE IN REPLICATE AQUARIA

	Treatment: Nominal Cd/AVS Ratio			
Replicates	Control	0.1	0.8	3.0
1	3.52	0.53	0.64	0.03
2	1.95	1.41	1.17	0.02
3	1.56	1.23	2.33	0.22
4	4.37	2.26	3.94	3.53
5	5.64	3.76	0.83	0.03
6	0.59	2.14	0.45	0.43
7	0.58	2.97	0.17	0.00
8	2.05	0.19	2.39	0.06
Geo. Mean	1.92	1.32	1.00	0.16[a]

[a] = Significantly different from control; $\sigma = 0.05$

A total of 14,347 individual macrobenthic benthic organisms, representing 54 species from 8 phyla, was collected from sediments sieved from all aquaria: eight control aquaria and eight aquaria for each of the three treatments that contained sediments spiked

at 0.1, 0.8, and 3.0 SEM/AVS (Tables 7-4 and 7-5). Annelids, arthropods, and chordates were most abundant; over half (27 of 52) of the species were polychaetes. Most individuals of all species were subadult; only Nereis succinea, Polydora socialis and Molgula manhattensis had significant numbers of adults. Individuals of all feeding types, suspension feeders, deposit feeders, selective deposit feeders, omnivores, and carnivores, were collected.

TABLE 7-4. TOTAL NUMBER OF SPECIES AND INDIVIDUALS (IN PARENTHESES).

	Treatment: Nominal Cd/AVS			
PHYLUM	CONTROL	0.1	0.8	3.0
Annelida	18(347)	19(330)	21(265[a])	8[a](159[a])
Mollusca Gastropoda	2(4)	1(4)	5(7)	3(4)
Bivalvia	4(6)	2(3)	1(5)	0(0)
Arthropoda	7(3640)	5(2078)	8(4228)	6(1294[a])
Nematoda	?(563)	?(432)	?(254[a])	?(128[a])
Sipuncula	1(1)	1(2)	1(1)	0(0)
Cnidaria	0(0)	1(1)	0(0)	1(4)
Rhynocoela	1(1)	0(0)	0(0)	0(0)
Chordata	4(197)	4(59)	3(102)	3(469[a])
TOTAL	37(4196)	33(2909)	39(4862)	19[a](2058)

[a]Significantly different from controls; $\alpha = 0.05$

Species richness and abundance decreased with increasing concentration of cadmium in the sediment (Tables 7-4 and 7-5). In the nominal 0.1 SEM/AVS treatment, no effect on either number of species or individuals, relative to the control, was detected in the colonized benthic communities. In the nominal 0.8 SEM/AVS treatment, no significant effects were detected in the overall total number of individuals or species. However, there were significantly fewer polychaetes (Mediomastus ambiseta, Streblospio

TABLE 7-5. NUMBER OF INDIVIDUALS OF BENTHIC SPECIES THAT COLONIZED SEDIMENTS IN EIGHT CONTROL AQUARIA AND EIGHT AQUARIA CONTAINING SEDIMENTS WITH CADMIUM SPIKED AT NOMINAL MOLAR RATIOS OF CADMIUM TO ACID VOLATILE SULFIDE OF 0.1, 0.8, OR 3.0. NUMBER OF AQUARIA CONTAINING THAT SPECIES IN PARENTHESES.

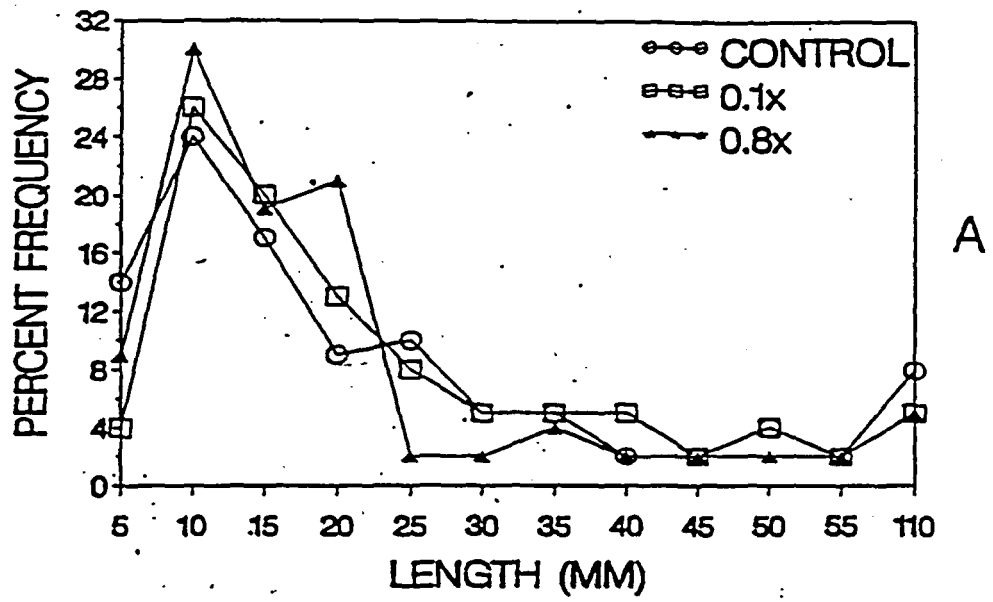
		Cd/AVS		
Taxon	Control	0.1	0.8	3.0
Macroinvertebrates:				
Annelida				
Nereis succinea	133(8)	194(8)	161(8)	113(8)
Polydora socialis	77(8)	46(8)	47(7)	28(7)
Mediomastus ambiseta	48(7)	32(7)	22*(8)	1*(1)
Polydora ligni	12(6)	8(6)	4(2)	11(7)
Polydora cauleryi	6(2)	7(4)	12(6)	3(1)
Ctenodrilus serratus	22(4)	1(1)	4(2)	0(0)
Streblospio benedicti	18(7)	9(3)	2*(1)	0*(0)
Podarke obscura	15(8)	13(6)	1(1)	0*(0)
Eunice sanguinea	6(3)	6(3)	3(2)	0(0)
Sabella microphthalma	2(1)	4(3)	2(2)	0(0)
Boccardia sp.	3(3)	2(2)	1(1)	0(0)
Tharyx sp	1(1)	2(1)	1(1)	0(0)
Polycirrus sp.	1(1)	0(0)	1(1)	1(1)
Sthenolais boa	0(0)	1(1)	1(1)	1(1)
Nephtys picta	0(0)	1(1)	1(1)	1(1)
Hydroides dianthus	1(1)	0(0)	2(1)	0(0)
Pectinaria gouldii	0(0)	1(1)	2(2)	0(0)
Capitella capitata	1(1)	1(1)	0(0)	0(0)
Ampharete arctica	0(0)	1(1)	1(1)	0(0)
Dodecaceria concharum	0(0)	0(0)	3(3)	0(0)
Pista cristata	2(2)	0(0)	0(0)	0(0)
Ereone heteropoda	0(0)	1(1)	0(0)	0(0)1
Potamilla neglecta	0(0)	0(0)	1(1)	0(0)
Spio setosa	0(0)	1(1)	0(0)	0(0)
Sabaleria vulgaris	1(1)	0(0)	0(0)	0(0)
Neanides tridentata	1(1)	0(0)	0(0)	0(0)
terebelid	0(0)	0(0)	3(2)	0(0)
Mollusca				
Gastropoda				
Acteocina canaliculata	3(1)	4(3)	2(1)	2(1)
Caliche oryza	1(1)	0(0)	1(1)	0(0)
Anachis lafresnayi	0(0)	0(0)	2(2)	0(0)
Crepidula fornicata	0(0)	0(0)	1(1)	0(0)
Bittium sp.	0(0)	0(0)	1(1)	0(0)
Odostomia sp.	0(0)	0(0)	0(0)	1(1)
Nudibranchia	0(0)	0(0)	0(0)	1(1)
Bivalvia				
Petricola pholadiformis	2(2)	1(1)	5(3)	0(0)
Nucula annulata	1(1)	2(1)	0(0)	0(0)
Macoma tenta	1(1)	0(0)	0(0)	0(0)
bivalvia sp	2(2)	0(0)	0(0)	0(0)
Arthropoda				
Crustacea				
Harpacticoida	3,406(8)	2,036(8)	4,098(8)	1,189*(8)
harpacticoid bb	104(6)	8(4)	35(6)	2(2)
harpacticoid al	34(4)	16(4)	20(4)	0(0)
harpacticoid gel				
Cumacea				
Diastylis sculpta	0(0)	0(0)	0(0)	1(1)
Amphipoda				
Jassa falcata	87(8)	17(2)	68(4)	99(8)
Corophium acutum	7(1)	0(0)	2(2)	2(1)
Corophium sp	0(0)	0(0)	1(1)	1(1)
Ampelisca abdita	2(2)	0(0)	1(1)	0(0)
Decapoda				
Neopanope texana	1(1)	2(2)	3(3)	0(0)
Nematoda				
nematode	563(8)	432(8)	264*(8)	128*(8)
Sipuncula				
Phascolion strombi	1(1)	2(2)	1(1)	0(0)
Cnidaria				
Edwardsia elegans	0(0)	1(1)	0(0)	4(1)
Rhynchocoela				
Micrura sp	1(1)	0(0)	0(0)	0(0)
Chordata				
Ascidiacea				
Molgula manhattensis	248(7)	64(4)	183(8)	627*(8)
Ciona intestinalis	4(2)	7(5)	2(2)	2(2)
Botrylus schlosseri	5(5)	0(0)	3(3)	6(4)
Styela partita	3(3)	5(3)	0(0)	0(0)
Hemichordata				
Saccoglossus kowalevskii	0(0)	1(1)	0(0)	0(0)
Total	4,268	2,917	4,948	2,223

*Statistically different from controls; $\alpha = 0.05$

benedicti and Podarke obscura) and unidentified meiofaunal nematodes in this treatment (Table 7-4). Sediments containing a nominal SEM/AVS ratio of 3.0 were colonized by fewer macrobenthic species (19) than controls (37), but the total number of individuals was not significantly affected (Table 7-4 and 7-5). This was principally because the number of polychaete species and their total abundance was significantly diminished. There were significantly fewer individuals of the polychaete species M. ambiseta, S. benedicti, P. obscura and the unidentified harpacticoid copepod species. Bivalve molluscs were absent in this highest treatment. The number of chordates, principally the tunicate M. manhattensis, was significantly greater in the 3.0 SEM/AVS treatment (Table 7-5). Numbers of these tunicates would have been even higher if myriads of small (< 1 mm diameter) tunicates, attached to large individuals but having no direct contact with sediment as well as those contacting sediments, had been counted.

The length-frequency distributions for the polychaete Nereis succinea in control, 0.1 and 0.8 SEM/AVS treatments indicates recruitment was continuous with no effect on abundance or growth (Figure 7-3a). In the 3.0 SEM/AVS treatment, there were no worms over 45mm in length; whereas 8.5 percent of the worms in other treatments exceeded this length (Figure 7-3b). Only 15.3 percent of the worms in the 3.0 SEM/AVS treatment were over 15mm in length, whereas 45.8 percent exceeded this length in other treatments. Extremely small (0 to 5mm) worms predominated (37.8 percent) in the 3.0 SEM/AVS treatment compared to 11.6 percent for other treatments. The absence of large (> 45mm) worms, markedly reduced occurrence of worms of intermediate lengths, preponderance of very small worms and absence of visible colonizers of any macrobenthic species for the first half of this study suggests that the sediments in the highest treatment were initially lethal but could later be tolerated by resistant species. Therefore, polychaete length-frequency distributions may indicate delayed recruitment, not decreased growth.

The response of these communities to cadmium-spiked sediments can be assessed by evaluating changes in abundance of individual species and phyla as was done above, or by summarizing organism abundance in the entire assemblage using an index. Cluster analyses that compare the species present or absent in each replicate with those in other



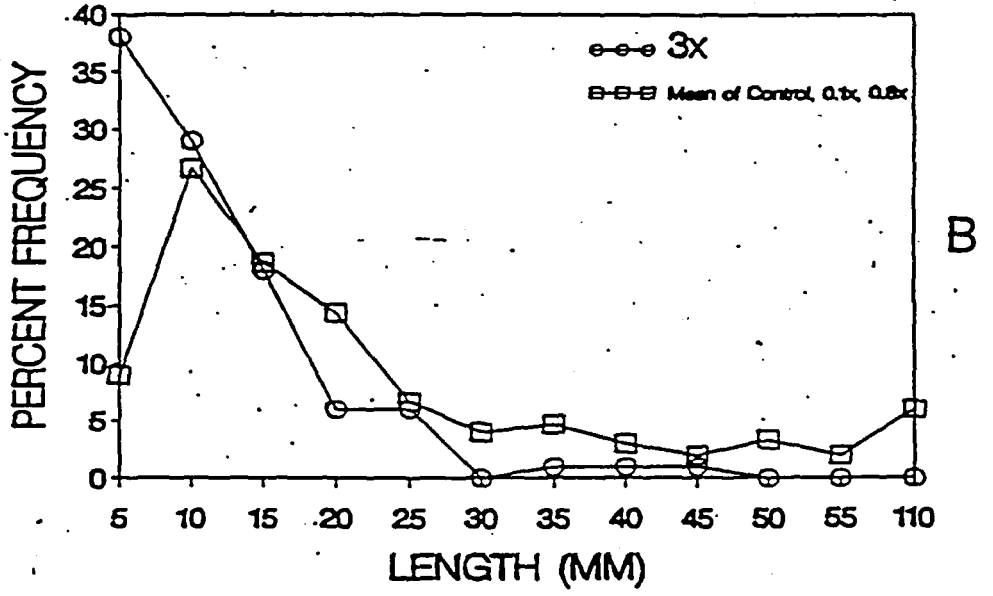


Figure 7-3. (A) Frequency distribution of length of the polychaete Nereis succinea that colonized control aquaria containing clean sediments or aquaria containing cadmium-spiked sediment with nominal SEM/AVS ratios of 0.1 or 0.8. (B) Frequency distribution of length of the polychaete Nereis succinea from control and 0.1 and 0.8 SEM/AVS treatments pooled vs. the 3.0 SEM/AVS treatment.

replicates from the same or different treatments, indicate that three clusters may exist. Although all treatments have many species in common, the kinds of species in the control treatment are most similar to those in the 0.1 SEM/AVS treatment. Species present or absent from replicate aquaria in these treatments are different from those in the 0.8 and 3.0 SEM/AVS treatments (Figure 7-4). Further, the clusters of presence-absence data for the species in aquaria in the 0.8 and 3.0 SEM/AVS treatments indicate differences in species composition between these highest treatments. Numbers of species in the control, 0.1, 0.8, and 3.0 SEM/AVS treatments were 37, 33, 39, and 19 respectively, based on raw counts (Table 7-4) and 51, 46, 57, and 34 respectively, based on Jackknife estimates of maximum species richness [13]. Because numbers of species in the control, and 0.1 and 0.8 SEM/AVS treatments are similar, shifts in community structure detected in the 0.8 SEM/AVS treatment compared to these two lower treatments probably occurred because of changing species composition and not the number of species present. In the 3.0 SEM/AVS treatment, there was a change in both species abundance and composition.

Discussion

Concentrations of AVS in marine sediments vary with depth as a function of seasonal processes [14]. Iron sulfide is formed by the anaerobic diagenesis of organic matter. As a result of bacterial sulfate reduction, concentrations of AVS increase in surficial sediments during warm months of greatest productivity and sediment oxygen demand. AVS is readily oxidized in cold months when productivity is minor and oxidizing conditions greatest. Therefore, in winter AVS concentrations in the surficial sediments decrease. For example, in the Pettaquamscutt River, Rhode Island AVS concentrations in the upper 3 cm of sediment may vary 15 to 25 fold between summer and winter [11]. Maximum concentrations occur in surface sediments between 2 and 5 cm depth and concentrations below these depths down to 15 cm decrease only marginally with season.

Vertical profiles of AVS in the cadmium colonization experiment in week 2 (July 17, 1991) and week 4 (July 31, 1991) were qualitatively and, to a lesser extent, quantitatively similar to those measured in the Pettaquamscutt River, Rhode Island by Boothman and

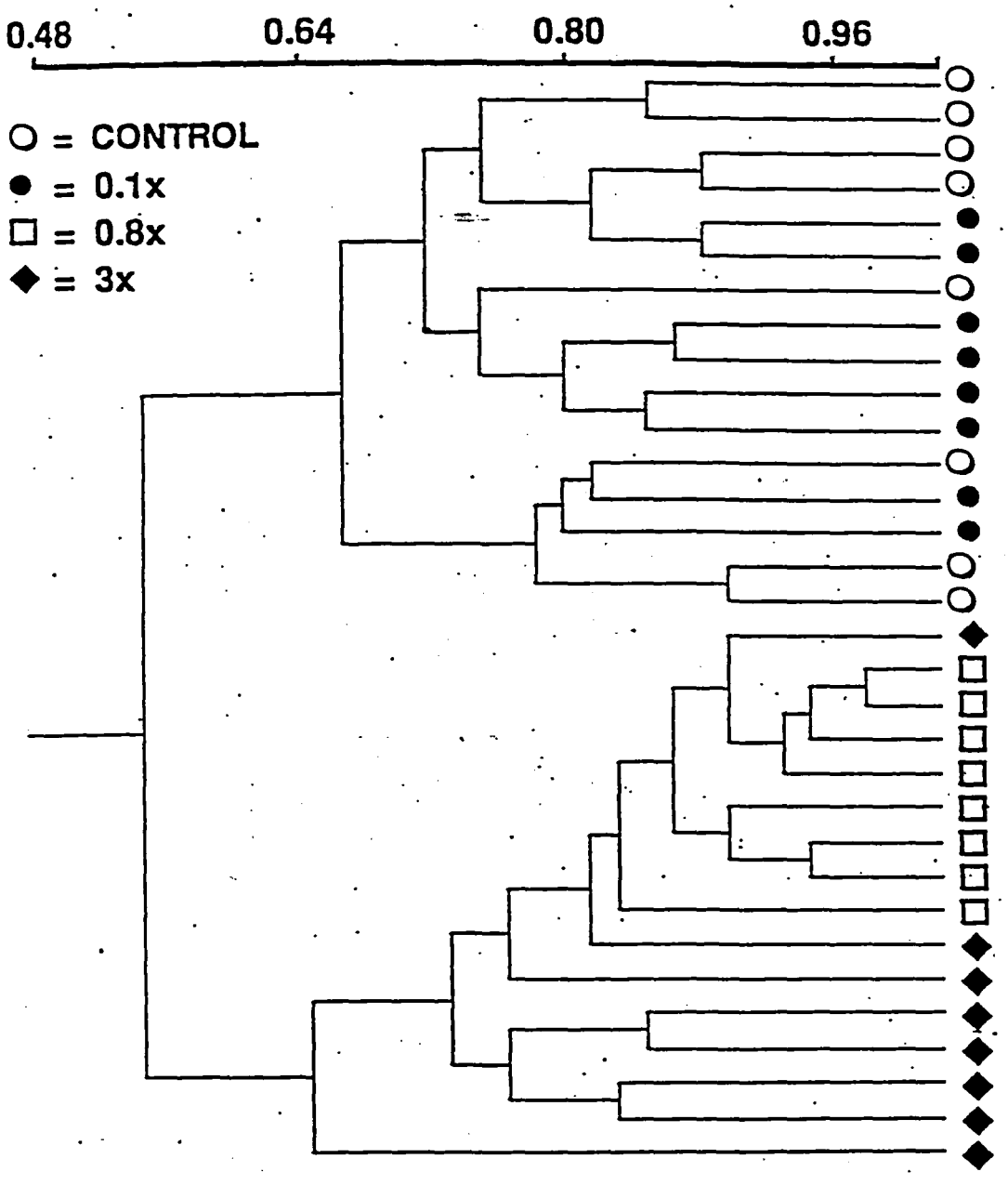


Figure 7-4. Cluster analysis of presence-absence data for species from sediments from control and nominal 0.1, 0.8, and 3.0 SEM/AVS treatments.

Helmstetter [11] at the same time as our experiment. Oxidation of AVS in surficial sediments in our experiment proceeded rapidly, with most occurring within two to four weeks of test initiation. The oxidation of sediments observed initially must be associated with passive oxygen diffusion and not be biotically driven as organisms large enough to bioturbate the sediments were not present during the first few weeks of the experiment. Their presence later apparently did little to change existing AVS profiles. Lesser oxidation of AVS early and throughout the experiment in the 3.0 SEM/AVS treatment, and the loss of cadmium from only the surficial 1.2 cm compared to 2.4 cm for AVS, agrees with laboratory sediment suspension experiments that demonstrate rapid (100 percent in 60 to 90 minutes) oxidation of iron sulfide versus slow (10 percent in 300 hours) oxidation rates for cadmium sulfide [10]. Further oxidation of sediments should result in release of only a portion of sulfide-associated cadmium to interstitial water because sedimentary Fe and Mn are transformed into their oxyhydroxides which, along with organic carbon, can bind released cadmium in oxic sediments [15]. In this and other laboratory experiments [16], AVS gradients and the complex microhabits associated with sediment geochemical processes and organism burrowing developed rapidly. These observations indicate that the opinion that bioassays are simplistic because they do not have the vertical gradients and microhabits that occur as part of naturally occurring geochemistry and biological processes [17] may not apply to all laboratory exposures.

The bioavailability and toxicity of divalent metals in field sediments can not be predicted using metals concentrations on a sediment dry weight basis [18]. However, Di Toro et al. [19] in laboratory studies using spiked sediments, observed that acute toxicity and interstitial water concentrations of cadmium were related to sediment concentrations on a μmol cadmium per μmol acid volatile sulfide basis. They hypothesized that this normalization should apply to other divalent metals in both freshwater and marine anoxic sediments, where the metals concentrations are expressed as the ratio of the sum of the molar concentrations of all divalent metals to the molar concentration of AVS, with the metal-sulfide solubility products providing insights into the likely metal of concern in a mixture. These observations were further extended to apply to copper, lead, nickel, and zinc, as well as metal mixtures, in acute lethality tests with spiked sediments and

saltwater amphipods and polychaetes [1,16,20,21] and freshwater oligochaetes and snails [22,23]. Studies revealed the requirement that metals concentrations be expressed as the molar concentration of metal simultaneously extracted with AVS, not total metal. Acute lethality tests with homogenized sediments from freshwater and marine locations consistently demonstrated an absence of toxicity when SEM/AVS ratios were ≤ 1.0 and that sediments having a ratio > 1.0 were sometimes toxic, but frequently were nontoxic [2,20,22,24,25]. Absence of toxicologically significant concentrations of metal in interstitial water in nontoxic sediments and the presence of interstitial metals concentrations of concern in toxic sediments highlighted the utility of the toxic unit concept as applied to interstitial metal in predicting sediment toxicity when SEM/AVS is > 1.0. Absence of toxicity when SEM/AVS is > 1.0 suggested the presence of other binding phases in these sediments. Ankley et al. [26] summarized much of the above information and proposed methodologies for assessing the potential bioavailability of metals in sediments. The studies above have involved exposures of 10 days or less and homogenized sediments, therefore, extrapolations using SEM/AVS ratios or interstitial water concentrations to chronic responses of benthic organisms in laboratory or field sediments with vertical gradients and microenvironments should be done with caution. Because of these limitations, this colonization experiment and those of Hare et al. [3] and Liber et al. [4] were conducted.

Biological effects of cadmium-spiked sediments observed in our colonization experiment are consistent with the previous interpretation of SEM/AVS ratios, when vertical gradients are considered, and with interstitial water cadmium concentrations and the relative sensitivities of benthic taxa in water-only aquatic toxicity tests (Table 7-6; Figure 7-5). In the nominal 0.1 SEM/AVS treatment, molar concentrations of AVS in vertical profiles of sediment were always in excess of those of cadmium; interstitial cadmium concentrations (ND to 10 μg/L) were either below detection limits, or less than known concentrations of toxicological significance in water-only tests [12]; and no significant effects were observed on sediment colonization by benthic species. In the nominal 0.8 SEM/AVS treatment, measured SEM/AVS ratios averaged 0.60 in homogenized sediments. However in surficial sediments, molar concentrations of cadmium

TABLE 7-6. SUMMARY OF EXPOSURE CONDITIONS AND EFFECTS OBSERVED IN THE CADMIUM COLONIZATION EXPERIMENT RELATIVE TO POTENTIAL EFFECTS GIVEN OBSERVED INTERSTITIAL CADMIUM CONCENTRATIONS AND KNOWN SENSITIVITIES OF BENTHIC ORGANISMS IN WATER-ONLY TESTS.

Exposure				Observed Biological Effects		Potential Effects Interstitial Cadmium Versus Water-Only Data[b]
Nominal Cd/AVS	Measured SEM/AVS 0 - 9.0 cm	Measured SEM/AVS 0 - 1.8 cm	Interstitial Cadmium[a]	Macroinvertebrates	Diatoms	
Control	0.00	0.00	ND (ND-7 μg/L)	7 Phyla, 37 species 4,259 individuals	1.92 x 10^6 Diatoms/cm^2	--------
0.1	0.10(0.07-0.12)	0.38(0.22-0.58)	4μg/L(ND-10 μg/L)	No Effects: 7 Phyla, 33 species 2,917 individuals	No Effects: 1.32 x 10^6 Diatoms/cm^2	Acute or chronic effects unlikely
0.8	0.60(0.55-0.67)	1.47(1.01-1.94)	33μg/L(24-157 μg/L)	Fewer polychaetes (Mediomastus, Streblospio, Podarke) and nematodes. Species presence/absence altered.	More spheroid foraminifera	Acute lethality unlikely. Chronic lethality or sublethal effects possible for sensitive polychaetes or crustaceans.
3.0	2.63(2.08-3.52)	2.29(1.88-2.53)	94,000μg/L (28,000-174,000 μg/L))	Fewer species, polychaetes (Mediomastus, Streblospio, Podarke), nematodes and harpacticoid copepods. Bivalves absent. More ascidians (Molgula). Length frequency distribution (Nereis) altered. Species presence/absence altered.	Reduced diatom density (0.16 diatoms/cm^2)	Acute lethality for most macroinvertebrate species including polychaetes, bivalve molluscs, snails, arthropods, and echinoderms. Algal growth inhibition.

[a]Mean of interstitial water concentrations derived using one-half the detection limit (ND = 3.0μg/L) for samples where Cadmium concentrations were not detectable.
[b]From "Ambient Water Quality Criteria for Cadmium" 1984 (U.S. EPA, 1985): Chronic criteria concentrations 9.3 μg/L, acute 42 μg/L.

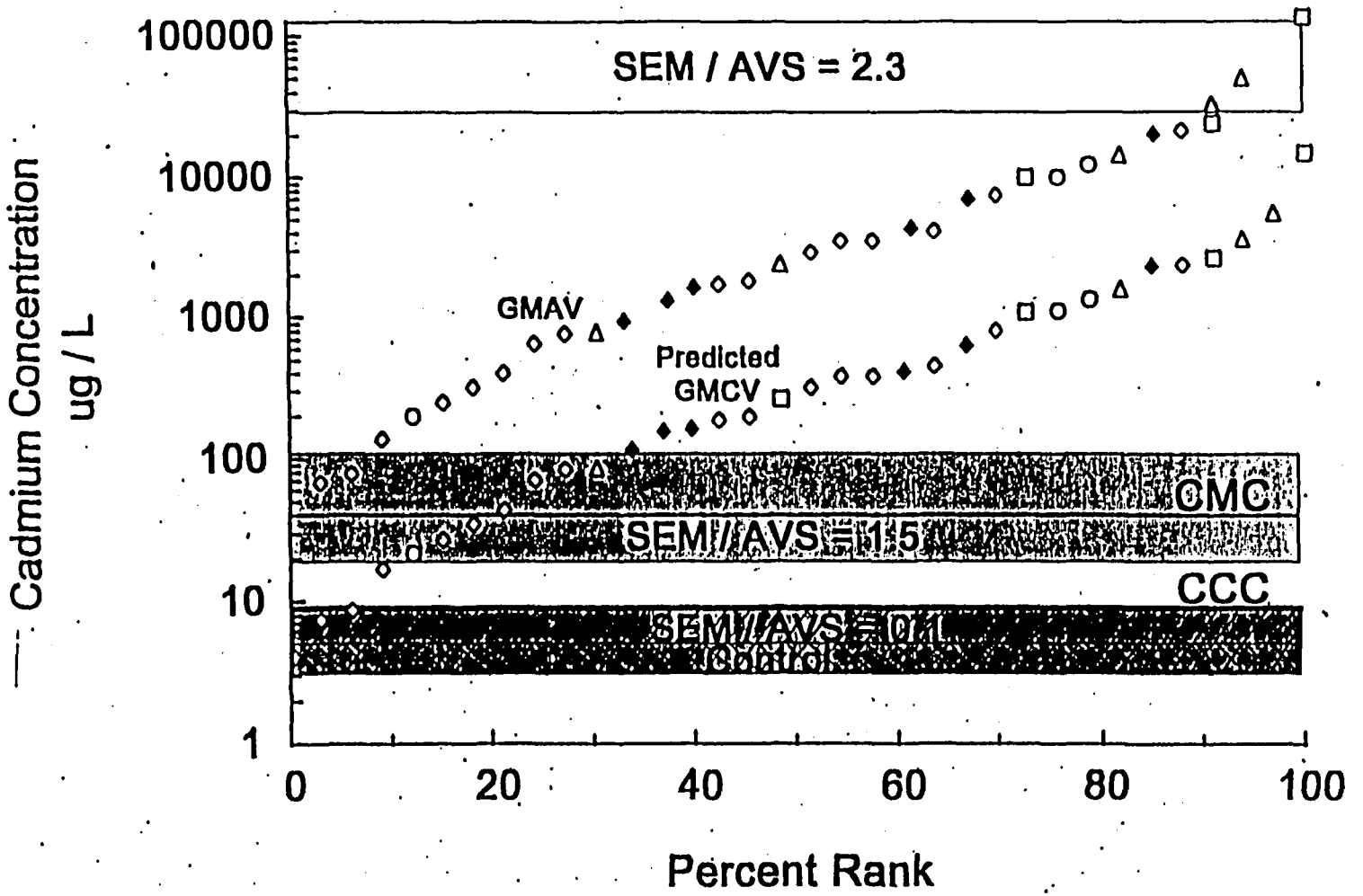


Figure 7-5. Comparison of genus mean acute values (GMAV) and predicted genus mean chronic values (GMCV) from water-only toxicity tests as a function of the percent rank sensitivity of the genus and ranges of interstitial water concentrations in sediments from control and nominal 0.1, 0.8, and 3.0 Cd/AVS treatments; measured SEM/AVS ratios were 0.0, 0.1, 1.5, and 2.3, respectively.. GMAV's are geometric means of LC50 values for water-only tests with species within any genus as reported in Table 3 of the cadmium water quality criteria (WQC) document (U.S. EPA, 1985). Predicted GMCV's are derived as the GMAV divided by the final acute-chronic ratio of 9.1 from the cadmium WQC document. Values for arthropod genera are indicated by open diamonds, molluscs solid diamonds, polychaetes circles, other invertebrates squares, and fishes triangles. Ranges of interstitial cadmium concentrations for each SEM/AVS treatment are indicated by horizontal shaded zones. The WQC criteria maximun concentration (CMC = acute criterion) of 85 µg/L and criteria continuous concentration (CCC = chronic criterion) of 9.3 µg/L are indicated by horizontal lines. To interpret this figure, if the sensitivities of various genera in water-only tests are indicative of sensitivities to interstitial cadmium concentrations in sediment tests, taxa potentially at risk in the sediment treatments in our experiment are those whose GMAVs and GMCVs are within and below the ranges in interstitial cadmium.

frequently exceeded those for sulfide and cadmium concentrations in interstitial water (ND to 157 μg/L) often exceeded those that in water-only tests are known to be acutely toxic to sensitive species. Chronic effects may be projected to occur to many sensitive arthropods and polychaetes if acute toxicity and acute-chronic ratios are used to estimate chronically toxic concentrations (Figure 7-5). Significant reductions in the abundance of polychaetes and nematodes, but not arthropods, and alterations in species composition were observed. In the nominal 3.0 SEM/AVS treatment, molar concentrations of cadmium always exceeded those of sulfide in both homogenized sediments and in sediment profiles, and interstitial water concentrations of cadmium were of sufficient magnitude (28,000 to 174,000 μg/L) to pose significant acute and chronic risks to almost all algal and macrobenthic saltwater organisms for which data are reported in the water quality criteria document [12]. Biological effects observed in our study were severe, with numbers of species reduced by about one-half. Significant reductions occurred in total polychaete species, abundance and size of certain polychaete species and abundance of nematodes and harpacticoid copepods. Bivalve molluscs were absent and diatom density was reduced 10-fold. Interestingly, the total number of individuals of benthic organisms was similar to that of controls. This suggests that tolerant benthic species that could avoid exposure by their epibenthic habits replaced more sensitive species. For example, the tunicate Molgula, known to be resistant to many substances in this test [6], rests on sediments utilizing water from above the sediment surface and was particularly abundant in 3.0 SEM/AVS. Alternatively, organisms may seek micro-environments known to occur in the surface 1 to 2 cm of sediments [14], as was observed in the polychaete Neanthes arenaceodentata exposed to cadmium or nickel-spiked sediment [16].

We conclude that the present theories used to predict the acute biological consequences of divalent metals in sediments may be applicable to chronically exposed benthic organisms. Predictions of the toxicological significance of metals in laboratory and field sediments must consider vertical profiles of SEM and AVS relative to biologically active sediment strata, interstitial water metal concentrations and the potential for release of nonavailable metal as a result of oxidation of AVS (including both iron and cadmium and

other toxic metal sulfides) as a part of the normal seasonal sulfide cycles and sediment bioturbation.

In addition to the marine colonization study described in this chapter, there have been two colonization experiments with freshwater sediments that have examined the role of AVS in determining metal bioavailability [3,4]. Because these experiments only recently have been completed, they are not described in detail herein; however, the studies will be presented in full at the SAB meeting. For the sake of completeness, below we briefly describe the freshwater colonization experiments, including major results and conclusions.

Hare et al. [3] conducted an experiment in which cadmium was spiked into clean field-collected sediments, which were then placed in trays and put in the Precambrian shield lake from which the sediments were initially collected. Nominal SEM:AVS ratios in the samples were 0.05 (control), 0.1, 0.5, 2, and 10. SEM:AVS ratios and pore water cadmium concentration were measured in 3 cm horizons of the sediment over the course of slightly greater than one year, after which macroinvertebrate samples were collected to evaluate benthic community structure and cadmium bioaccumulation by the benthos. The results of the bioaccumulation study are addressed in Chapter 8. Except for the sample with a nominal SEM:AVS ratio of 10, water overlying the sediments (collected with "peepers") contained non-detectable levels of cadmium. At all the test concentrations, oxidation of AVS in surficial sediments resulted in greater SEM:AVS ratios in the shallowest horizon than in deeper portions of the core. Pore water cadmium concentrations in the control and 0.1 treatment were consistently low. However, in the 0.5 treatment, pore water cadmium concentration were elevated, particularly in the shallowest sediment horizons, presumably due to surficial oxidation of AVS. In the samples with nominal SEM:AVS ratios of 2 and 10, pore water cadmium concentrations were consistently elevated; however, there appeared to be little if any impact of the cadmium on organism abundance (Figure 7-6). One of the explanations suggested by the authors for the seeming lack of impact was that SEM:AVS ratios actually can be quite misleading. Although samples with very small AVS concentrations (such as those in their study, ca., 0.2 umol AVS/g) might exceed an SEM:AVS ratio of 1, the actual amount of

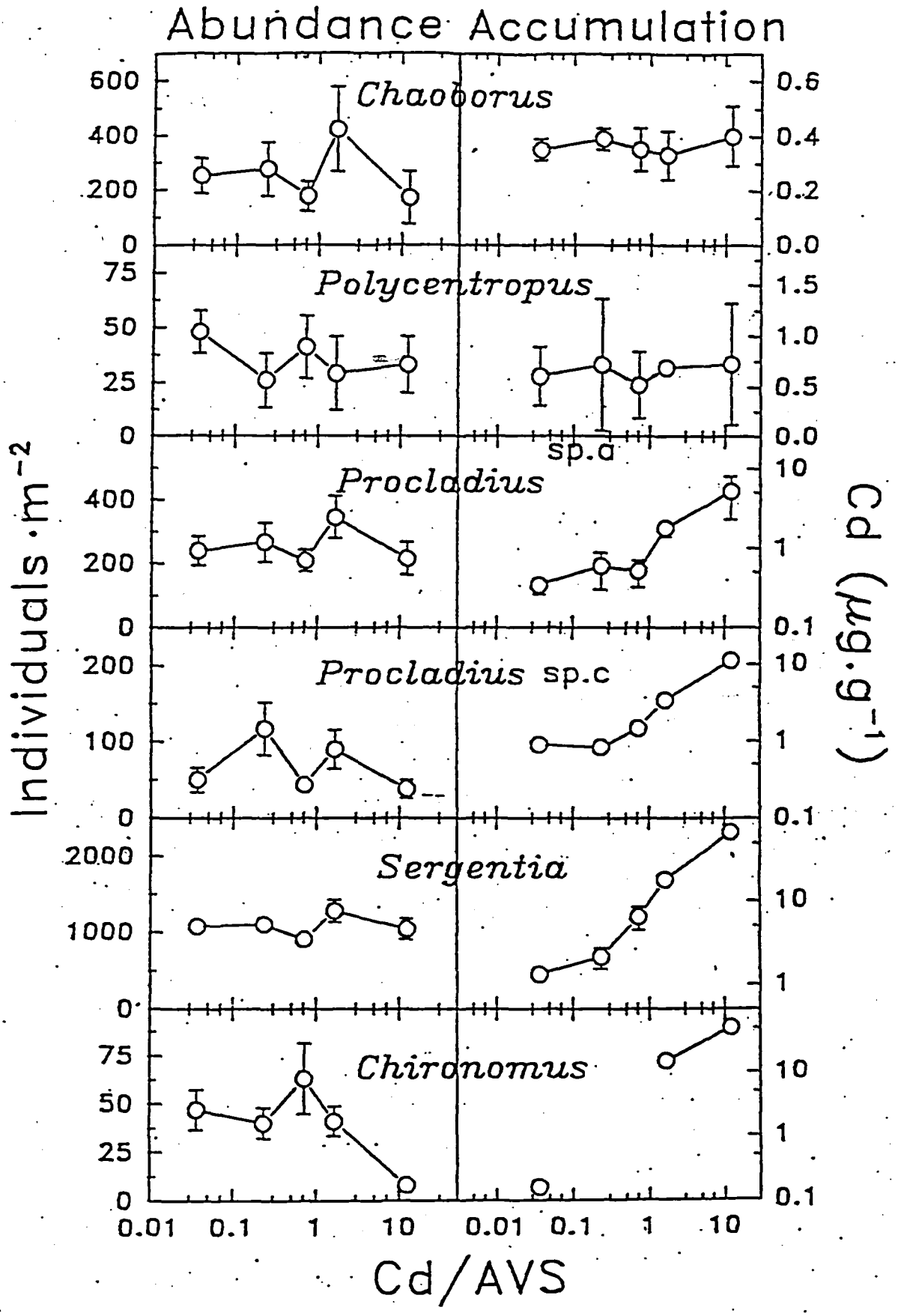


Figure 7-6. Comparison of SEM (cadmium):AVS to abundance of, and bioaccumulation of cadmium by six taxa of benthic macroinvertebrates from a field study.

total free metal could be quite small. This led the authors to conclude that it may be more appropriate to use the absolute difference between SEM and AVS to predict the presence of bioavailable metal [3].

Liber et al. [4] conducted a colonization experiment with zinc spiked into clean sediments from a small mesotrophic pond near Duluth, Minnesota. The spiked sediments were replaced in the pond in trays, and sampled periodically over the course of about 14 months for determination of SEM:AVS ratios and zinc pore water concentrations, and benthic community structure. Five zinc concentrations, ranging from 0.8 to 12 umol/g were tested in order to cover the expected seasonal range in AVS concentrations. However, the zinc-sulfide complex proved to be exceptionally stable to oxidation relative to iron monsulfide, (see Chapter 9), in that there was a concentration-dependent increase in sediment AVS content with increasing zinc concentration (Figure 7-7). The net result of this was that SEM:AVS ratios at the four lowest treatments never exceeded one, and only slightly exceeded one in the highest zinc spiking regime. This exceedence occurred only in surficial (0 to 2 cm) sediments; similar to the study of Hare et al. [3], AVS concentrations in the shallowest horizons, irrespective of the zinc treatment, were smaller than those in deeper sediments (Figure 7-7). Regardless of the measured SEM:AVS ratio, zinc was rarely detected in the pore water, and never at biologically significant concentrations. Sediment cores, collected during each sampling period, were not toxic to Chironomus tentans or Hyalella azteca in laboratory bioassays, nor was there any discernable impact on diversity of abundance of benthic communities in the zinc-spiked samples (Figure 7-8). Results form the study confirmed that when molar AVS concentrations exceed those of SEM, little or no free metal is present in pore water, and toxicity to benthic organisms does not occur.

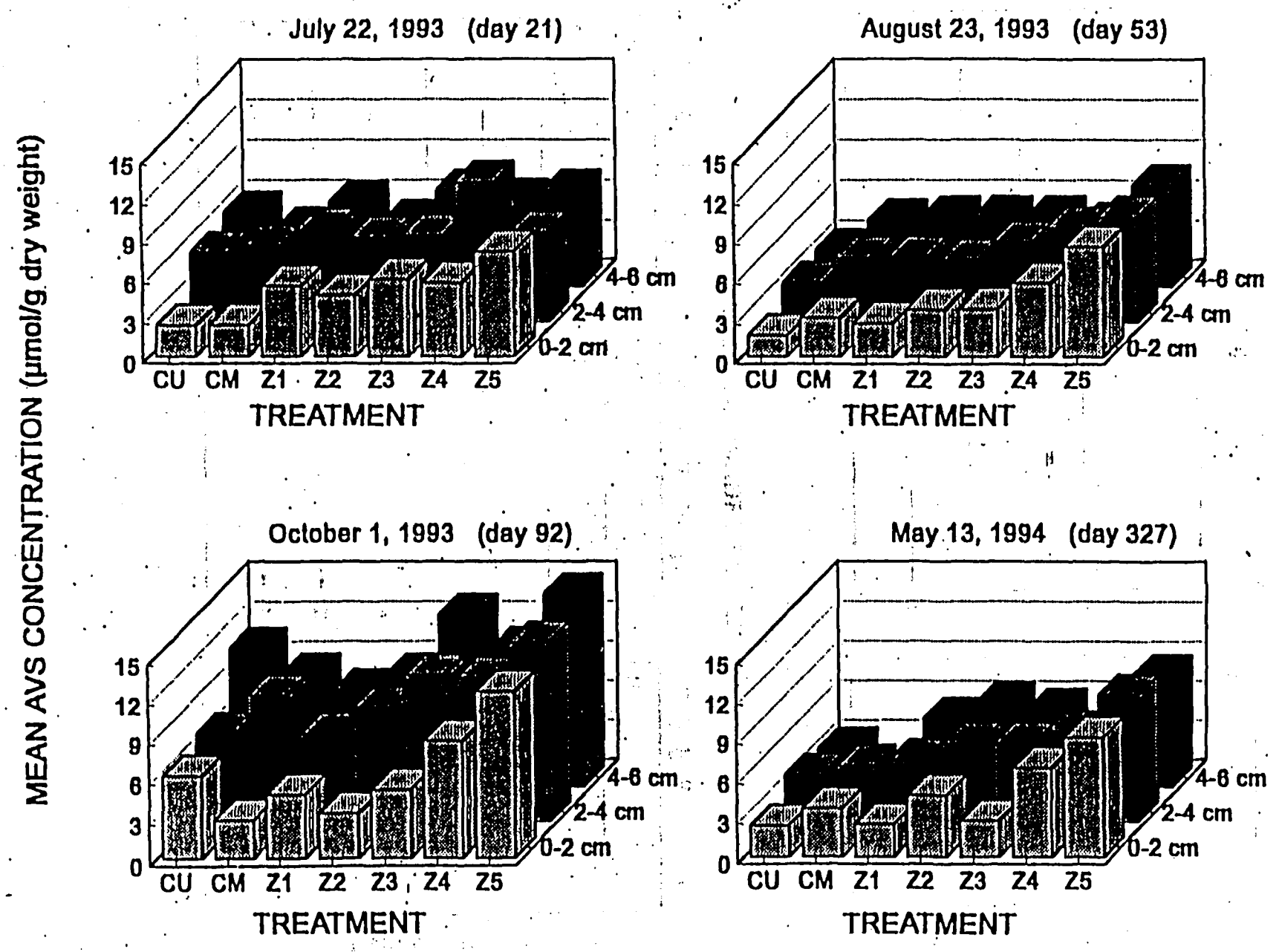


Figure 7-7. Average AVS concentrations at various depths in test sediments (controls and zinc-spiked) on four of the five sample dates.

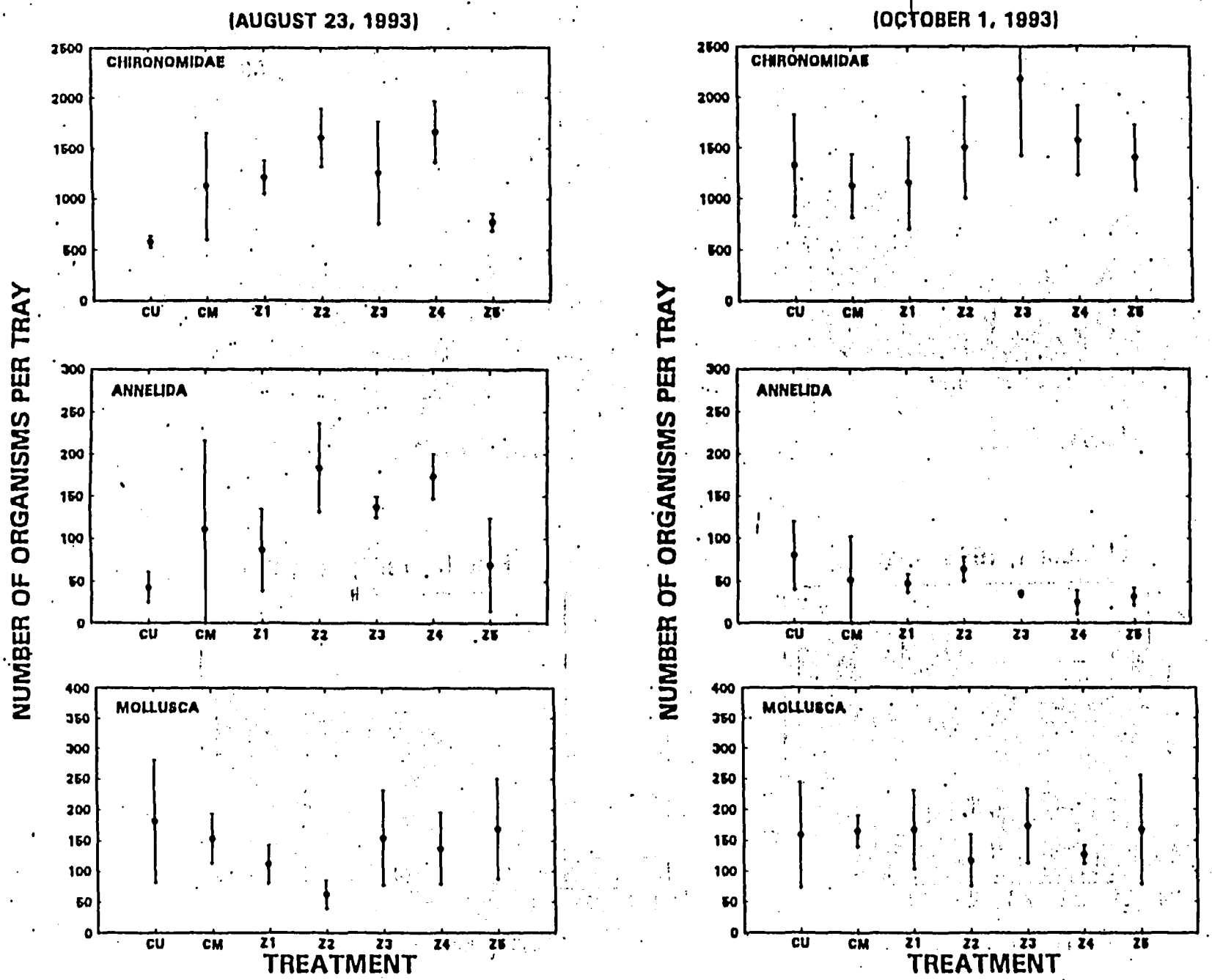


Figure 7-8. Benthic macroinvertebrate abundance ($\bar{x} \pm SD$) in sediment trays on two of the five sampling dates.

APPENDIX 7A
METHODS

Effects of cadmium spiked into sediments on macrobenthic organisms that colonized sediments was tested in a 118-day (July 4 to October 21, 1991) experiment using a control and three cadmium-spiked sediment treatments, with nominal SEM/AVS ratios of 0.1, 0.8, and 3.0. There were 12 replicate, 8 biological and 4 chemical, aquaria (13.3 x 30 x 15 cm high) for each treatment (Figure 7A-1). A stratified random placement strategy was used for location of treatments and replicates among the four test apparatuses was used. Approximately four liters of sediment from central Long Island Sound south of Milford, Connecticut (5.6 percent sand, 70.7 percent silt, 23.7 percent clay and 1.0 percent TOC), defaunated by freezing, were added to a depth of 8 cm to each aquarium. A splitter box delivered unfiltered saltwater, (29 to 32ppt salinity; 16 to 23.5°C) from the West Passage of Narragansett Bay to one end of each aquarium at 200 ml/min (about 300 volume additions per day). This unfiltered saltwater contained planktonic larvae and other lifestages of benthic organisms. A drain hole at the opposite end maintained water depth over the sediment at 2 cm.

Sediment from central Long Island Sound (mean 17.2 μmol AVS/g dry weight) was spiked with cadmium chloride dissolved in seawater, homogenized, and stored at 20°C for 26 days prior to test initiation. Treatments were nominal μmol SEM cadmium/μmol AVS ratios of 0.0 (control), 0.1, 0.8, and 3.0. The Long Island Sound sediment has low levels of metals (about 0.4 μg/g cadmium, 40 μg/g copper, 60 μg/g lead, 15 μg/g nickel, and 130 μg/g zinc) that contribute 3.17 μmol/g to the total SEM and 0.18 to the total divalent metal SEM/AVS ratio. Hereafter, SEM/AVS ratio used will be μmol SEM cadmium/μmol AVS. Sediments from this location have proven biologically acceptable as control or reference sediment in a great number of tests conducted previously at U.S. EPA, Narragansett, Rhode Island. The experiment began after addition of sediments to aquaria and initiation of water flow.

Replicate chemical aquaria were sampled on days 14, 28, 56, and 117. Each chemical replicate contained six interstitial water diffusion samplers (peepers), three

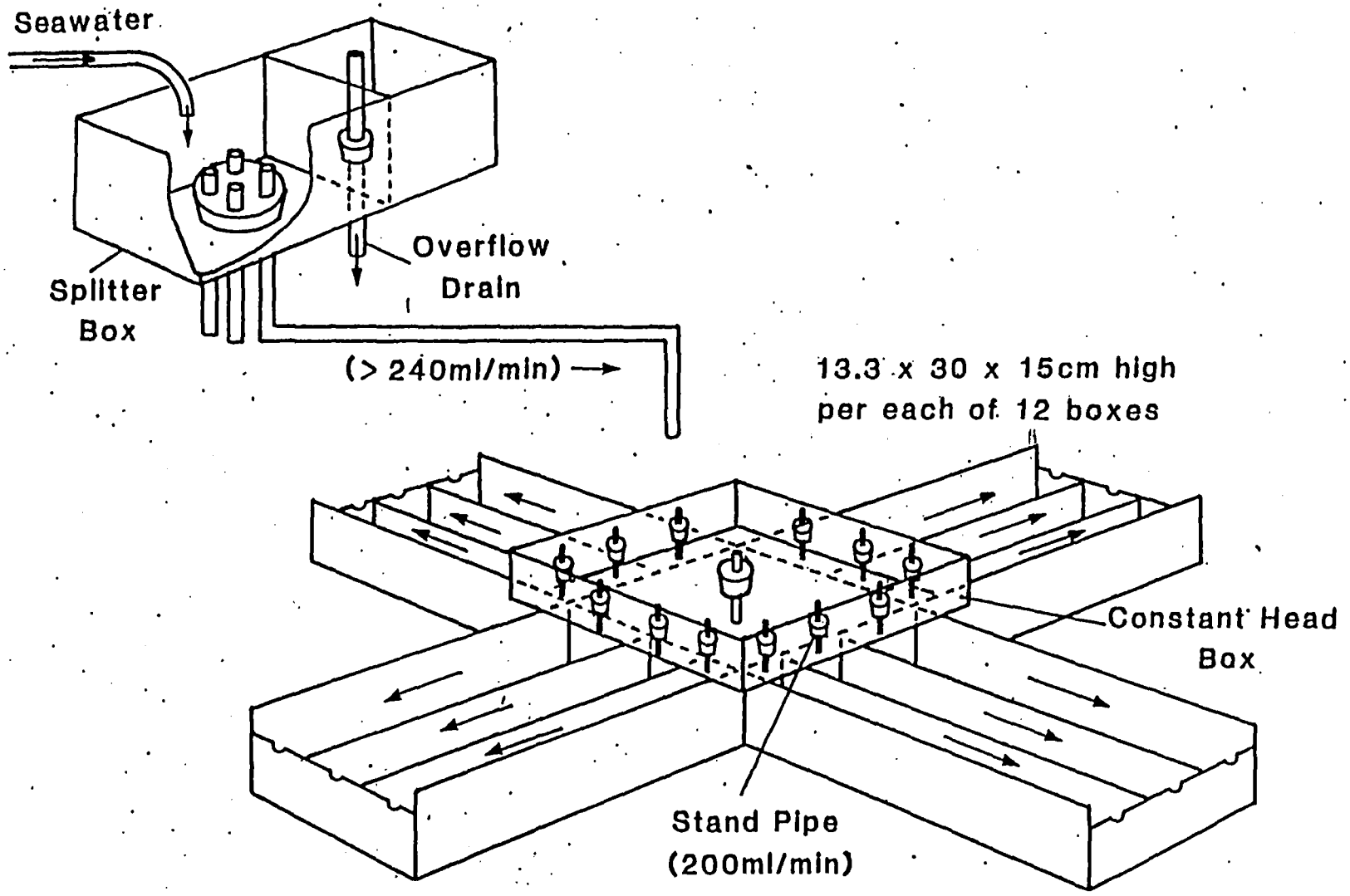


Figure 7A-1. One of four identical apparatuses each consisting of twelve aquaria used to test the effects of cadmium in sediment on colonization by benthic organisms. The splitter box supplied unfiltered seawater to the four apparatuses. Each apparatus contained two biology and one chemistry replicate for the control, 0.1, 0.8 and 3.0 SEM/AVS treatments. Each chemistry replicate contained three interstitial water diffusion samplers (peepers) near the sediment surface and three peepers 2 cm from the bottom of the sediment.

immediately below the sediment surface and three 2 cm above the bottom of the test aquaria (Figure 7A-1). Peepers were polyethylene vials containing 6.3 ml of filtered seawater with 1-micron pore size polycarbonate mesh across the top. On each sampling day, three core tubes, 6.5-cm ID, were first inserted into the sediment in the front, middle and end of the chemistry replicate for each treatment and the top capped. Next, peepers were withdrawn, rinsed with seawater to remove adhering sediment, the membrane punctured with a disposable pipette tip, the water withdrawn, acidified, and stored for analysis. Cores were removed, the bottom capped, and frozen. Remaining sediments were homogenized and an aliquot frozen. Before chemical analysis, sediment cores from days 28, 56, and 117 were extruded from core tubes and sliced into five 0.6 cm horizons in the first 3.0 cm of sediment and in 2.0 cm horizons for the remainder of the core. Cores from day 14 were sliced at a variety of depth horizons. Each horizon from each core was homogenized before chemical analyses. Homogenized remaining sediments and cores were analyzed for SEM cadmium, AVS, and interstitial water metal by AA or ICP using the methods of Boothman and Helmsletter [1], Allen et al. [27], and U.S. EPA [28].

All biological replicates were sampled on day 80 to obtain periphyton samples and on day 118 to remove the macrobenthos. Periphyton were pipetted from two 8-mm circles of surfical sediment from each aquarium at the midline and one-third the distance from each end. The volume of each these two samples was increased to 3.0 ml and the samples refrigerated. Diatoms in three aliquots containing 0.0636 μl from each sample were counted within 24 hours using a Palmer-Maloney cell. Counts were adjusted to cells/cm^2. Sediments were sieved through stacked 2.5, 0.5, and 0.3-mm sieves to remove macrobenthic organisms. The organisms were relaxed in magnesium sulfate and preserved in 10 percent buffered formaldehyde with rose bengal stain. Organisms were identified to species except for a few small or damaged specimens. Relaxed polychaetes, Nereis succinea, were measured for length prior to preservation. For tunicates, only individuals immediately in contact with sediment were counted; myriads of extremely small tunicates attached to larger tunicates-hence not in contact with sediment and present only in one control and five 3.0 SEM/AVS replicates-were not counted.

Analysis of variance was used to detect differences in the abundance of periphyton and individual macrobenthic animal species and phyla. Cluster analyses were performed to compare the kinds of macrobenthic species present or absent in each replicate or treatment using the simple matching coefficient [29].

$$S_{jk} = \frac{a + d}{a + b + c + d}$$

where, a = number of species present in both replicates,

b = number of species present in replicate k only,

c = number of species present in replicate j only,

d = number of species absent in both the replicate j and replicate k but that occur in at least one other replicate in the experiment, and

(a + b + c + d) = the total number of species found in the experiment.

Numbers calculated by this measure range from 0 (dissimilar) to 1 (similar).

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CHAPTER 8

BIOACCUMULATION OF METALS

Although the presence and/or absence of toxicity can, to some extent, be inferred as a barometer of contaminant bioavailability, in many instances a more accurate endpoint for assessing bioavailability is bioaccumulation. Even if a chemical is bioavailable, if the test species of concern is not particularly sensitive and/or the length of the test is too short, toxicity may not be manifested. Therefore, bioaccumulation also should be considered when assessing whether a particular model is appropriate for predicting metal bioavailability in sediments. This issue is of particular relevance to the bioavailability paradigm presented in previous Chapters of this document. Basically, if interstitial water concentrations of metals are small or non-detectable and/or (divalent) metal:AVS ratios measured in appropriate sediment horizons are less than one, significant accumulation of metals by macrobenthos should not occur. If significant bioaccumulation does occur this would suggest that, regardless of the results of toxicity studies, the bioavailability model which has been advanced for metals in sediments is not completely accurate.

Because bioaccumulation is a convenient endpoint for biomonitoring, the literature is replete with observations of metal bioaccumulation by vertebrate and invertebrate species associated with metal-contaminated sediments. In many instances, researchers have attempted to correlate concentrations of metals in field-collected animals with some measure of sediment metal concentrations. However, as is true for toxicity, total extractable metal concentrations in sediments are relatively poor indicators of that fraction of metal which apparently is available for bioaccumulation (for reviews see Tessier and Campbell, [1]; Luoma, [2]; Hare, [3]). Differential extraction techniques in conjunction with speciation models sometimes have improved correlations between concentrations of metals in animals and sediments, however, in most instances these types of models tend to be empirical and somewhat site-specific.

Definition of the true bioavailable fraction of metals is only part of the difficulty in quantitatively linking metal bioaccumulation by organisms to metals in sediments, either

in the laboratory or field. Although assessing bioaccumulation of metals from sediments theoretically should be a relatively straight-forward process, if not adequately controlled, a number of key variables can bias interpretation of observed results. One issue which is particularly problematic in field studies is the separation of exposure to sediment-associated metals (either from pore water or particulates) from exposure to metals in the water column. In the majority of systems contaminated by metals, both the sediments and overlying water have elevated metal concentrations. Because most benthic organisms have the potential for exposure via both media, it is difficult to separate the relative contribution of the two routes. This is compounded by the fact that while relatively accurate sediment chemistry can be obtained with single samples, it is very difficult to collect meaningful overlying water quality data temporally. This is not to say that from a holistic standpoint metals bioaccumulated by organisms from overlying water are not important; in fact, an overall model for assessing the impacts of metals on benthic organisms should incorporate exposure both from sediment and overlying water [4,5]. However, to develop a mechanistic understanding of factors mediating metal bioavailability in sediments, the contribution from overlying water must be monitored or controlled.

A number of biological/physiological factors also can complicate the interpretation of sediment bioaccumulation studies with benthic organisms. For example, species which ingest sediment must have their gut contents physically removed, or purged (e.g., by holding in clean water or sediment) in order to effectively separate metal that actually has been bioaccumulated from that associated with sediments in the gut [6,7]. Another potential bias in metal bioaccumulation studies with some species is that a sizable percentage of the metals measured on a total body basis may actually only be adsorbed to the outer integument [8]. A final problem with metal bioaccumulation as an endpoint for assessing bioavailability is that many invertebrate species are capable of regulating body burdens of essential trace metals (e.g., zinc, copper) to some extent (e.g., Timmermans et al., [9]). Hence, the lack of bioaccumulation does not always necessarily indicate a lack of bioavailability.

A number of studies have been conducted which permit the critical evaluation of metal bioaccumulation by macroinvertebrates relative to sediment pore water metal concentrations and SEM:AVS ratios. These studies include short-term laboratory experiments with cadmium- or nickel-spiked marine and freshwater sediments, short- and long-term laboratory experiments with field-collected marine and freshwater sediments variously contaminated with cadmium, nickel, copper, lead, and zinc, and a long-term field study with cadmium-spiked freshwater sediments. Species assessed included molluscs, oligochaetes, polychaetes, amphipods, and chironomids. In these experiments, the potential confounding variables described above, in particular clearance of gut contents, were controlled to varying degrees, which in some instances causes ambiguity in the interpretation of the study results.

Laboratory Spiking Experiments-Freshwater

Carlson et al. [10] exposed oligochaetes (Lumbriculus variegatus) and snails (Helisoma sp) to freshwater sediments, containing three different AVS concentrations, which each had been spiked to achieve nominal cadmium:AVS ratios of 0, 0.1, 0.3, 1.0, 3.0, and 10. Assays were conducted for 10 d in a system which provided approximately 11.5 turnovers of clean Lake Superior water/d. At test conclusion, mortality of the two organisms was assessed and tissue samples were collected for residue analysis. As discussed elsewhere in this document (Chapter 5), significant mortality of the two test species only occurred at cadmium:AVS ratios greater than one. However, even at cadmium:AVS ratios less than one, dissolved concentrations of cadmium in pore water from the spiked sediments were often greater than in unspiked sediments. Cadmium concentrations in surviving oligochaetes and snails were below those tissue concentrations expected to result in toxicity based upon comparison to concurrent water-only cadmium tests with the two species. However, cadmium residues in both species appeared to increase in a concentration-dependent manner at cadmium:AVS ratios less than one for all three test sediments (Figure 8-1). Comparison of the actual magnitude of these increases in worms and snails from the cadmium-spiked sediments is complicated by the fact that a complete set of cadmium concentrations in organisms from unspiked (control) samples

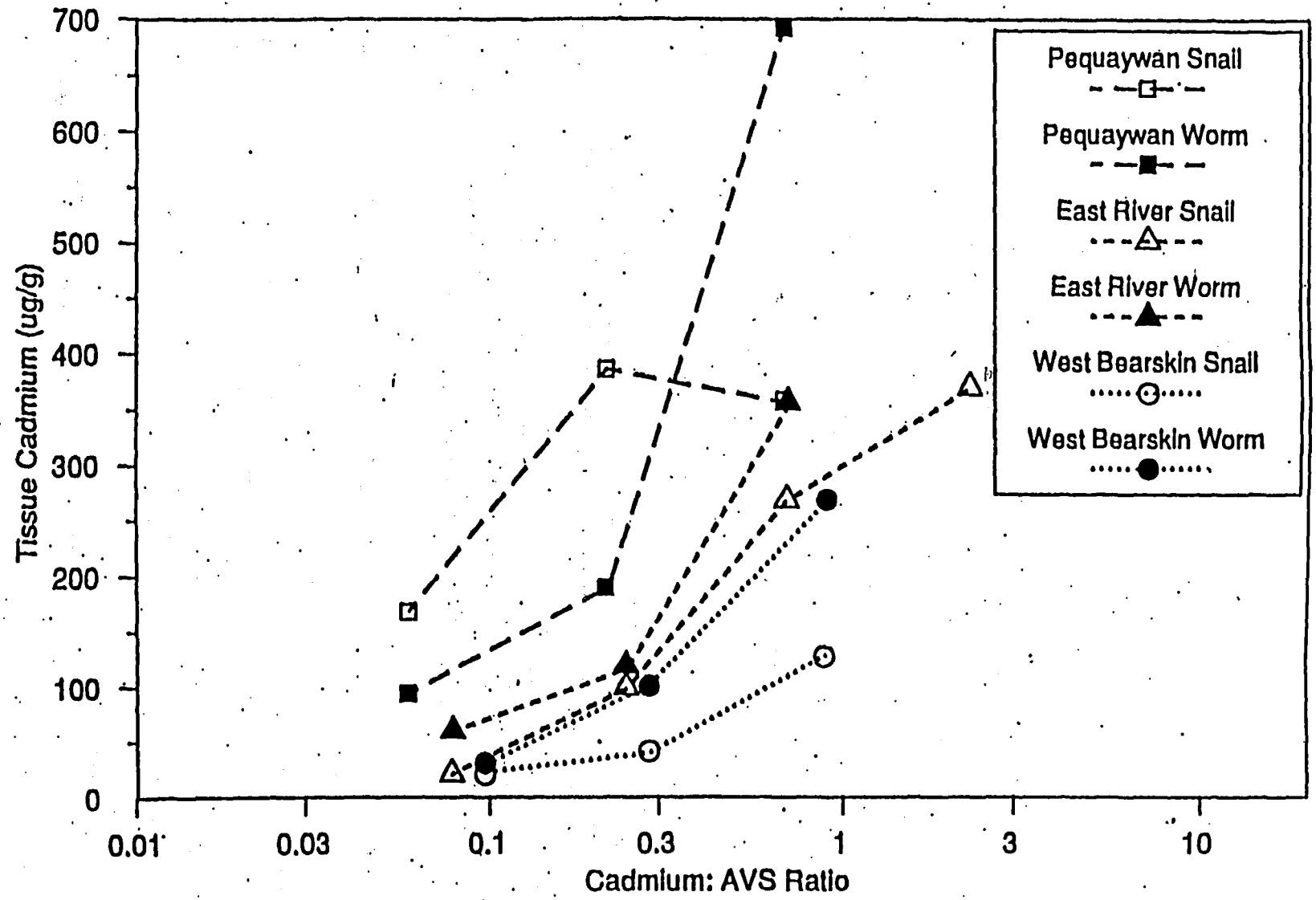

Figure 8-1. Comparison of cadmium:AVS ratios in three (spiked) freshwater sediments to bioaccumulation of cadmium by Lumbriculus variegatus and Helisoma sp.

are available for only one of the three test sediments. However, if concentrations of cadmium in organisms from this one sediment, which were on the order of 0.5 to 5 ug/g dry weight, are taken to be indicative of those in all the sediments, then cadmium concentrations were as much as two orders of magnitude greater than background in surviving test organisms from sediments with SEM:AVS ratios less than one.

An important shortcoming in the study by Carlson et al. [10] was that cadmium residues measured in the oligochaetes and snails included all gut contents, i.e., the organisms were removed directly from the sediment without allowance for gut purging. Data are not available with which to evaluate the potential contribution of gut contents to the total body weight of the snails; however, recent studies by Brooke et al. [11] indicate that in L. variegatus which have not been gut purged, approximately 10 percent of the dry weight of the worms may be sediment. Using this estimate, if it is assumed that the cadmium concentration in sediment in the gut of the oligochaete was similar to the cadmium concentration in the surrounding sediment, depending upon the test sediment, as little as 2 percent or as much as 50 percent of the total cadmium body burden in the oligochaetes could have been due to gut contents. It should be noted that the assumption that sediment in the gut is equivalent to that outside the organism becomes increasingly tenuous as the selectivity of feeding increases.

Laboratory Spiking-Marine

Pesch et al. [12] conducted experiments in which the toxicity and bioaccumulation of cadmium or nickel spiked into marine sediments were evaluated using the polychaete Neanthes arenaceodentata. Two different sediments, with relatively low and high AVS concentrations, were spiked so as to achieve final SEM (cadmium or nickel):AVS ratios of 0, 0.1, 0.3, 1.0, 3.0, 10, 30, and 100. Exposures were conducted for 10 d in a system which provided 30 to 50 turnovers of clean sea water/d. At the end of the exposure, surviving organisms were removed from the test sediments, and placed in clean sea water for 4 h. At this time, visual inspection suggested that the polychaetes had completely purged their gut contents. As discussed elsewhere (Chapter 5), no significant mortality

occurred at SEM:AVS ratios less than one; at SEM:AVS ratios greater than one and when interstitial water toxic units (TU) also were greater than one, the polychaetes either died or avoided burrowing in the cadmium- or nickel-spiked sediments. At SEM:AVS ratios less than one, dissolved concentrations of cadmium and nickel in pore water from the two sediments were comparable to values from unspiked sediments. Bioaccumulation of cadmium and nickel was most pronounced in sediments with SEM:AVS ratios greater than one; cadmium concentrations in polychaetes from sediments with ratios greater than one typically were more than an order of magnitude greater than concentrations in worms from sediments with ratios less than one (Figure 8-2). Nickel concentrations in animals from sediments with SEM:AVS ratios greater than one were approximately two- to 10-fold greater than nickel concentrations in polychaetes from sediments with ratios less than one (Figure 8-3).

Although bioaccumulation of both cadmium and nickel was most pronounced at SEM:AVS ratios greater than one, there also was a concentration-dependent increase in tissue metal concentrations in the polychaetes at SEM:AVS ratios less than one (Figures 8-2 and 8-3). There are a number of possible explanations for this. Metal residues in polychaetes from sediments with the lower SEM:AVS ratios could have been derived via ingestion and digestion of contaminated particulate matter. Alternatively, uptake of the two metals could have been directly from interstitial water; the burrowing activity of the animals could have served to effectively oxidize metal-sulfide complexes thereby releasing metal to the immediate environs of the polychaetes. Because this phenomenon would occur only in the microenvironment of the organisms, the release of metals may not have been manifested in measurements of cadmium and nickel concentrations in the pore water collected via "peepers." One other possible explanation for the observation of apparent metal bioaccumulation by the worms in samples with SEM:AVS ratios less than one, and pore water metal concentrations similar to control values, may be that the metals were adsorbed to the chitinous sheath of the polychaetes, and were not actually in the organism. This type of phenomenon has been documented for freshwater invertebrates such as chironomids [8], but to our knowledge, has not been investigated for N. arenaceodentata.

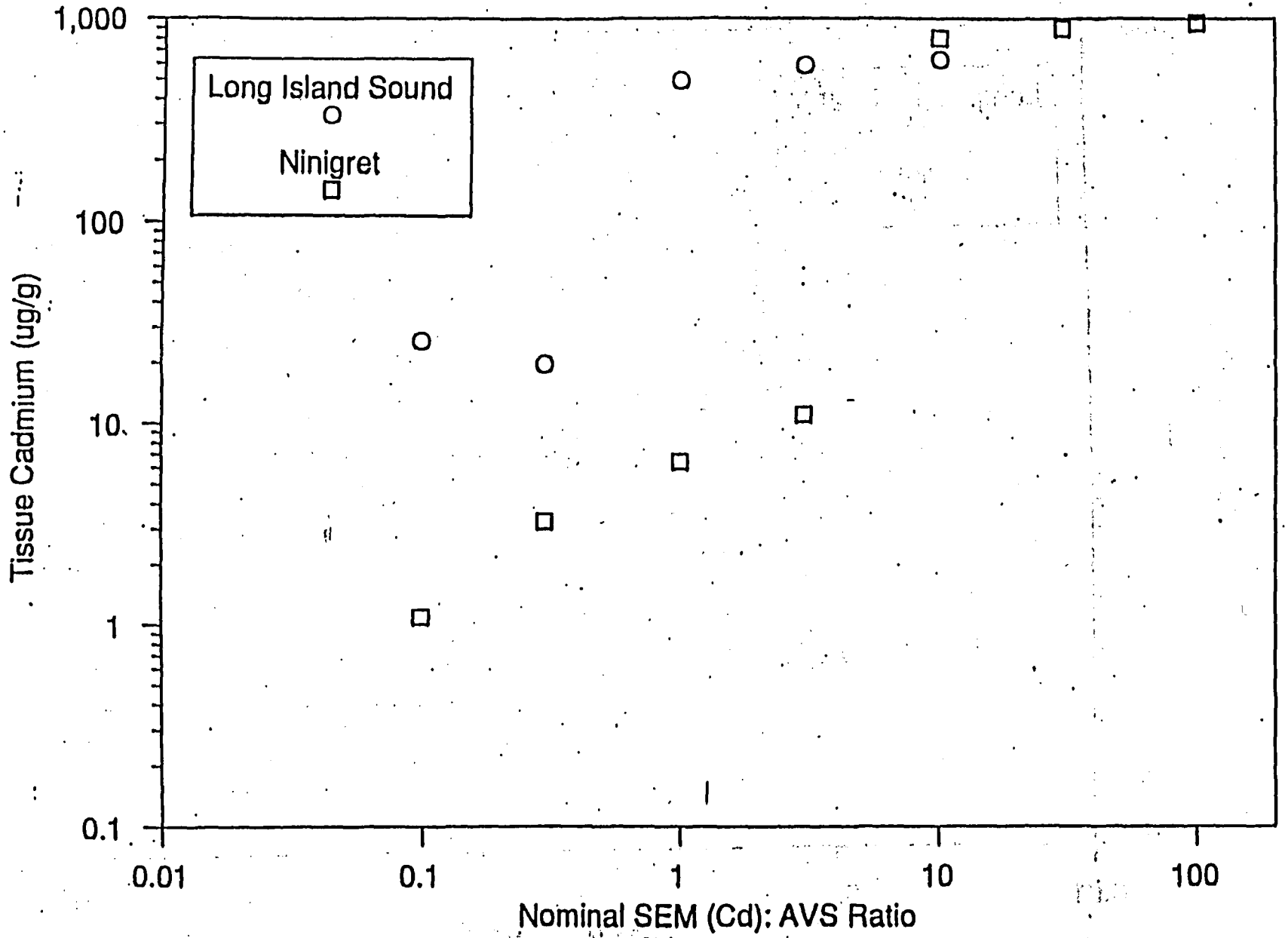

Figure 8-2. Comparison of SEM(cadmium):AVS ratios in two (spiked) marine sediments to bioaccumulation of cadmium by [illegible]nthes arenaceodentata.

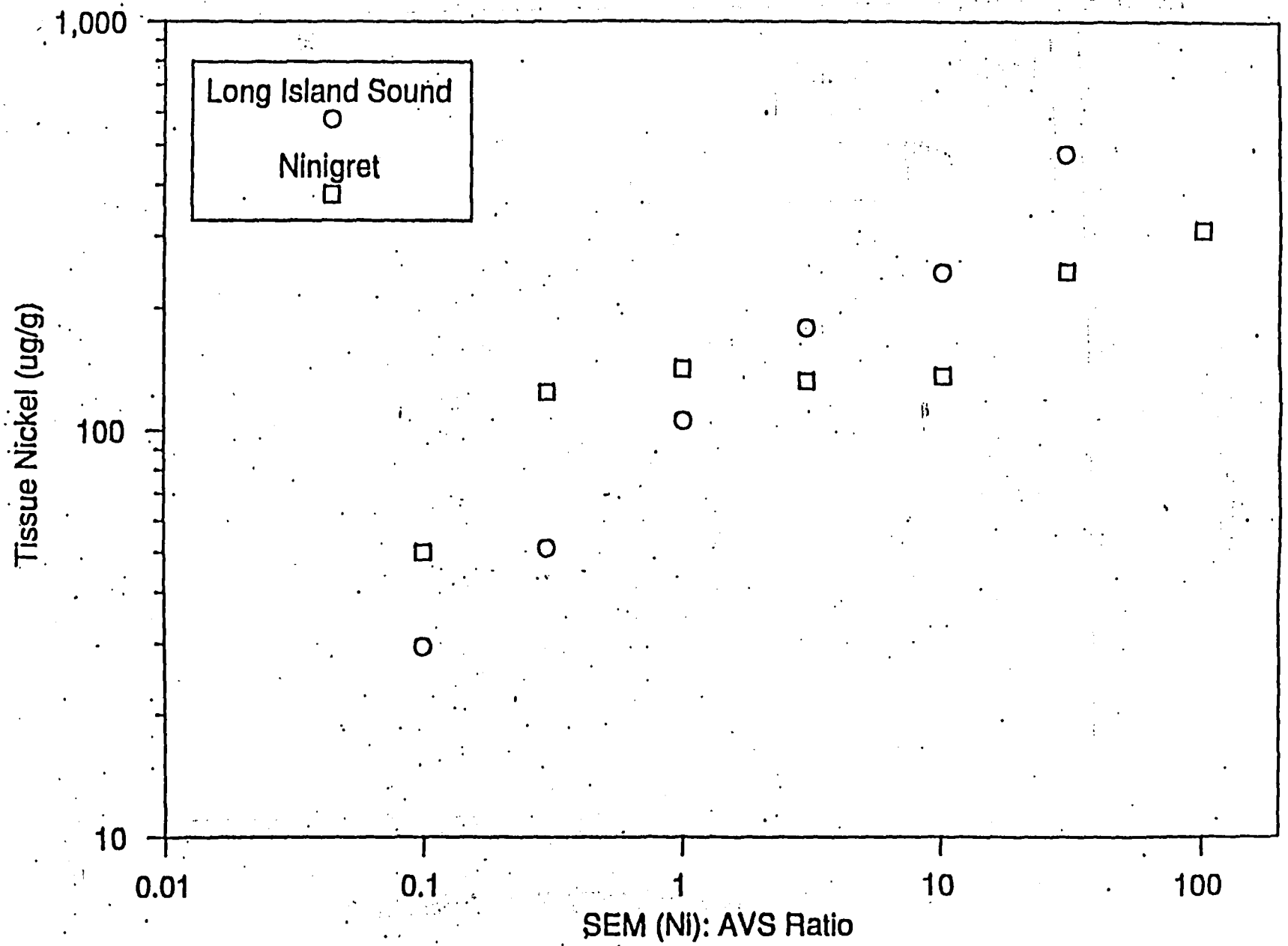

Figure 8-3. Comparison of SEM(nickel):AVS ratios in two (spiked) marine sediments to bioaccumulation of nickel by Neanthes aceodentata.

Field Sediments-Freshwater

Ankley et al. [13] evaluated bioaccumulation of cadmium and nickel by L. variegatus from 17 sediment samples from the upper (freshwater) end of a marine tidal estuary contaminated by a battery plant. Exposures were conducted for 10 d in a system which provided 12 turnovers of clean Lake Superior water/d. At test completion, the surviving oligochaetes were removed from the test sediments and placed in clean water for 24 h before residue analysis. Brooke et al. [11] have shown that this sampling regime should result in >90 percent clearance of gut contents of L. variegatus. As described elsewhere (Chapter 6), toxicity of the 17 sediments to the oligochaete was minimal; although 13 of the 17 samples had SEM (cadmium plus nickel):AVS ratios greater than one, only at the two highest ratios was significant mortality observed, which was consistent with pore water metal TU calculations for the worm. Bioaccumulation of metals (cadmium plus nickel) from the test sediments by L. variegatus was not predictable based upon total sediment metal concentrations (Figure 8-4a), however, bioaccumulation of metals by the worm did appear to be related to the sediment SEM:AVS ratios (Figure 8-4b). Metal concentrations in oligochaetes from sediments with ratios less than one were consistently small; significant bioaccumulation only occurred in those sediments where SEM:AVS ratios were greater than one. However, marked bioaccumulation of cadmium and nickel by L. variegatus was not observed in all samples with ratios greater than one, suggesting perhaps the presence of additional binding phases in excess of AVS for the metals in some of the test sediments.

Ankley et al. [14] also conducted a series of longer term sediment bioaccumulation tests with L. variegatus. In these experiments, three sediments from the lower Fox River, Wisconsin were tested; based upon "typical" background concentrations of metals in freshwater sediments, the three samples had greatly elevated concentrations of cadmium, copper, zinc, nickel, and lead. However, the sediments also had very high concentrations of AVS for fresh water sediments (ca., 20 umol/g), with the net result being that SEM:AVS ratios were in the range of approximately 0.4 to 0.6. Based upon this, Ankley et al. [14] hypothesized that (a) pore water concentrations of the metals should be low or

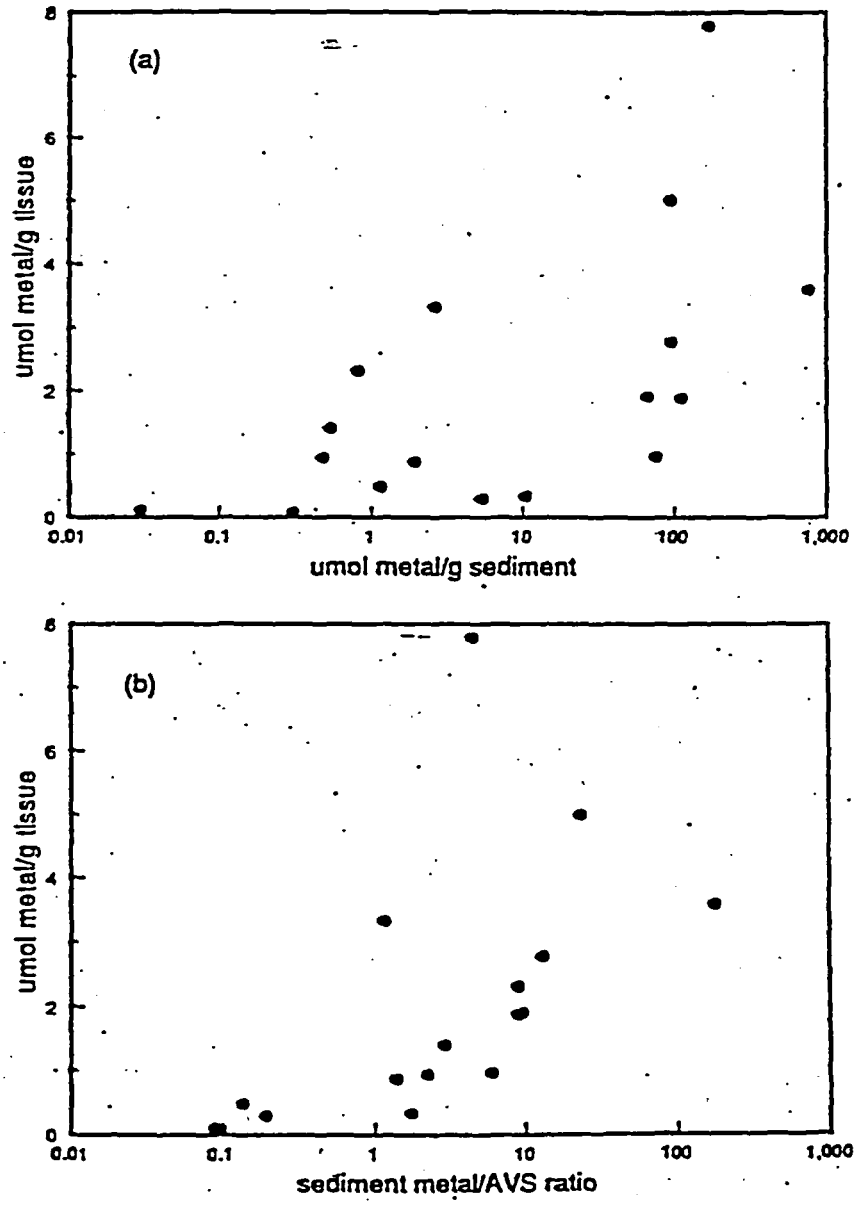

Figure 8-4. Comparison of metal (cadmium plus nickel) bioaccumulation by Lumbriculus variegatus to (a) total sediment metal (cadmium plus nickel) concentrations and (b) SEM(cadmium plus nickel):AVS ratios in 17 field-collected sediments.

non-detectable, and (b) in laboratory exposures, oligochaetes should not accumulate significant concentrations of the five cationic metals. Tests were conducted for 30 d with eight renewals of clean overlying (Lake Superior) water/d. The control for the experiment consisted of worms held in Lake Superior water only. At conclusion of the test, the oligochaetes were held for 24 h in clean water to purge gut contents. Sediment SEM:AVS ratios were relatively constant over the 30 d test; all ratios remained less than one. Pore water concentrations of dissolved cadmium, lead and nickel were non-detectable throughout the test; however, concentrations of both zinc and copper were consistently detectable, and higher than background (Lake Superior water) concentrations. The explanation for the elevated dissolved copper and zinc concentrations in pore water, in the presence of excess concentrations of AVS in the sediments, is uncertain. However, at completion of the 30 d exposure, concentrations of the five metals in tissues of the oligochaetes were similar to or smaller than control values, i.e., no apparent bioaccumulation of any of the metals occurred (Figure 8-5). This suggests that if copper and zinc in the pore water truly were bioavailable and not simply complexed, for example with DOC, then L. variegatus must possess some mechanism for effectively regulating tissue concentrations of these two metals.

Ingersoll et al. [15] conducted a long-term bioaccumulation test with six sediments from the Clark Fork River, MT using the amphipod Hyalella azteca. SEM:AVS ratios in the six samples ranged from 0.07 to 960 (Table 8-1), with copper and zinc comprising >97 percent of the SEM. Exposures were conducted for 28 d in a system which provided 1.25 renewals of clean overlying reconstituted water/d. Gut contents of the amphipods were not purged at test completion. In sediments with SEM:AVS ratios of one or greater, dissolved pore water concentrations of both copper and zinc were consistently elevated, while pore water concentrations of the two metals were comparable to control values in the sediment with the lowest SEM:AVS ratio (Table 8-1). However, as was the case in the study by Ankley et al. [14], concentrations of both metals also were increased over control values in two sediments (CF2, CF5) with SEM:AVS ratios slightly less than one. Concentrations of both copper and zinc were significantly increased in the amphipods from the three sediment samples with SEM:AVS ratios of one or greater (Table 8-1). Tissue

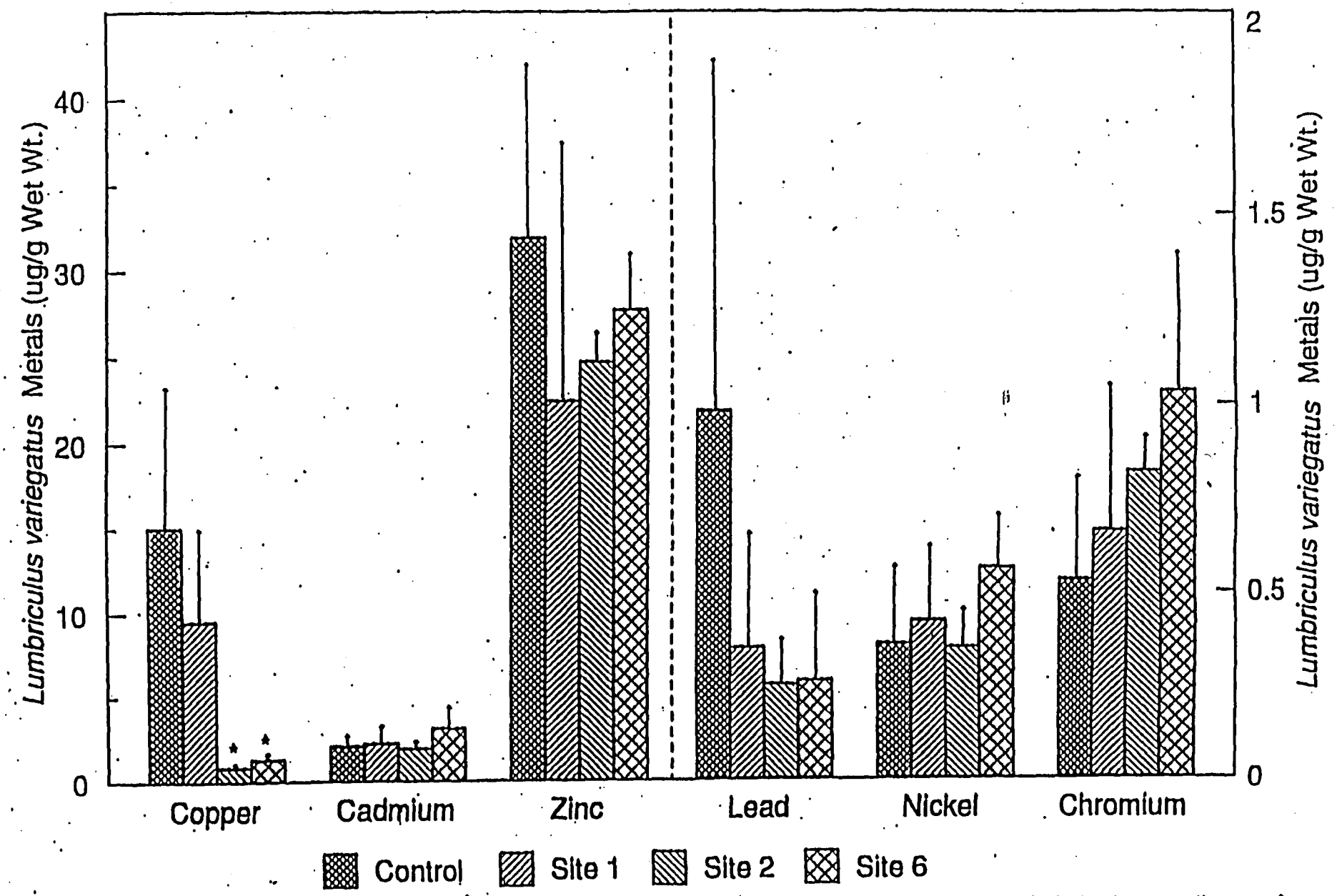

Figure 8-5. Comparison of tissue of concentrations of five metals in Lumbriculus variegatus held in three sediments from the lower Fox River, Wisconsin versus concentrations in worms held in clean water. Asterisks indicate significant difference from control.

concentrations of zinc, but not copper, were significantly higher than control values in H. azteca from a sediment with an SEM:AVS ratio of 0.85, while the converse was seen in sediment with a ratio of 0.75. Neither metal was bioaccumulated in amphipods exposed to a sediment with a SEM:AVS ratio of 0.07. Because the amphipods were not purged at test completion, the slight increases in copper or zinc concentrations observed in organisms from the two sediments with SEM:AVS ratios less than one could have been due largely to gut contents.

TABLE 8-1. SUMMARY OF CHEMISTRY AND TOXICITY DATA FOR SIX SEDIMENT SAMPLES FROM THE CLARK FORK RIVER (CF), AND A CONTROL.

	SEM[1]:AVS	Pore Water (µg/L)		Tissue (µg/g dry wt)	
Site	(SEM, AVS, µmol/g)	Copper	Zinc	Copper	Zinc
Control	–	4.3	3.9	80	57
CF1	960 (250, 0.26)	79	2603	249*	259*
CF2	0.85 (16.2, 19.1)	36	166	87	106*
CF3	2.15 (11.1, 5.16)	16	40	124*	80*
CF4	0.99 (12.9, 13.0)	8.7	28	127*	79*
CF5	0.75 (5.88, 7.84)	8.7	19	124*	74
CF6	0.07 (0.47, 6.66)	1.5	2.0	84	56

[1] Copper plus zinc.
* Differed significantly from control.

Field Sediments-Marine

Only one study has been conducted using field-collected sediments to evaluate bioaccumulation of metals by marine invertebrates relative to sediment SEM:AVS ratios or pore water metal concentrations. Pesch et al. [12] tested N. arenaceodentata with the same set of samples evaluated by Ankley et al. [13]. Test conditions were essentially the same as those described above for the polychaete. Results of the study by Pesch et al. [12] were remarkedly similar to those of Ankley et al. [13]; at SEM (cadmium plus

nickel):AVS ratios less than one, tissue concentrations of cadmium and nickel were low and comparable to control values (Figure 8-6). At SEM:AVS ratios greater than one, tissue concentrations of both metals increased markedly. Comparison of the bioaccumulation of cadmium and nickel by the polychaete also showed a reasonable correspondence with pore water concentrations of the two metals.

Field Spiking-Freshwater

Hare et al. [4] conducted an experiment in which cadmium was spiked into clean field-collected sediments, which were subsequently replaced in the field to evaluate trends in colonization by benthos, as well as bioaccumulation of the cadmium by select taxonomic groups. The study was conducted in a Precambrian shield lake near Quebec City, Quebec. Sediments were spiked to achieve nominal SEM:AVS ratios of 0.05 (control), 0.1, 0.5, 2, and 10. SEM:AVS ratios and pore water cadmium concentrations were measured in 3 cm horizons of the sediment over the course of slightly more than 1 year, at the end of which macroinvertebrate samples were collected to evaluate benthic community structure and cadmium bioaccumulation. Except for the sample with a SEM:AVS ratio of 10, water overlying the sediments (ca., 1 cm) had non-detectable dissolved cadmium concentrations. At all the test concentrations, oxidation of AVS in surficial sediments resulted in slightly greater SEM:AVS ratios in the shallowest horizon than in deeper sections of core samples. Pore water concentrations of dissolved cadmium in the control sediment and the sediment with a ratio of 0.1 were consistently low. Cadmium concentrations in pore water from the sediment with the SEM:AVS ratio of 0.5 were slightly elevated, particularly in the shallow sediment horizons, likely due to the surface oxidation of AVS. In the two samples with SEM:AVS ratios greater than one, pore water cadmium concentrations in all horizons were consistently elevated, particularly in the sample with the ratio of 10. Results of the colonization portion of the study are briefly presented in Chapter 7, and described in detail by Hare et al. [4]. There was little impact of the spiked cadmium on organism abundance, however, there was a significant bioaccumulation of cadmium by several different taxa at SEM:AVS ratios greater than one (Figure 8-7). The source of these metals was not gut contents, as the animals were purged in clean water for 2 to 5 d before preservation. The

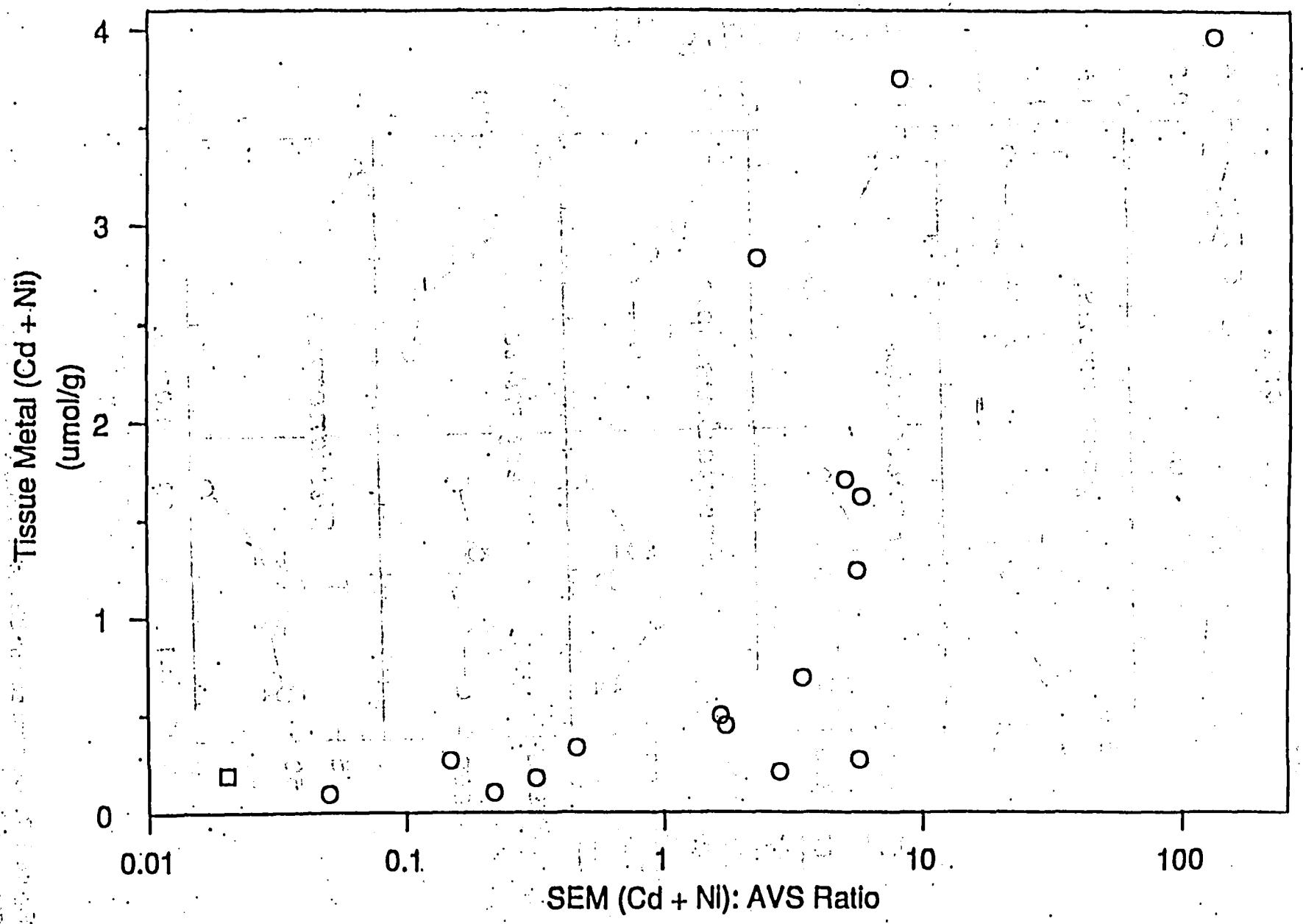

Figure 8-6. Comparison of metal (cadmium plus nickel) bioaccumulation by Neanthes arenaceodentata to SEM (cadmium plus nickel):AVS ratios in 16 field-collected sediments.

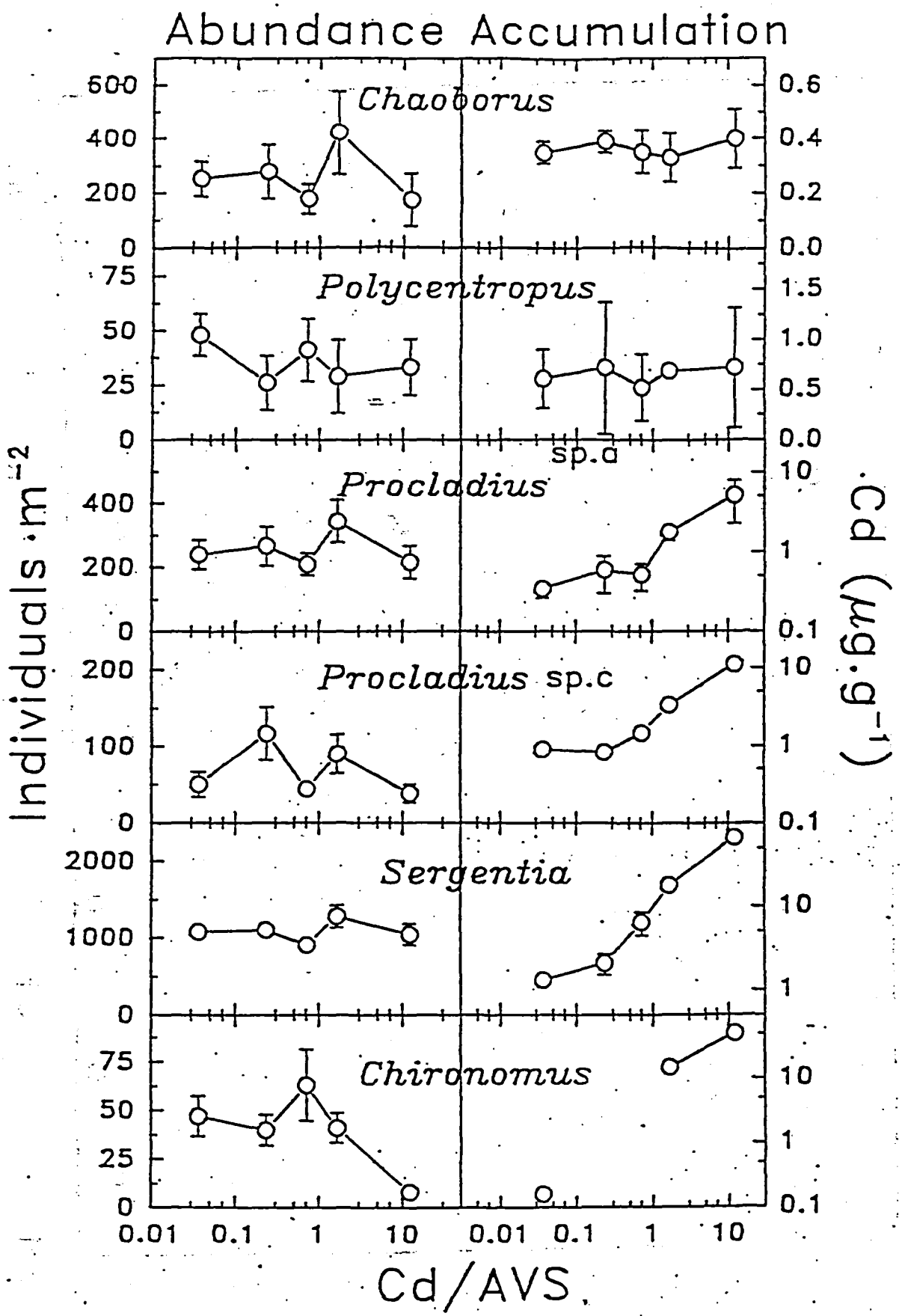

Figure 8-7. Comparison of SEM(cadmium):AVS to abundance of, and bioaccumulation of cadmium by six taxa of benthic macroinvertebrates from a field study.

two taxa which did not appear to bioaccumulate cadmium (Chaoborus, Polycentropus) are both predatory and have limited contact with sediments, while the three taxa which showed significant cadmium bioaccumulation were all burrowing midges. There also appeared to be an increase in tissue residues of cadmium in Sergentia from the sediment with a SEM:AVS ratio of 0.5, which was consistent with the slight increases in pore water cadmium observed at this ratio. Interestingly, the majority of cadmium accumulated by this species was associated with gut tissue.

Summary and Conclusions

In an effort to summarize bioaccumulation data from the above studies in a "global" framework, two different approaches were used. In the first, metal bioaccumulation data from the various laboratory studies were compared to SEM:AVS ratios in the test sediments. To normalize for differences in the concentration of metals in control organisms from the different tests, bioaccumulation data were expressed as the ratio of the concentration in organisms from test sediments to that in control animals from the same experiment. Hence, if AVS were critical in controlling metal bioaccumulation by the various benthic invertebrates tested, this bioaccumulation ratio should be near one at SEM:AVS ratios less than one, while at SEM:AVS ratios greater than one, bioaccumulation may be expected to increase. Due to uncertainties about control values and the lack of gut clearance of the test organisms, data from the study by Carlson et al. [10] were excluded from this and subsequent analyses.

The bioaccumulation of lead, zinc and copper appears to be explained reasonably well by a model based on AVS binding, i.e., at SEM:AVS ratios less than one, differences between control and experimental organisms are minimal, while at ratios between one and 10 bioaccumulation increases (Table 8-2). However, the total dataset for these three metals, in particular lead, is quite small. By far the most data are available for nickel and cadmium. The uptake of both of these metals clearly increases with increasing SEM:AVS ratios; however, the amount of metal bioaccumulated at ratios less than one is higher than controls (Table 8-2). Interestingly, if data only from field-collected sediments are

TABLE 8-2. SUMMARY OF BIOACCUMULATION RATIOS (EXPERIMENTAL/CONTROL) AT VARIOUS SEM:AVS RATIOS IN LABORATORY EXPOSURES WITH METAL-CONTAMINATED SPIKED AND FIELD COLLECTED SEDIMENTS.

				Nickel		Cadmium	
SEM/AVS	Lead	Zinc	Copper	All[2]	FC[3]	All	FC
<1	0.3±0.06(1)	1.1±0.4(7)	0.9±0.6(7)	2.4±2.6(16)	1.2±0.45(12)	4.2±7.4(16)	1.5±1.8(12)
1-10	-	3.0±2.2(2)	2.4±1.1(2)	7.6±7.0(24)	6.2±6.4(20)	73.5±158(24)	34.0±73.1(20)
>10	-	--	-	22.2±17.2(9)	21.9±20.7(6)	342±303(8)	72±133(4)

[1] $\bar{x}$ ± SD (n)
[2] Ratios from all laboratory exposures
[3] Ratios from laboratory exposures with just field-collected sediments.

considered, the relationship between metal bioaccumulation and SEM:AVS ratios appears much more consistent, i.e., little if any bioaccumulation of nickel or cadmium is observed at SEM:AVS ratios less than one (Table 8-2). It is worth noting that the absolute concentrations of nickel and cadmium used in the spiking experiments by Pesch et al. [12] were extremely high; even at SEM:AVS ratios less one, concentrations of the two metals were as great as approximately 200 and 700 ug/g (dry wt), respectively. Given these test concentrations, it is possible that even minimal contributions from residual gut contents and/or surface adsorption could contribute significantly to the total body burden of nickel or cadmium measured in the polychaete.

Bioaccumulation of the five metals also was compared to measured pore water concentrations for the various laboratory studies. In this analysis, the use of bioaccumulation ratios serves not only to correct for different control values for a given metal, but also to normalize for differences in the propensity for absolute concentrations of essential trace metals (e.g., zinc) to be naturally higher than those for non-essential trace metals. Non-detectable pore water concentrations were set at study-specific detection limits. Regression of the $\log_{10}$ bioaccumulation ratios for the five metals versus the $\log_{10}$ pore water metal concentrations resulted in a significant linear model which explained approximately 45 percent of the variability in the data (Figure 8-8). The fact that this model is not more robust could be related to a number of sources of among-study variation including differences in pore water sampling methodology, differences in analytical detection limits (particularly between freshwater and marine studies), and among-species differences in ability to regulate trace metal concentrations.

Although relationships between SEM:AVS ratios and/or pore water metal concentrations are not as conclusive as for the toxicity data described in Chapter 6, it appears that trends in the bioaccumulation of divalent cationic metals by benthic macroinvertebrates in laboratory exposures are clearly related to these two measures of bioavailability. The one field study that has been conducted to test this hypothesis also suggests that the long-term bioaccumulation of metals by different taxa can be related to pore water metal concentrations, which in turn, appear to be controlled by metal-sulfide

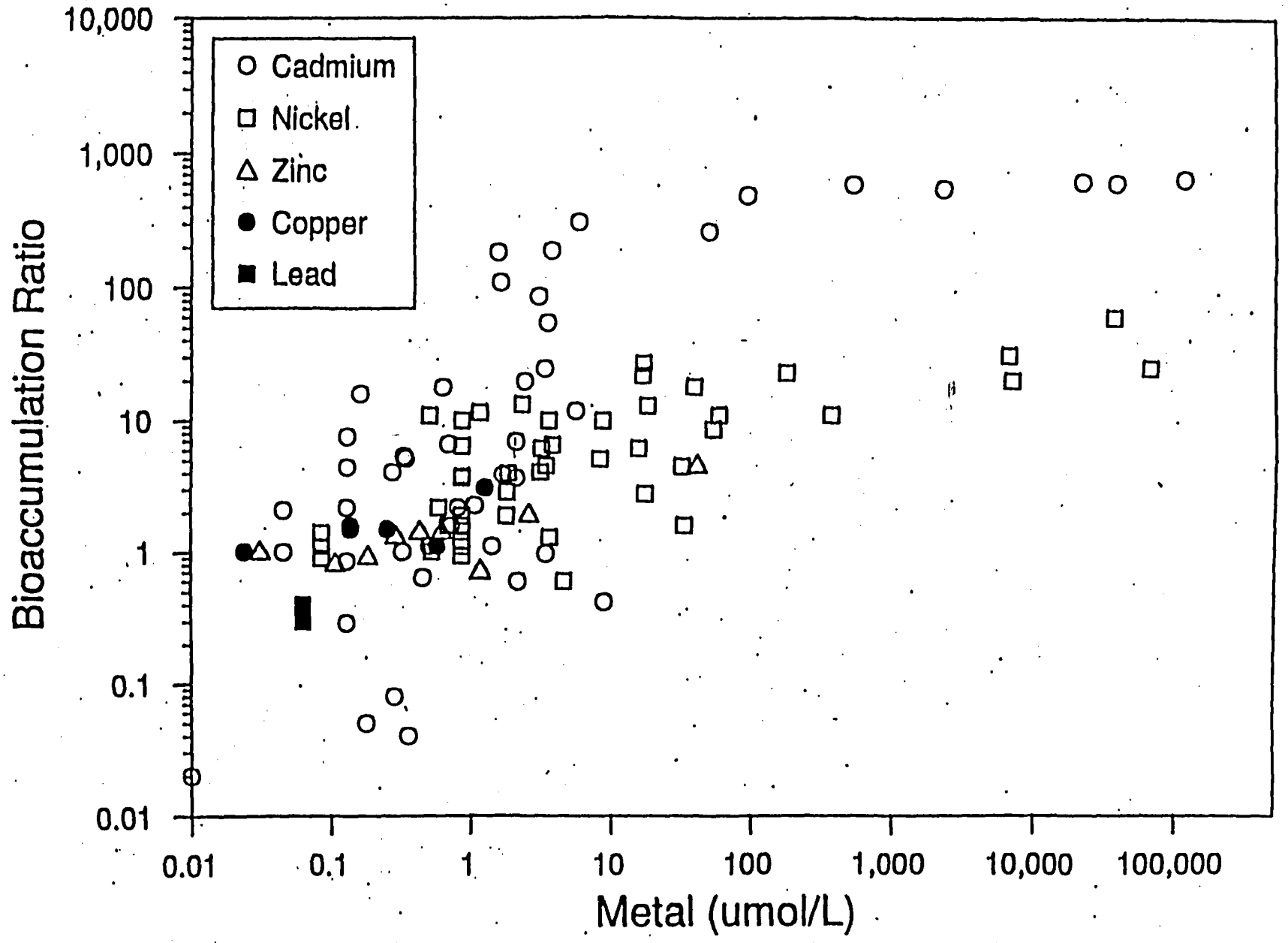

Figure 8-8. Bioaccumulation of metals versus pore water metal concentrations.

interactions. However, even though this analysis broadly supports the metal bioavailability model described elsewhere in this document, there are enough inconsistencies in the various studies described above to warrant future research in this area. In particular, more studies need to be conducted with field-collected sediments, and in the field. These studies need to be done with attention to details such as (a) defining appropriate sediment horizons for sampling pore water metals, and SEM:AVS concentrations, to better approximate exposure of organisms to metals in aerobic zones of sediments, and (b)determining the contribution of adsorbed and/or ingested material to the total body burden of metals in test organisms.

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CHAPTER 9

AVS AND OTHER BINDING PHASES

The previous chapters have addressed the theoretical and experimental evidence in support of establishing sediment quality criteria for metals using Equilibrium Partitioning. It was shown that both sediment AVS and interstitial water concentrations are important in assessing sediment toxicity. Determinations of AVS levels in sediments and interstitial water concentrations will play an important role in the application of SQC for metals.

This chapter addresses some additional considerations pertaining to characteristics of AVS sediment distributions and other factors that are important in the application of SQC for metals. These issues include the seasonal and depth variability of AVS, and the correlation of AVS to sediment organic carbon. Oxidation kinetics of iron sulfide and metal sulfide are presented. Experiments and their results pertaining to organic carbon binding for copper, cadmium, and lead are discussed. Experimental results for metals in low organic carbon sediments are presented to define a minimum partition coefficient. Lastly, pore water and SEM and AVS sampling are discussed.

Vertical and Seasonal AVS Distributions

Several factors contribute to variability in AVS distributions. The amounts of organic matter, sulfate, iron, and oxygen in sediments affects the potential amount of AVS that can be formed. An example of this is the difference in AVS concentrations in freshwater versus saltwater systems. Sulfate is present at higher levels in saltwater systems and the AVS concentrations can be expected to be higher in these sediments. A literature review by Leonard et al. [1], found that concentrations of AVS in unpolluted freshwater sediments were in the range of about 4 to 13 umol S/g, while AVS concentrations in coastal marine sediments have been reported in the range of about 0.1 to 100 μmol/g [2]. AVS also varies with depth and season. AVS concentrations tend to increase with depth up to about 20 cm and then decrease with depth. The following chapter summarizes three studies that have explored both seasonal and vertical

distributions of AVS. Two studies were done in freshwater systems and one study was done in a marine system.

Leonard et al. [1] measured seasonal and depth dependent AVS variations in three freshwater lakes in northeastern Minnesota; Caribou Lake, Fish Lake, and Pike Lake. The lakes were sampled approximately monthly from May 1990 to September 1991 for a total of 16 months. Sediment cores were sectioned into three 15 cm sections to represent the 0 to 15 cm depth, 15 to 30 cm depth and 30 to 45 cm depth. Particle size, total organic carbon and pore water pH and ammonia were measured for each 15 cm section. Overlying water was sampled for pH, alkalinity, hardness, conductivity, dissolved oxygen and primary productivity.

Temporal profiles of overlying water temperature and AVS at the three depths for each of the three lakes are presented in Figure 9-1. Average AVS concentrations in the 0 to 15 cm segments were <0.1 to 9.8 umol S/g in Caribou Lake, 0.1 to 6.0 umol S/g in Fish Lake, and 1.3 to 36.2 umol S/g in Pike Lake. Variability in AVS concentrations was most dramatic in the top 0 to 15 cm with less variability in the 15 to 30 cm and 30 to 45 cm segments in each of the lakes.

Leonard et al. [1] found that AVS in the upper two segments of Fish and Pike lakes was correlated to overlying water temperature and though not statistically significant, AVS did vary with overlying water temperature in Caribou Lake as well. During periods of ice cover overlying water temperatures were 0.2 to 1.5°C as shown in Figure 9-1 and AVS was at lowest levels (0.1 to 2.0 umol S/g). AVS increased to maximum concentrations as overlying water temperature increased to 20 to 25°C. Generally, when overlying water temperatures were at highest levels in June through August so were the AVS levels. AVS decreased with the onset of ice cover. Leonard et al. [1] note that the generation of AVS in the summer can be expected as sulfate reducing bacteria have an optimal temperature for growth in the 15 to 20°C range and a minimal temperature for growth at 0°C [3]. Figure 9-1 shows that AVS concentrations in the 15 to 30 cm depths were less influenced by temperature and almost no changes were seen in the 30 to 45 cm depths.

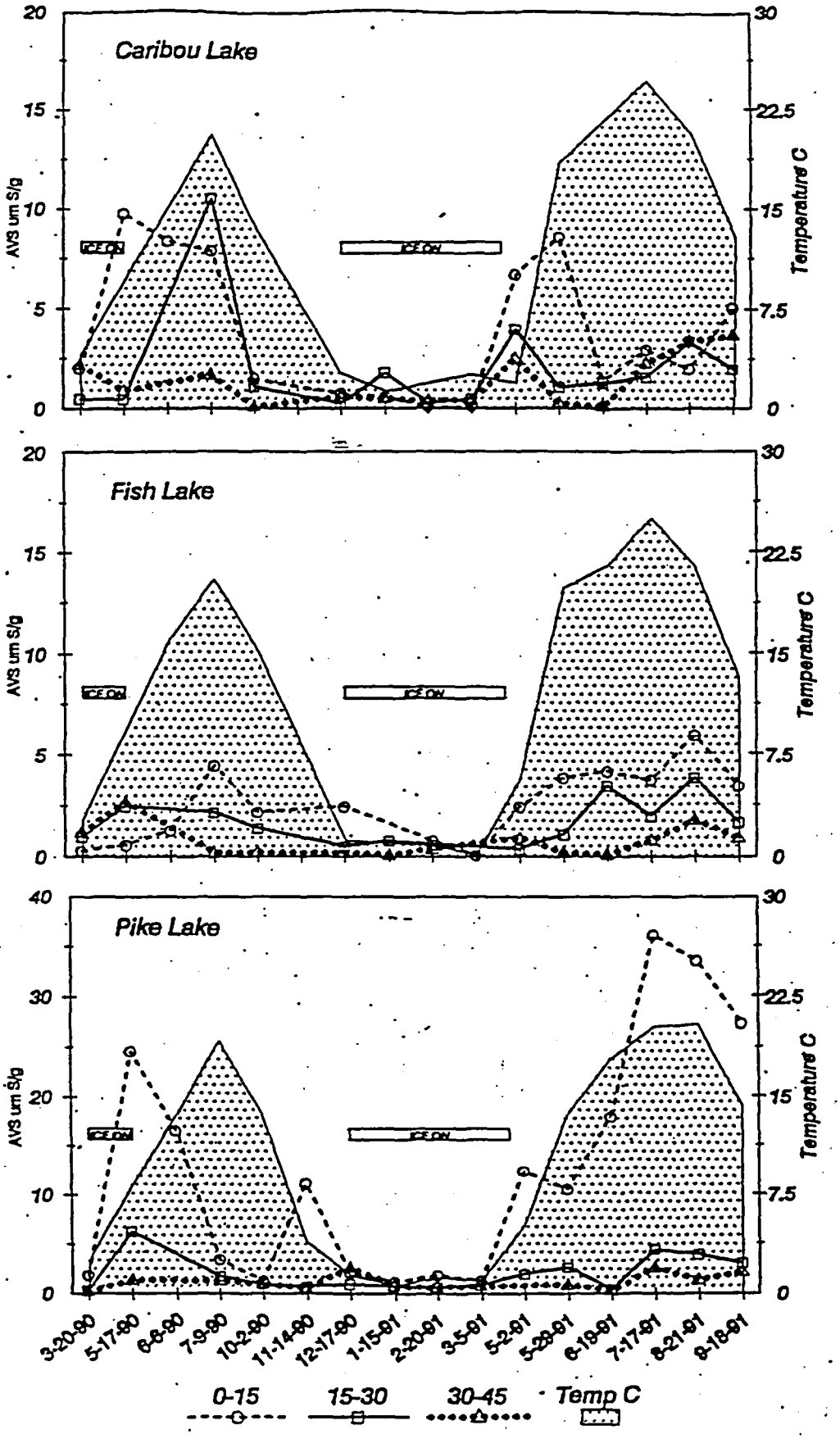


Figure 9-1. Seasonal AVS and temperature profiles for Caribou Lake, Fish Lake, and Pike Lake, Minnesota at 0 to 15 cm, 15 to 30 cm, and 30 to 45 cm. Periods of ice cover are indicated. Note that sampling dates (x axis) are not to scale. Source: [1].

Boothman and Helmstetter [4] studied the vertical and seasonal variability of AVS in uncontaminated marine sediments. Sediment cores were collected in the Pettaquamscutt Cove in Narragansett, Rhode Island five times between July 1990 and May 1991 and biweekly in June, July, and August 1991. The top 15 cm were collected and sliced into sections of 1 cm. Sections of 1 cm were analyzed for the top 5 cm as well as the 9 to 10 cm and 14 to 15 cm sections.

AVS distributions are presented in Figure 9-2. Replicate cores for 5 of the 11 sampling dates are represented by dashed lines. A general trend in depth variability is seen for each of the sampling periods. AVS is always lowest in the top 1 cm slice which may indicate the oxic sediment layer. Then AVS increases generally to the 10 cm slice and remains fairly constant from the 10 cm section to 15 cm section. Most of the variability is seen in the top 0 to 5 cm.

The profiles in Figure 9-2 indicate a seasonal variability in AVS levels. AVS concentrations in the top 5 cm increased from June to August with concentrations of 15 to 35 umol/g. The winter cores (top row) show lower AVS concentrations (10 to 25 umol/g) except for one measurement in the January 1991 core of about 30 umol/g. Boothman and Helmstetter [4] also found a strong correlation of AVS levels with overlying water temperature. They attribute vertical and seasonal variability of AVS in an uncontaminated marine sediment to two competing processes: microbial diagenetic sulfate reduction and oxidation of sulfides. In oxic water bodies diffusion of oxygen into the sediment from overlying water results in sulfide oxidation. Sulfide oxidation occurs in both the colder and warmer periods but rates of microbial activity and the production of sulfides are much greater, so that AVS levels increase in the summer months [1]. Sulfide oxidation is dependent on the presence of oxygen, diffusion rates, bioturbation, and the oxidation potential of the metal sulfides. A discussion of the oxidation of metal sulfides will be presented subsequently.

An AVS spatial and seasonal study was done using three freshwater lakes having seasonally anoxic hypolimnia and varying periods of stratification; Crosson Lake,

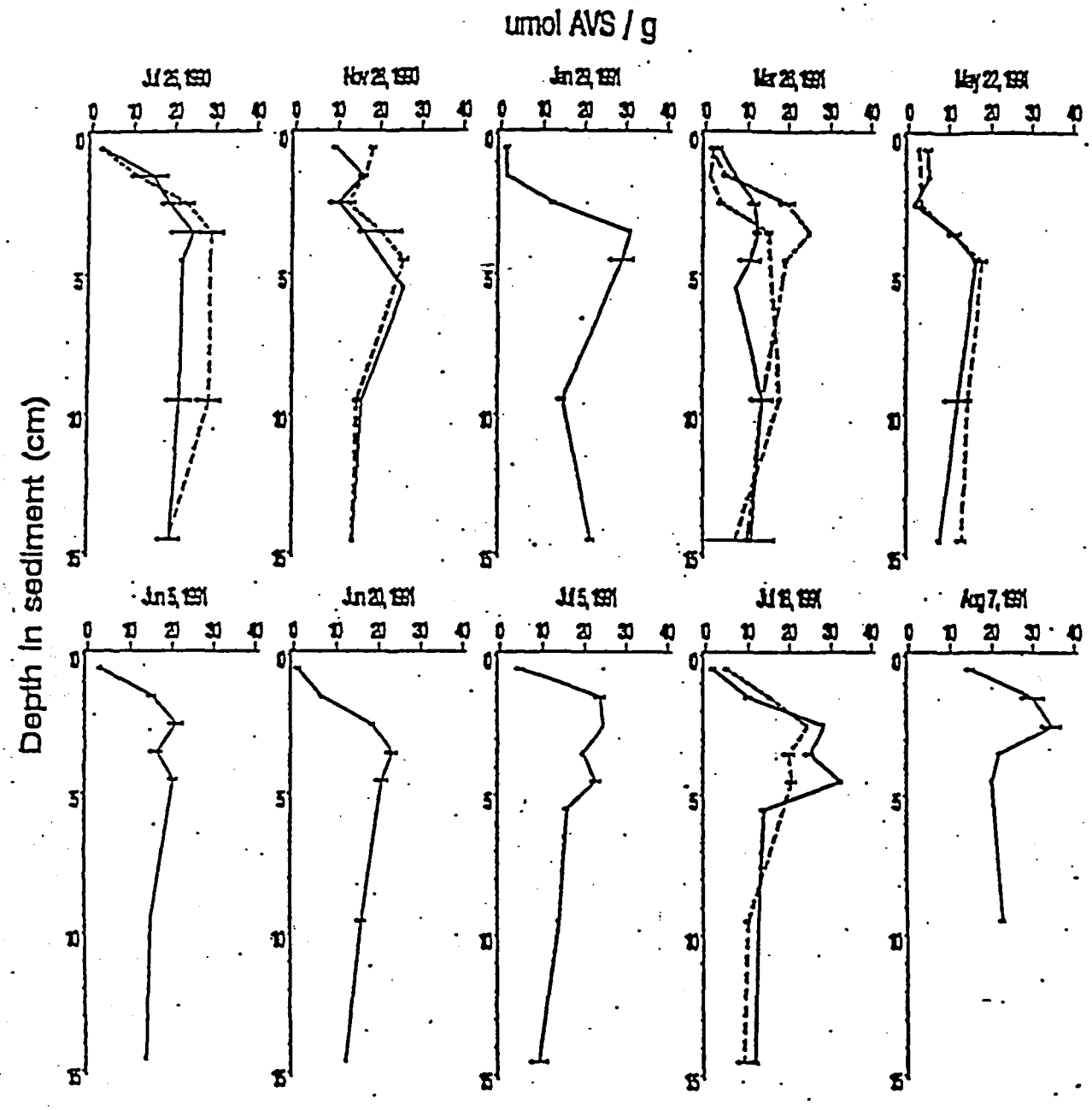


Figure 9-2. Vertical profiles of AVS in Pettaquamscutt Cove horizontal lines represent standard deviations for individual samples and dashed lines are results for replicate cores. Source: [4].

Gullfeather Lake, and Jake Lake, in Ontario [5]. For the spatial comparison sediments in all three lakes were sampled for AVS at various water column depths from the littoral zone to the main depositional basin of each lake during periods of anoxia. Crosson and Jake Lakes were also sampled during periods of no stratification. AVS results were reported as the mean of three replicates from the top 15 cm of sediment. Figure 9-3 presents AVS concentrations at various water column depths for the three lakes and comparisons of the anoxic (September) and oxygenated (May or August) periods at various water column depths for Crosson and Jake Lakes. Figure 9-3 indicates that AVS concentrations increase at greater overlying water depth in all three lakes during both anoxic and oxygenated periods. AVS concentrations were greatest during periods of anoxia.

For the AVS seasonal analysis, Jake Lake was sampled for AVS bimonthly from mid-April 1991 to mid-May 1992 at a lake depth of 21m. Figure 9-4 presents a temporal distribution of AVS. Turnover events and periods of anoxia as measured at the sediment/water interface are indicated. AVS was highest during periods of anoxia and began decreasing to a minimum following lake turnover. This is expected since as oxygen in the overlying water is depleted oxygen diffusion into the sediment ceases and sulfate reduces to sulfide thereby increasing the AVS. The key point here is that as the sediment becomes anaerobic and in the presence of sulfate and sulfate reducing bacteria AVS will form. This study did not report overlying water temperature. However the lowest AVS levels occur in May 1991 and December-January 1992 which is in agreement with other seasonal studies [1,4].

A 40 cm core was taken in Jake Lake on August 12, 1992 when the lake had just become anoxic to establish a profile of AVS concentration with sediment depth. Figure 9-5 presents this profile. The AVS sample at the sediment/water interface was less than 1.0 umol S/g wet sediment then increased to a high of 7.1 umol S/g wet sediment at about 8 cm. AVS concentrations showed less variability below 15 cm.

These three studies indicate the variability that can be expected in vertical and seasonal AVS concentrations. The studies indicate that AVS is low in the top 1 cm of

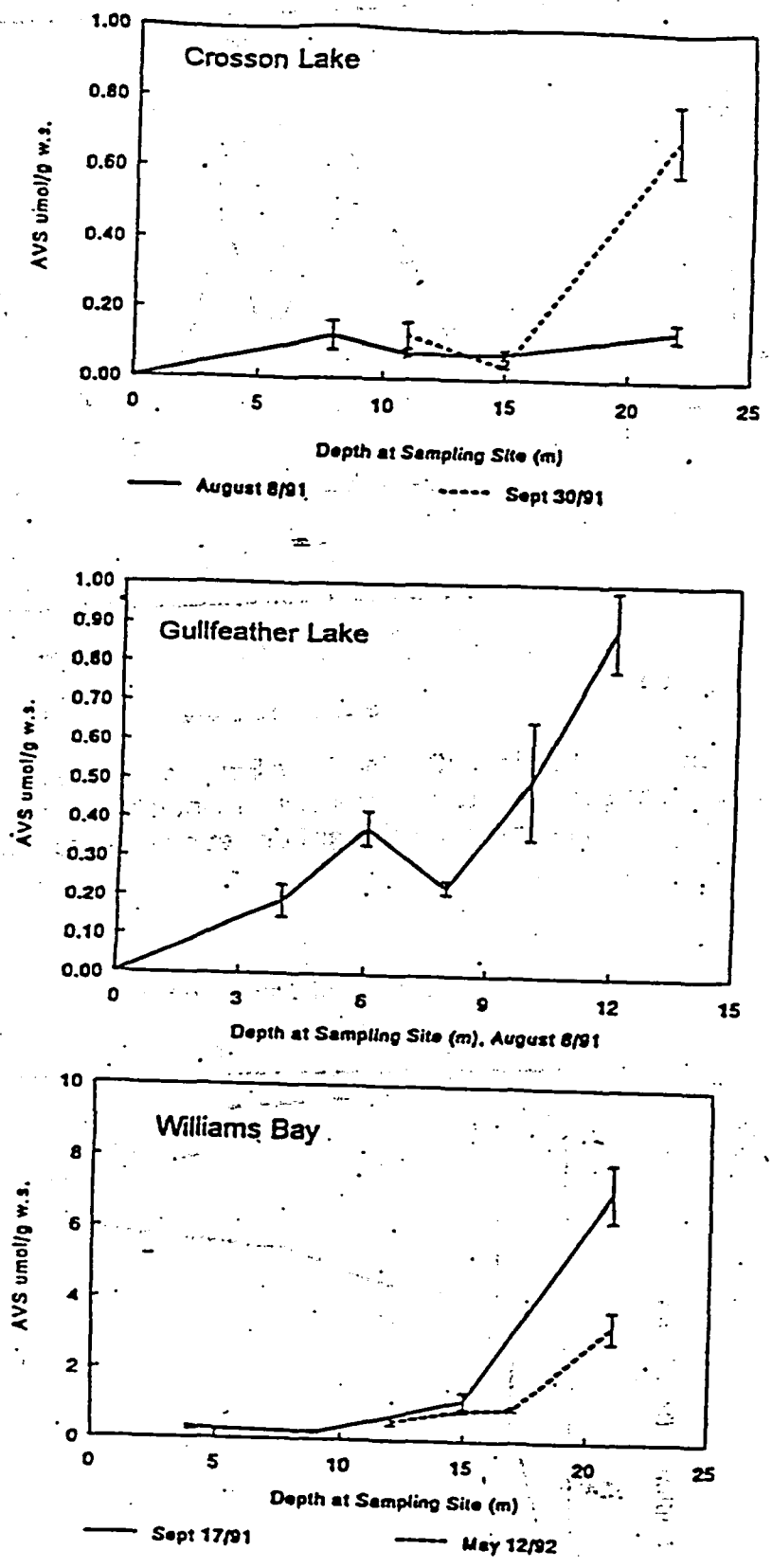


Figure 9-3. Spatial profiles of the top 0 to 15 cm of sediment AVS from the littoral zone to the main depositional basin in Crosson Lake (top panel), Gullfeather Lake (center panel), and Williams Bay, Jake Lake (bottom panel), Peterborough, Ontario. Samples for Crosson Lake were taken on August 8, 1991, before the hypolimnion went anoxic, and September 30, 1991, during the anoxic period. Samples for Gullfeather Lake were taken on August 8, 1991, when the hypolimnion was anoxic. Samples for Williams Bay were taken on September 17, 1991 during the anoxic period, and May 12, 1992 just after spring turnover. Error bars represent one standard deviation. Source: [5].

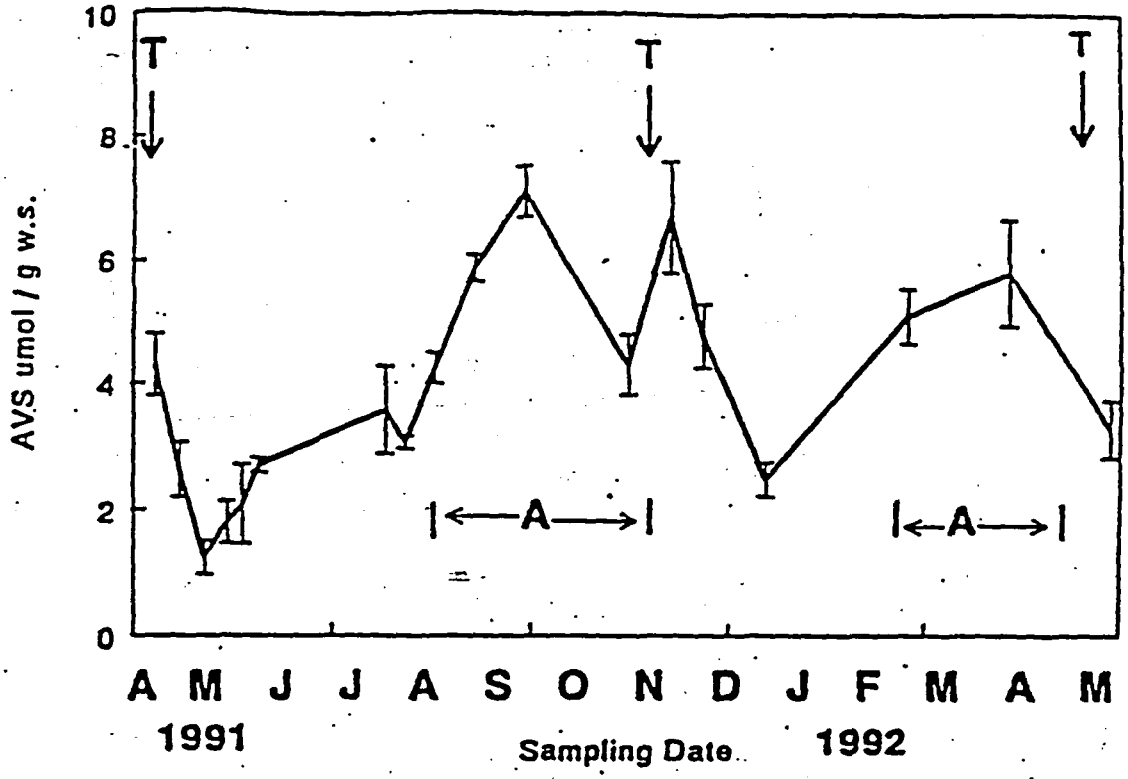


Figure 9-4. Seasonal variation in AVS in Williams Bay, Jake Lake at water depth of 21 m. Periods of anoxia at the sediment water interface are indicated by A and turnover events are indicated by T. Bars indicate one standard deviation. Source: [5].

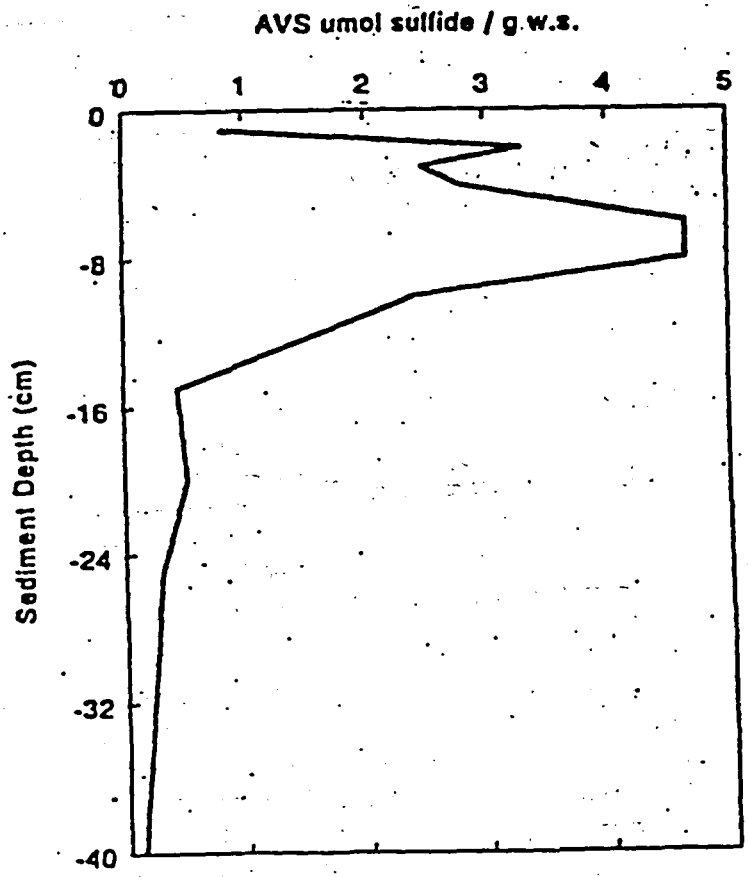


Figure 9-5. Vertical profile of AVS in Jack Lake at water depth of 21 m. Source: [5].

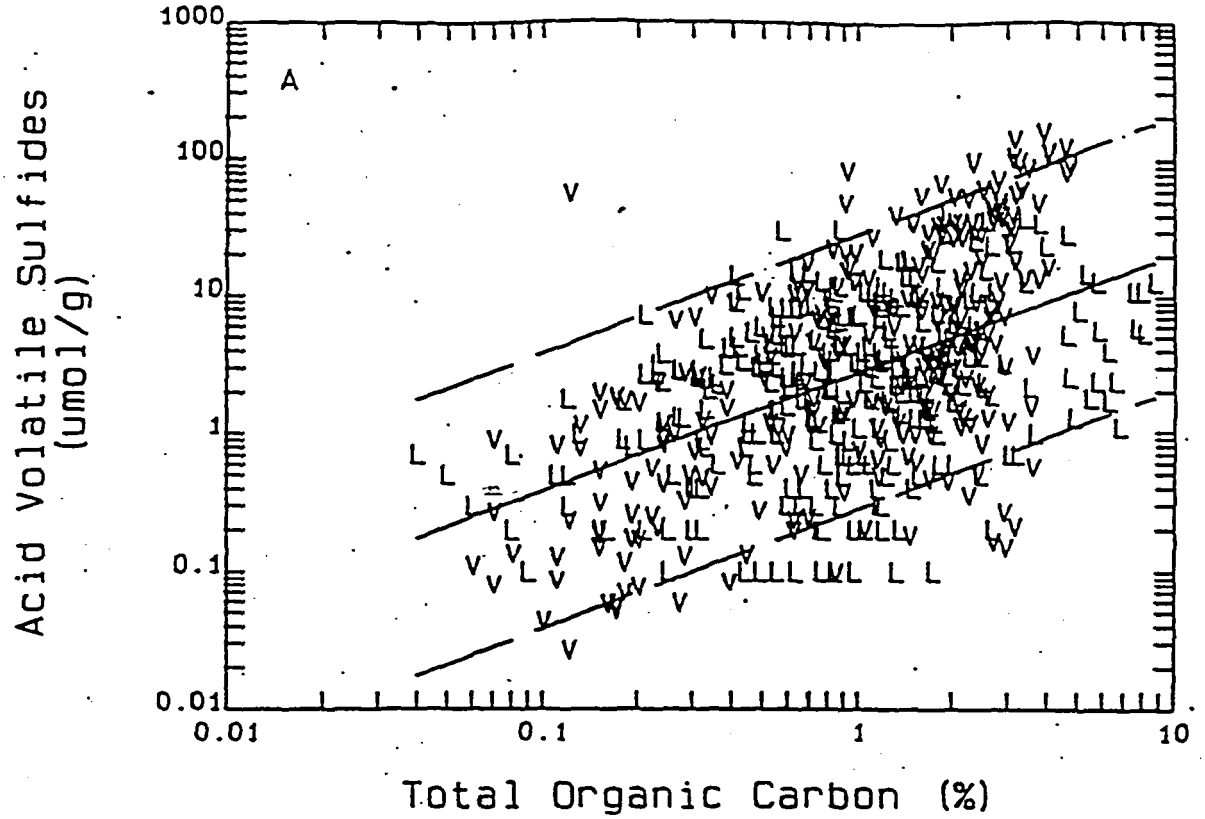
sediment. Presumably, oxygen at the sediment/water interface oxidizes the sulfides. The highest AVS levels are seen in the top 1 to 10 cm but then decrease and show less variability below 10 to 15 cm. In oxic water bodies AVS generally correlates to overlying water temperature. Microbial degradation of organic matter to produce sulfate and the reduction of sulfate to sulfide increases with increasing overlying water temperature and decreases as overlying water temperature decreases. As a result AVS can be expected to increase with increased water temperature and decrease as temperature decreases. Sulfide oxidation, which is dependent on the diffusion of oxygen into the sediment and the oxidation potential of the metal sulfides, also plays a role in vertical and seasonal AVS variability. In water bodies that have periods of anoxia AVS seems to correlate to overlying oxygen levels. Overlying water temperatures seem to affect AVS concentrations in the anoxic system presented.

The Correlation of AVS to Sediment Organic Carbon

Data from the US EPA Environmental Monitoring and Assessment Program (EMAP)[2] were summarized to examine possible relationships between total organic carbon (TOC) and AVS in marine sediments. Data are from the Gulf of Mexico (Louisiana Province) and from the Mid-Atlantic Coast (Virginian Province). The EMAP data was collected in the last week of July through the first week of September from 1990 through 1992. The data represent the top 2.0 cm.

In the EMAP data set TOC ranges from 0.1 to approximately 10 percent. The median TOC is approximately 1 percent. AVS ranges from approximately 0.1 to 100 umol/dry weight sediment with a median of approximately 3 umol/g. TOC and AVS measurements from the Virginian Province and the Louisianan Province had similar distributions.

AVS showed a positive correlation with TOC for the EMAP data. A linear regression of the log transformed AVS and TOC is shown on Figure 9-6 (solid line). The equation that relates TOC to AVS derived from this data set is:



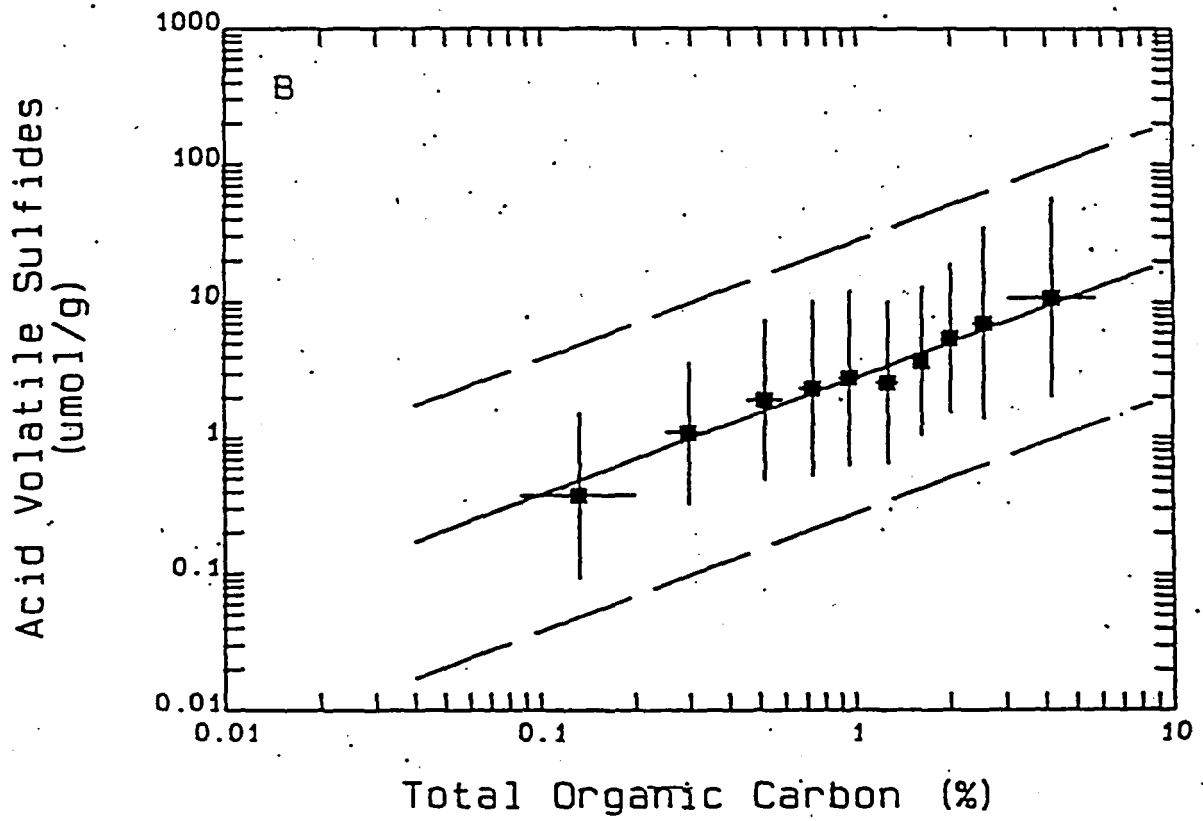


Figure 9-6. AVS versus percent TOC using EMAP [2] data, last week of July to first week of September 1990 to 1992. Data have been plotted by intervals having equal number of values. Horizontal bars represent TOC standard deviation and vertical bars represent AVS standard deviation. Line represents linear regression of log transformed AVS and % TOC.

$$\text{Log AVS} = 0.447 + 0.865 \text{ Log TOC} \quad (9\text{-}1)$$

The individual data from the Louisiana (L) and Virginia (V) Provinces are shown in Figure 9-6A. The data grouped into 10 intervals with an equal number of values and averaged is shown in Figure 9-6B. Although there is a roughly linear relationship between AVS and TOC (log slope = 0.87 which is almost 1.0), there is an enormous scatter. The lines in Figure 9-6 are a factor of 10 and 0.1 of the regression line as a visual aid to illustrate the variability in the data. Therefore, a prediction of AVS based on sediment TOC is highly uncertain. These data are in agreement with the results of Ankley et al. [6] who found no significant correlation between AVS and TOC in 17 sediment samples from an estuarine system contaminated with cadmium and nickel.

The basis of this analysis is that organic matter contributes to the formation of sulfides. Organic carbon exists in sediments in refractory and reactive forms. It is the reactive organic matter present in sediments that contributes to the formation of AVS. It, in turn, is the net result of the input of TOC by primary production plus terrestrial sources of TOC less particulate organic carbon (POC) loss by burial. Thus, the residual POC is a good index of the average concentration of reactive organic carbon but not the seasonal variation. The result in Figure 9-6A is not surprising considering the variability of AVS that has been shown in the previous discussion. By contrast, organic carbon concentrations are quite constant with respect to time [7]. The reason is that most of the organic carbon in sediments is very refractory with only a small percentage that is reactive [8].

Oxidation of Metal Sulfides

The oxidation of metal sulfides is an important component in the analysis of the ultimate fate and toxicity of metals in sediments. The oxidation of iron sulfide (FeS) controls the amount that is available to complex newly deposited metals. Also the seasonal cycle of AVS in natural sediments is controlled by a balance between the formation of AVS via the oxidation of organic carbon with sulfate as the electron acceptor, and the oxidation of AVS with oxygen as the oxidant. Thus a knowledge of the oxidation

kinetics and their interaction with other mass transport mechanisms in sediments is important to a proper use of sediment quality criteria based on AVS.

FeS(s) and CdS(s) Oxidation Kinetics

The rates of oxidation of iron and cadmium sulfides have been studied extensively at low pHs in the mining literature [9]. However, the oxidation of FeS in more natural settings has not received much attention with one notable exception. Nelson [10] studied the oxidation of synthetic FeS under a wide variety of conditions. Variations in pH, oxygen concentration, ionic strength, temperature, and the presence of catalytic metals were examined. His focus was on the initial rate of reaction. He proposed a surface complexation model which fit his experimental results quite successfully.

The entire time course of the reaction for synthetic FeS using Nelson's data and for AVS in sediments from other experiments, has recently been completed and a model for the kinetics of the oxidation has been proposed [11]. The model is based on the surface oxidation of FeS, as proposed by Nelson. The particles are assumed to have various particle size distributions. In particular a uniform and an exponential distribution of surface areas are considered. The equations and the solutions are listed in Table 9-1.

The results of fitting the model to synthetic FeS and sediment AVS are shown in Figure 9-7. The two model parameters are the zero order surface reaction rate, K, and the coefficient of variation of the particle size distribution. The symbols represent initial concentrations of FeS and AVS. The results indicate that the reaction rate is virtually the same for sediments and synthetic FeS at the same pH (Figures 9-7A, C, D). This suggests that all of the experimental information that has been generated for the pH, temperature, and O_2 dependence of the oxidation rate (Figure 9-8), is applicable to sediment AVS. In particular, the cadmium and iron oxidation kinetics used below assume that the oxidation rate is linear with respect to oxygen. The data in Figure 9-8B verify that assumption for synthetic FeS.

TABLE 9-1. FeS OXIDATION MODEL

Population balance equation:

$$\frac{\partial n}{\partial t} + \frac{\partial n}{\partial A}\frac{\partial A}{\partial t} = 0$$

where n(A,t) = number of particles with surface area in the interval A and A + dA, at time t. For a zero order rate of surface oxidation:

$$\frac{\partial A}{\partial t} = -k$$

the particle balance equation becomes:

$$\frac{\partial n}{\partial t} - k\frac{\partial n}{\partial A} = 0$$

For an initial particle size distribution: $n_o(A)$, the solution is:

$$n(A,t) = n_o(A + kt)$$

the concentration at any time t is found using the surface area concentration - surface area relationship:

$$c(t) = c_o\frac{\int_0^\infty n_o(A + kt)A^\gamma dA}{\int_0^\infty n_o(A)A^\gamma dA}$$

where γ is the volume to surface area exponent. For a uniform number density:

$$n_o(A) = \frac{n_o}{A_2 - A_1} \qquad A_1 \le A \le A_2$$

$$= 0 \qquad \text{elsewhere}$$

The result is:

$$c(t) + c_o\frac{p(A_2 - k't)^{\gamma+1} - p(A_1\ k't)^{\gamma+1}}{A_2^{\gamma+1} - A_1^{\gamma+1}}$$

where p(A), the positive function, is the positive portion of its argument A. Using the mean, μ, and coefficient of variation, v, of the uniform density yields:

$$c(t) = c_o\frac{p(1 + \sqrt{3}v - kt)^{\gamma+1} - p(1 - \sqrt{3}v - kt)^{\gamma+1}}{(1 + \sqrt{3}v)^{\gamma+1} - (1 - \sqrt{3}v)^{\gamma+1}}$$

where $k = k'/\mu$. The parameters are γ, the volume to surface area exponent; v, the coefficient of variation of the number density; and k, the decay rate.

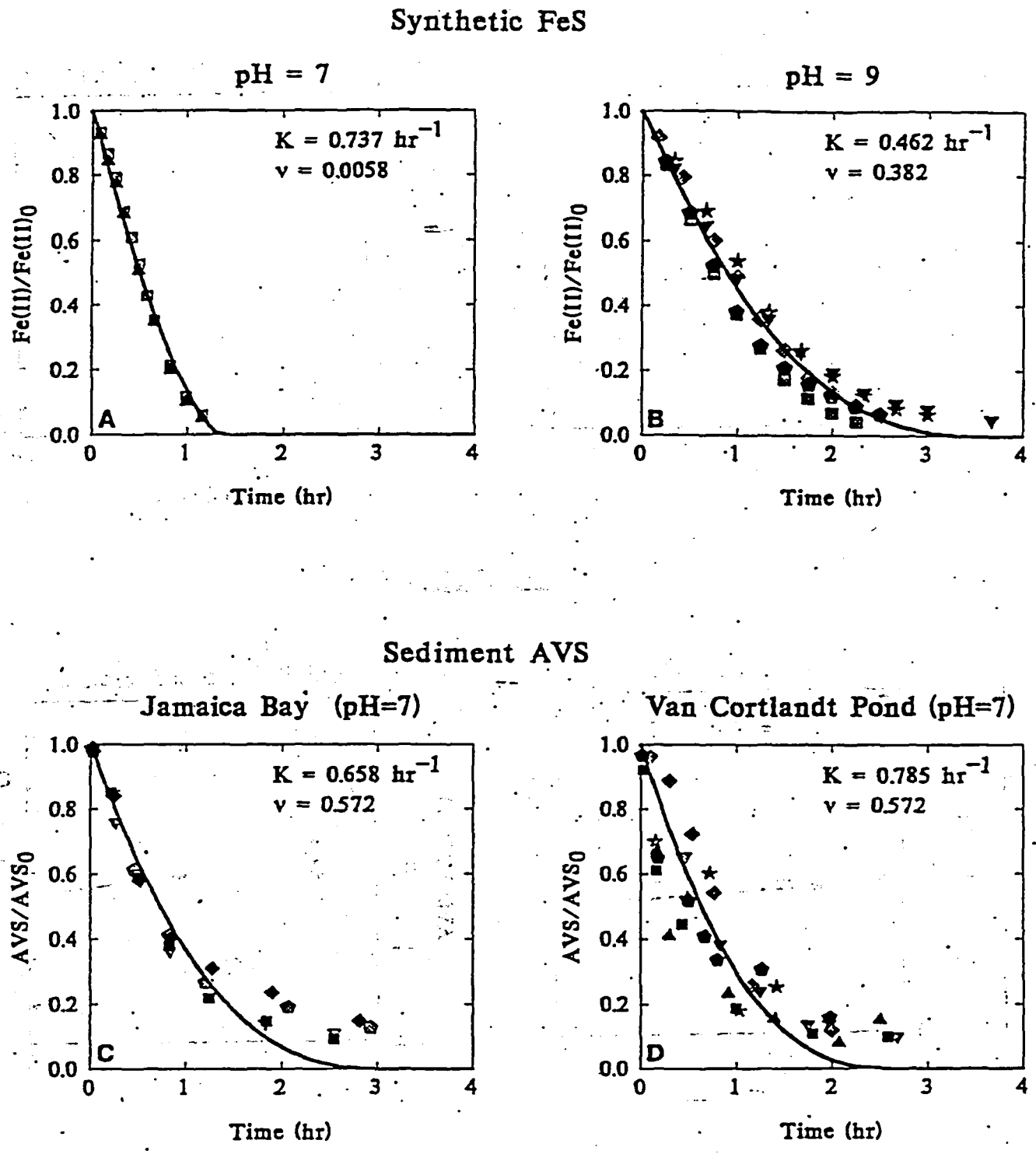


Figure 9-7. FeS oxidation polydisperse particle distribution model fitting synthetic FeS and sediment AVS. The zero order surface reaction rate, K and the coefficient of variation of the particle size distribution, v are shown for synthetic FeS at pH 6 and 7 and AVS for two sediments; Jamaica Bay and Van Cortlandt Pond.

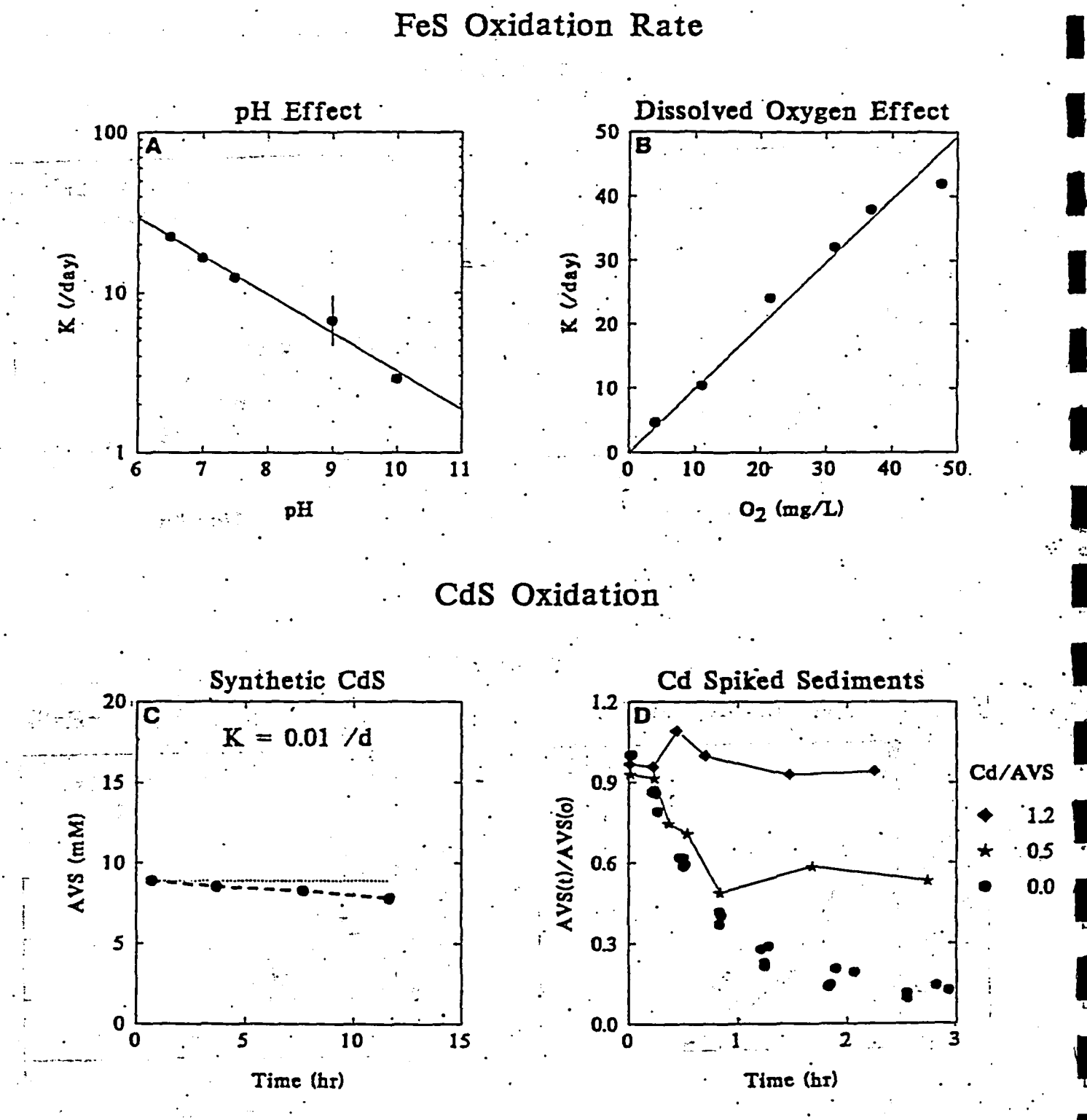


Figure 9-8. The effect of pH (panel A) and dissolved oxygen (panel B) on the FeS oxidation rate. Oxidation results of metal-sulfide oxidation experiments using synthetic CdS (panel C) and cadmium spiked sediments.

The initial results from a series of metal-sulfide oxidation experiments using synthetic CdS are presented in Figure 9-8C. The reaction rate is much slower than the rates found for FeS (Figure 9-7A). Cadmium spiked sediments show the same slow oxidation rate (Figure 9-8D). For Cd/AVS = 0, the AVS is all FeS and the oxidation is rapid. When a fraction (Cd/AVS = 0.5) or all (Cd/AVS = 1.2) of the FeS is converted to CdS by adding cadmium to the sediment, that fraction of the AVS does not oxidize in the time scale of this experiment. Also, Zhuang et al. [12] conducted a series of laboratory aeration experiments in batch reactors to investigate the effects of aeration of sediment on the sulfide content of sediment and on the partitioning of cadmium to the sediment. Aeration of the sediment resulted in a rapid decrease in AVS. Concentations of dissolved cadmium increased while concentrations of cadmium associated with AVS and with pyrite decreased.

Sediment Metal Oxidation Model

The rate at which cadmium sulfide oxidizes in sediments depends not only on the rate it oxidizes in an aerobic environment but also the rate at which FeS oxidizes, which controls the depth of the aerobic layer. This is the mechanism that can cause the cadmium-AVS molar ratio in the surface layer of the sediment to change from a value of less than one to a value of greater than one, with the possible concomitant increase in toxicity.

The oxidation kinetics of FeS and CdS are a necessary part of a model of the oxidation and release of metals from sediments. Work has been proceeding to develop such a comprehensive model. The model is based on a sediment flux model that has been developed for oxygen and nutrients [6]. The formulation for the cadmium flux model is illustrated in Figure 9-9. The sediment is idealized as having two layers: (1) an aerobic layer (1) where the oxygen concentration is greater than zero; and (2) an anaerobic layer where the oxygen is zero. Sulfate reduction in this layer produces sulfide which interacts with the iron present to form iron monosulfide (FeS).

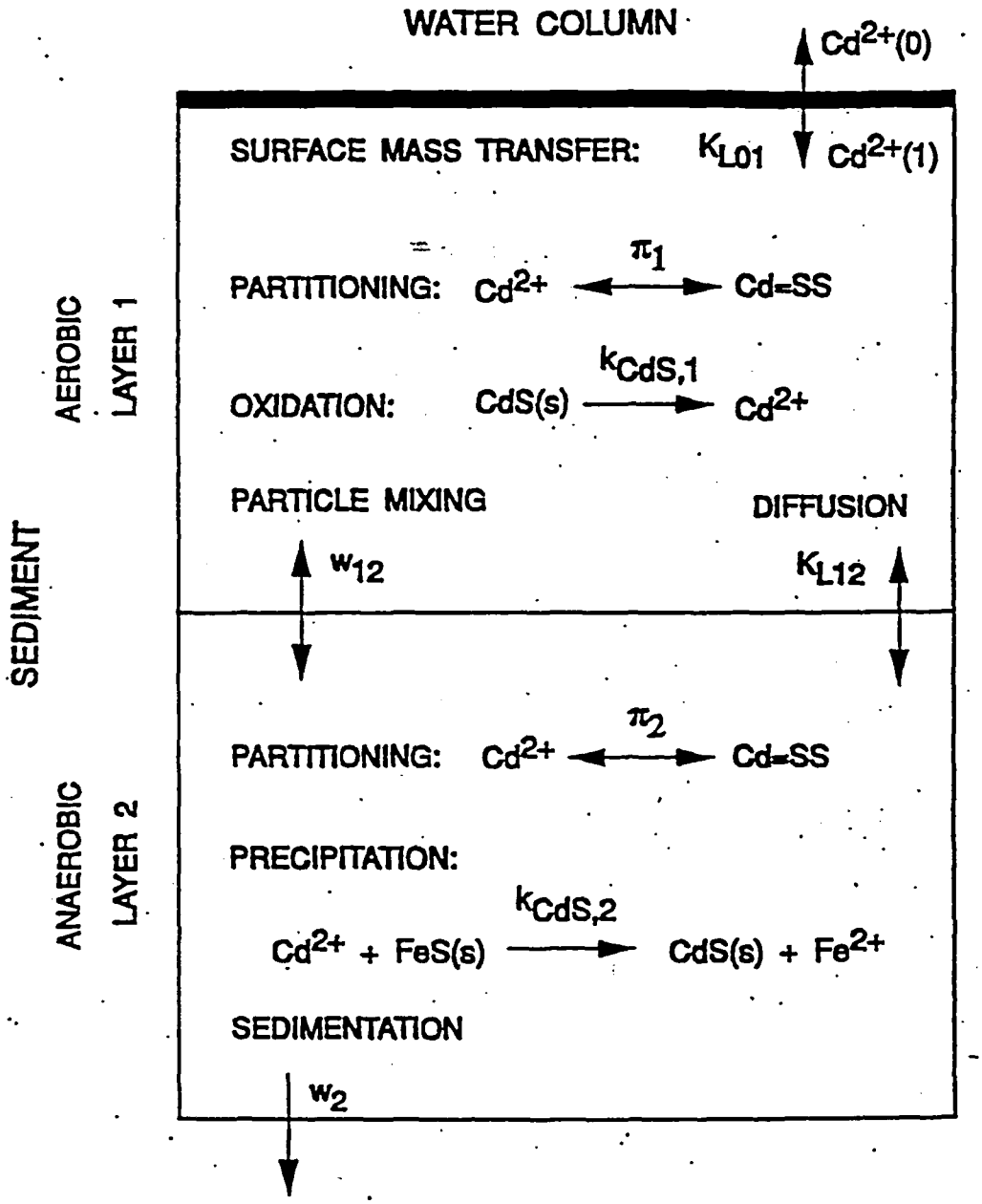


Figure 9-9. Cadmium flux model. The sediment is represented by an aerobic layer and an anaerobic layer.

Cadmium enters the sediment either by surface mass transfer from the overlying water, K_{L01}, or as particles settling to the sediment. The reactions in the aerobic layer are the partitioning of cadmium to the sediment solids. Particles and dissolved cadmium are biotically and abiotically, transported to the anaerobic layer where cadmium sulfide is formed. Cds transport to the aerobic layer is either by particle mixing, w_{12}, or by diffusion of dissolved cadmium, K_{L12}. Cadmium sulfide oxidation produces Cd^{2+} which, after partitioning, escapes from the sediment as a flux to the overlying water via surface mass transfer.

A one dimensional model for cadmium and iron sulfide, oxygen, and dissolved + sorbed cadmium is based on the mass balance equations listed in Table 9-2. The mechanisms for cadmium transport and kinetics are shown in Figure 9-9. Models of this sort have been employed before [13]. The novelty here is the inclusion of the sulfide reactions. The kinetics of oxidation of both iron and cadmium sulfide are first order in oxygen and sulfide concentration. The data used to justify these kinetics are shown in Figures 9-7 and 9-8. Cadmium sulfide oxidizes at a rate: $k_{CdS}[O_2][CdS]$ (Table 9-1; Equation 9-1) consuming oxygen (Equation 9-3) and liberating cadmium to the interstitial water and therefore becoming a source to the dissolved + sorbed cadmium (Equation 9-4). The fraction that is dissolved is determined by the partitioning expression (Equation 9-7) which affects the magnitude of the diffusion coefficient of total sorbed + dissolved cadmium. Iron sulfide oxidizes at a rate: $k_{FeS}[O_2][FeS]$ (Equation 9-2) and consumes oxygen (Equation 9-3). The formulation for particle mixing by bioturbation is conventional [14] - particle diffusion that exponentially decays in depth with characteristic mixing depth z_B (Equation 9-5). A source of FeS, J_{O2} from organic matter diagenesis, is added (Equation 9-2) to account for the generation of AVS during the experiment.

The solutions to the equations in Table 9-2 are obtained using an implicit finite difference formulation with the nonlinear terms lagged by one time step. The model vertical resolution is 1 mm. The parameters of the model are the oxidation rates: k_{CdS} and k_{FeS}, and the mixing parameters for particles, D_p and z_B, and interstitial water, D_d, and the AVS source, J_{O2}.

TABLE 9-2. MODEL OF CADMIUM AND AVS DISTRIBUTION

Mass balance equations for cadmium sulfide, CdS(z,t), iron sulfide, FeS(z,t) dissolved oxygen, $O_2(z,t)$ and dissolved + sorbed cadmium, C_T:

$$\frac{\partial[CdS]}{\partial t} = \frac{\partial}{\partial z} D_P \frac{\partial[CdS]}{\partial z} - k_{CdS}[O_2][CdS] \tag{1}$$

$$\frac{\partial[FeS]}{\partial t} = \frac{\partial}{\partial z} D_P \frac{\partial[FeS]}{\partial z} - k_{FeS}[O_2][FeS] + \frac{J_{O_2}}{H} \tag{2}$$

$$\frac{\partial[O_2]}{\partial t} = \frac{\partial}{\partial z} D_d \frac{\partial[O_2]}{\partial z} - k_{CdS}[O_2][CdS] - k_{FeS}[O_2][FeS] \tag{3}$$

$$\frac{\partial[Cd_t]}{\partial t} = \frac{\partial}{\partial z} D_t \frac{\partial[Cd_t]}{\partial z} + k_{CdS}[O_2][CdS] \tag{4}$$

where k_{CdS} and k_{FeS} are the oxidation rates of CdS and FeS, J_{O2}, is the source of FeS from organic matter diagenesis, H is the depth of the sediment, and:

$$D_P = D_{P_0} e^{-\frac{z}{z_B}} \tag{5}$$

is the particle mixing diffusion coefficient, z_B is the characteristic depth of bioturbation, D_d is the diffusion coefficient in porewater, and:

$$D_T = D_P f_P + D_d f_d \tag{6}$$

is the weighted diffusion coefficient for dissolved + sorbed cadmium. The dissolved, f_d, and particulate, f_p, fractions are:

$$f_d = \frac{1}{1 + m\pi} = 1 - f_P \tag{7}$$

with m = solids concentration and π = dissolved cadmium partition coefficient.

A set of data from the colonization experiment (Chapter 7) designed to test the toxicity of the sediment can be used for an initial evaluation of the model [15]. Raw seawater is allowed to flow over sediments that have been spiked uniformly with various concentrations of cadmium so that the initial concentrations of AVS and cadmium are constant with depth. The larval forms of benthic organisms settle and colonize the sediment. The experiment was carried out for 118 days. The vertical distribution of AVS and cadmium were measured in 6 mm slices, the smallest practical interval. Four concentrations of cadmium were dosed into the sediment: 0, 0.1, 0.8, and 3.0 times the moles of AVS in the sediment. The vertical profiles were measured at day 28, 57, and 118.

The observations and model computations are shown in Figure 9-10 for AVS, Figure 9-11 for cadmium, and Figure 9-12 for SEM to AVS ratio. The columns correspond to each of the three sampling days. The rows correspond to progressively increasing cadmium concentrations. The vertical distributions of AVS and cadmium are reproduced reasonably well by the model except for the bottom row where the Cd/AVS = 3 and the sediment was toxic to benthic biota. Presumably in this treatment the rate of bioturbation decreased and less oxidation occurred than predicted. The computed vertical distribution of dissolved oxygen is also shown as a dashed line in the AVS plot (Figure 9-10). The critical result is that in order to reproduce the vertical distribution of AVS it is necessary to mix the particles. Presumably this is the result of bioturbation by the organisms that colonized the sediment. The presence of significant impacts on many benthic organisms (Chapter 7) and lack of model fit for Cd/AVS = 3 supports this hypothesis. The model also reproduces the trend of increasing SEM/AVS ratio that occurs in the top 1 to 2 cm of the sediment, although the magnitudes of the calculated increases are not as large as is observed in the topmost 6 mm in the 0.8x treatment and larger than observed in the 0.1x treatment.

The parameters used in this simulation are listed in Table 9-3. In particular the rate of FeS oxidation is consistent with the kinetics obtained from synthetic and sediment AVS

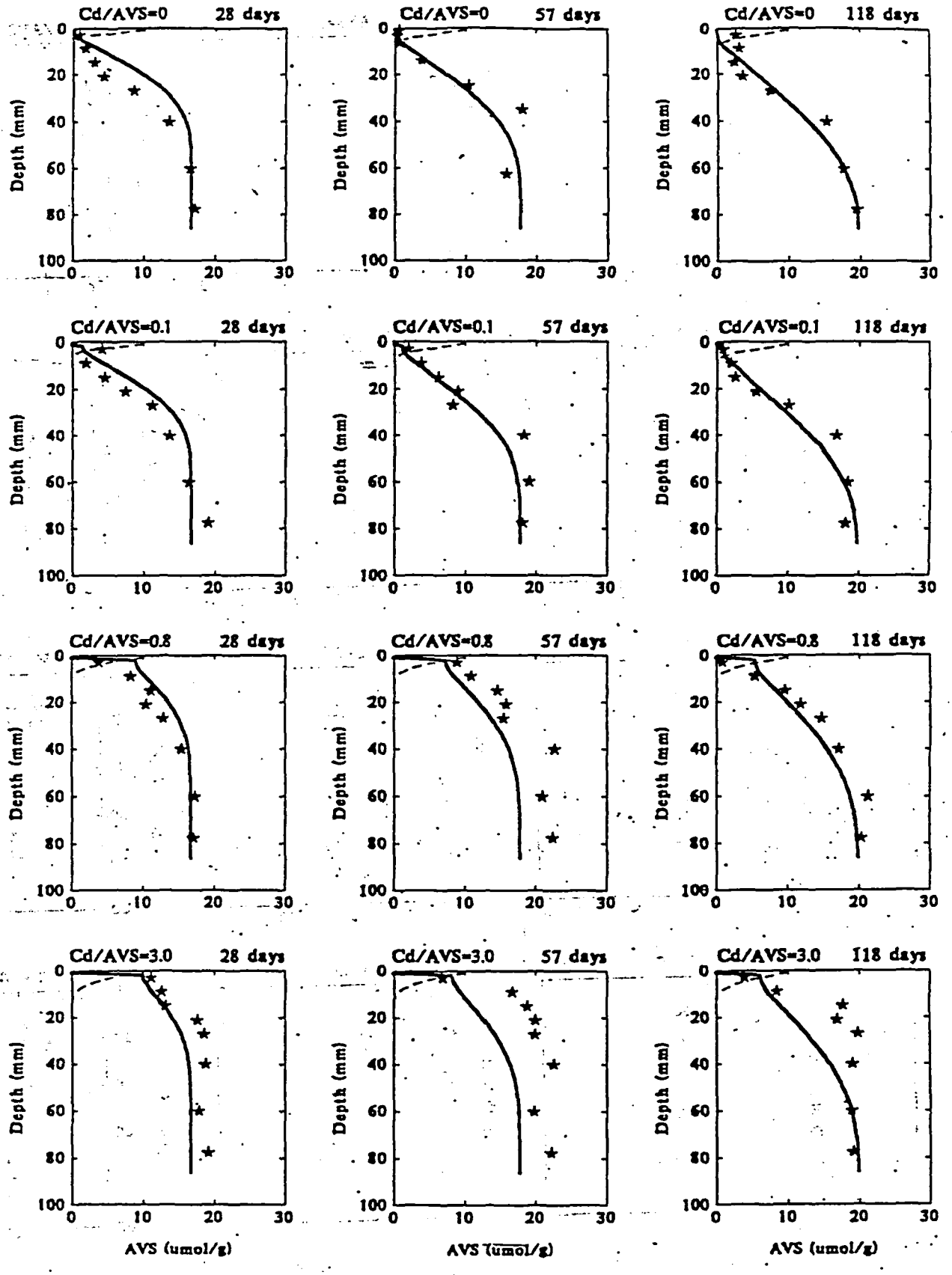


Figure 9-10. Vertical distributions of AVS for the field colonization experiment at days 28, 57, and 118 for nominal treatments of 0., 0.1, 0.8, and 3.0 Cd/AVS ratios (symbols) and cadmium flux model results (solid line). The dashed line is the computed vertical distribution of dissolved oxygen.

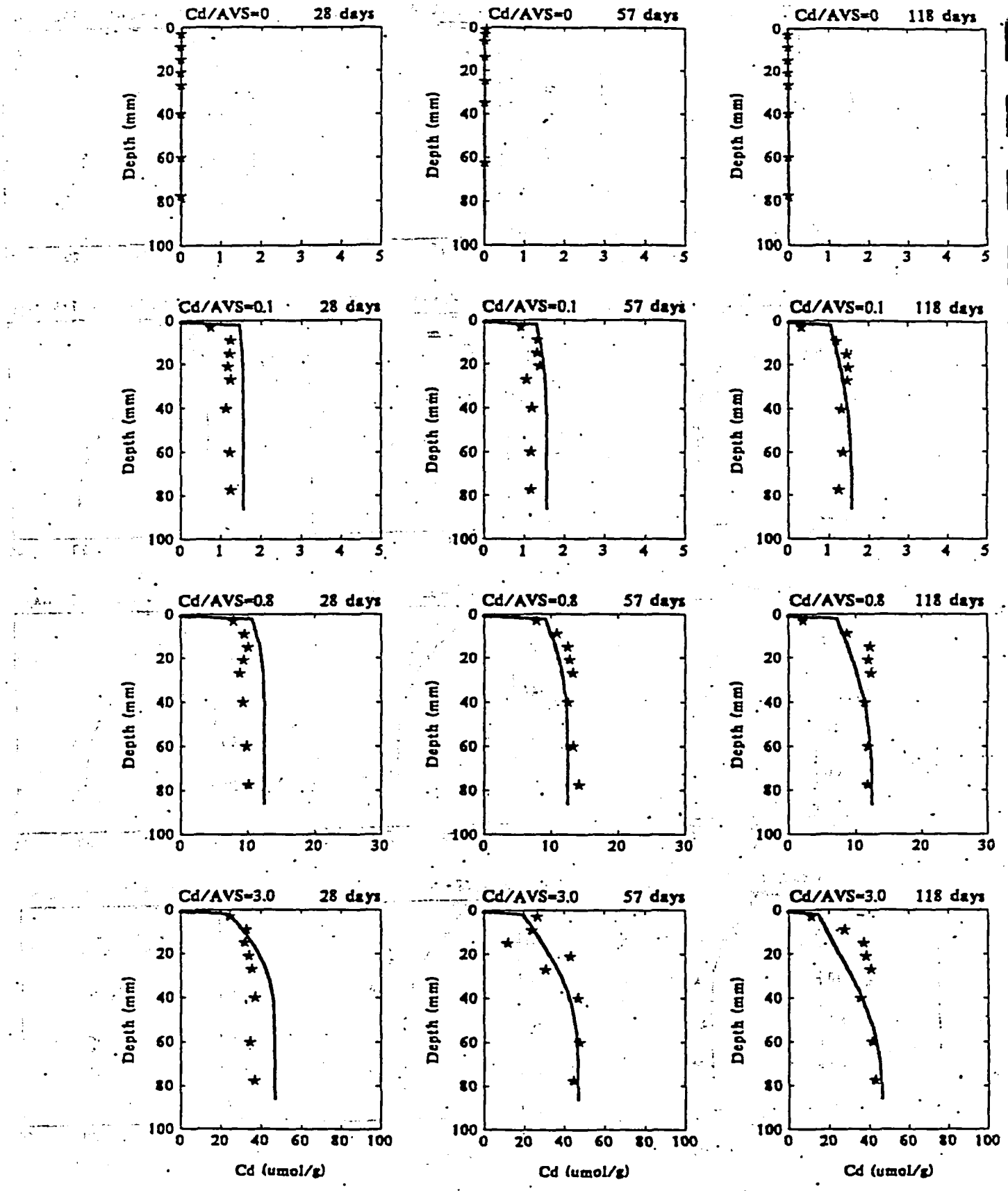


Figure 9-11. Vertical distributions of cadmium SEM for the field colonization experiment at days 28, 57, and 118 for nominal treatments of 0., 0.1, 0.8, and 3.0 Cd/AVS ratios (symbols) and cadmium flux model results (solid line).

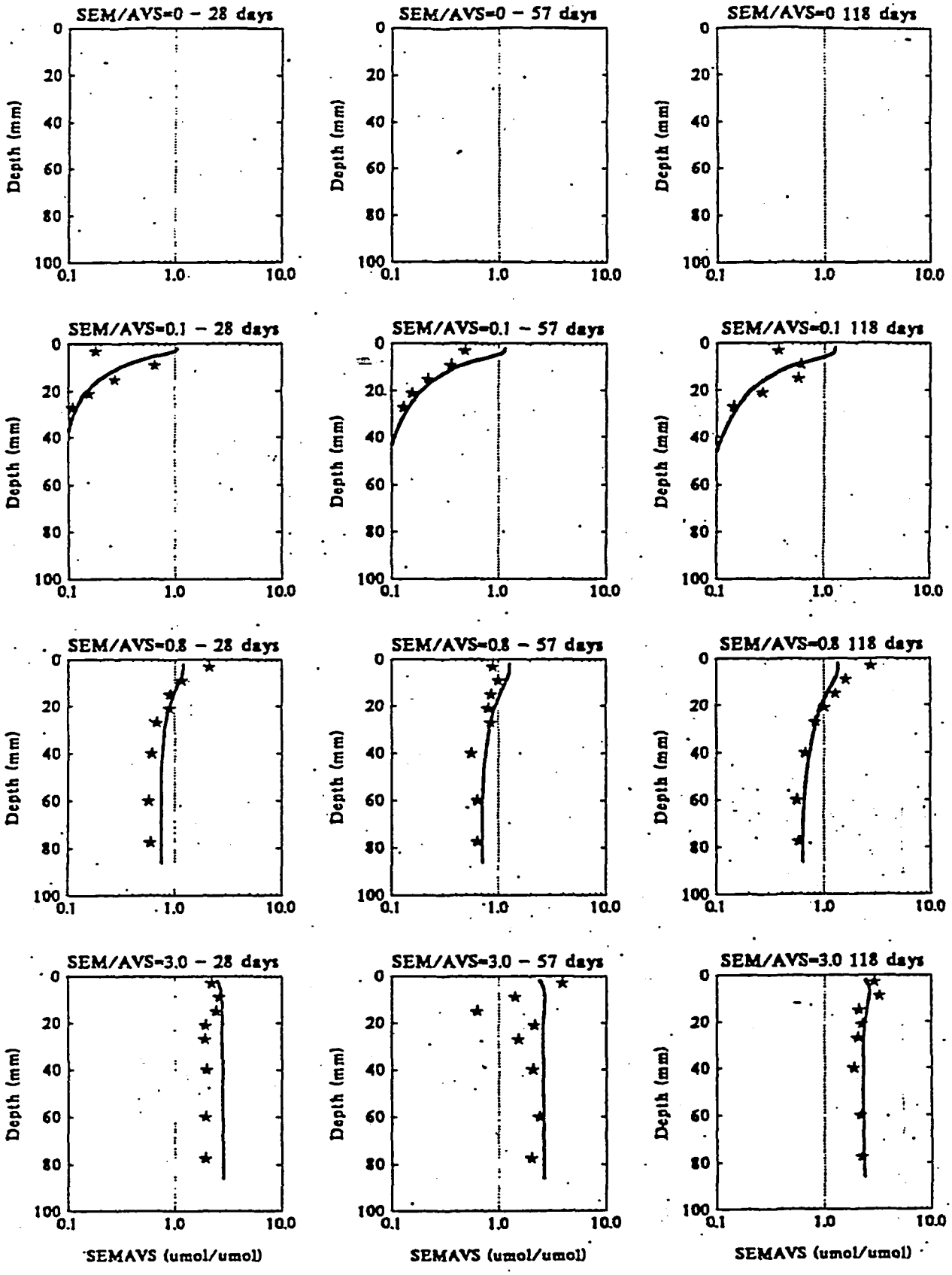


Figure 9-12. Vertical distributions of SEM/AVS ratios for the field colonization experiment at days 28, 57, and 118 for nominal treatments of 0., 0.1, 0.8, and 3.0 Cd/AVS ratios (symbols) and cadmium flux model results (solid line).

oxidation experiments reported above. The oxidation rate of cadmium sulfide is not inconsistent with the results of the initial experiments.

A preliminary application of this model to data from a year long field colonization experiment with zinc contaminated sediments was performed [16]. The purpose of the field colonization experiment was to investigate the seasonal realtionships between AVS and the toxicity of zinc to benthic organisms. The FeS oxidation rate and particule mixing parameters applied in the calibration were similar to those used in the cadmium colonization model calibration (Table 9-3). The zinc oxidation rate was then calibrated to the data. Data (symbols) from the sampling after 92 days (Figure 9-13) and near the end of the experiment (327 days, Figure 9-14) illustrate the fit of the model (solid line) to the data. A very low zinc oxidation rate (Table 9-3 which is indistinguishable from zero) provided the best model fit. The results indicate that very little zinc sulfide has oxidized.

TABLE 9-3. SEDIMENT MODEL

	Cd (Colonization Experiment)[15]	Cd (Effect of oligochaetes experiment) [17]	Zinc (Colonization Experiment)[16]
D_d (cm^2/d)	1.0	1.0	0.1
D_p (cm^2/d)	0.1	.01	0.1
Z_B (cm)	5.0	5.0	5.0
k_{FeS} (L/mg O_2-d)	3.4	3.8	3.4
k_{MS} (L/mg O_2-d)	0.01	0.01	1×10^{-7}
$\pi_1 = \pi_2$ (L/kg)	300	300	300
J_{O2} (gm/m^2d)	0.2	0	0.2

An initial experiment which was designed to emphasize the effect of bioturbation has been performed using oligochaetes [17]. It is well known that these organisms can rework the surface sediment which causes an increase in AVS oxidation. Initial results from these experiments are shown in Figure 9-15 which presents the vertical profiles of AVS and cadmium with and without oligochaetes added to the surface of the sediment. The lines are computed using the same coefficients as before (Table 9-3) with the exception of particle mixing. For the case without oligochaetes it is zero. For the case with oligochaetes it is a factor of 10 lower than the colonization experiment, reflecting the

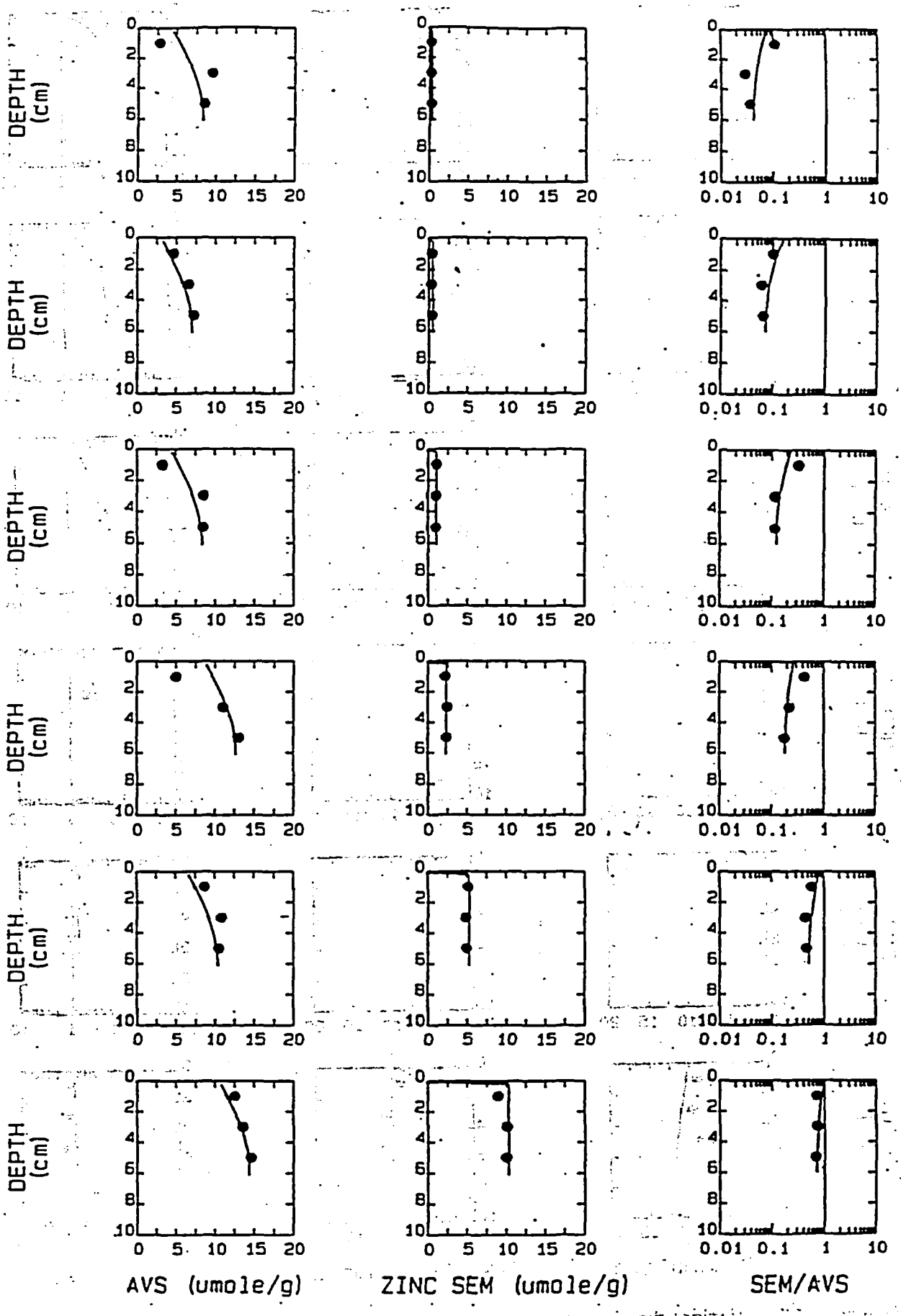


Figure 9-13. Vertical distributions of AVS, zinc SEM and SEM/AVS ratios at day 92 of the zinc field experiment for the control and five treatments.

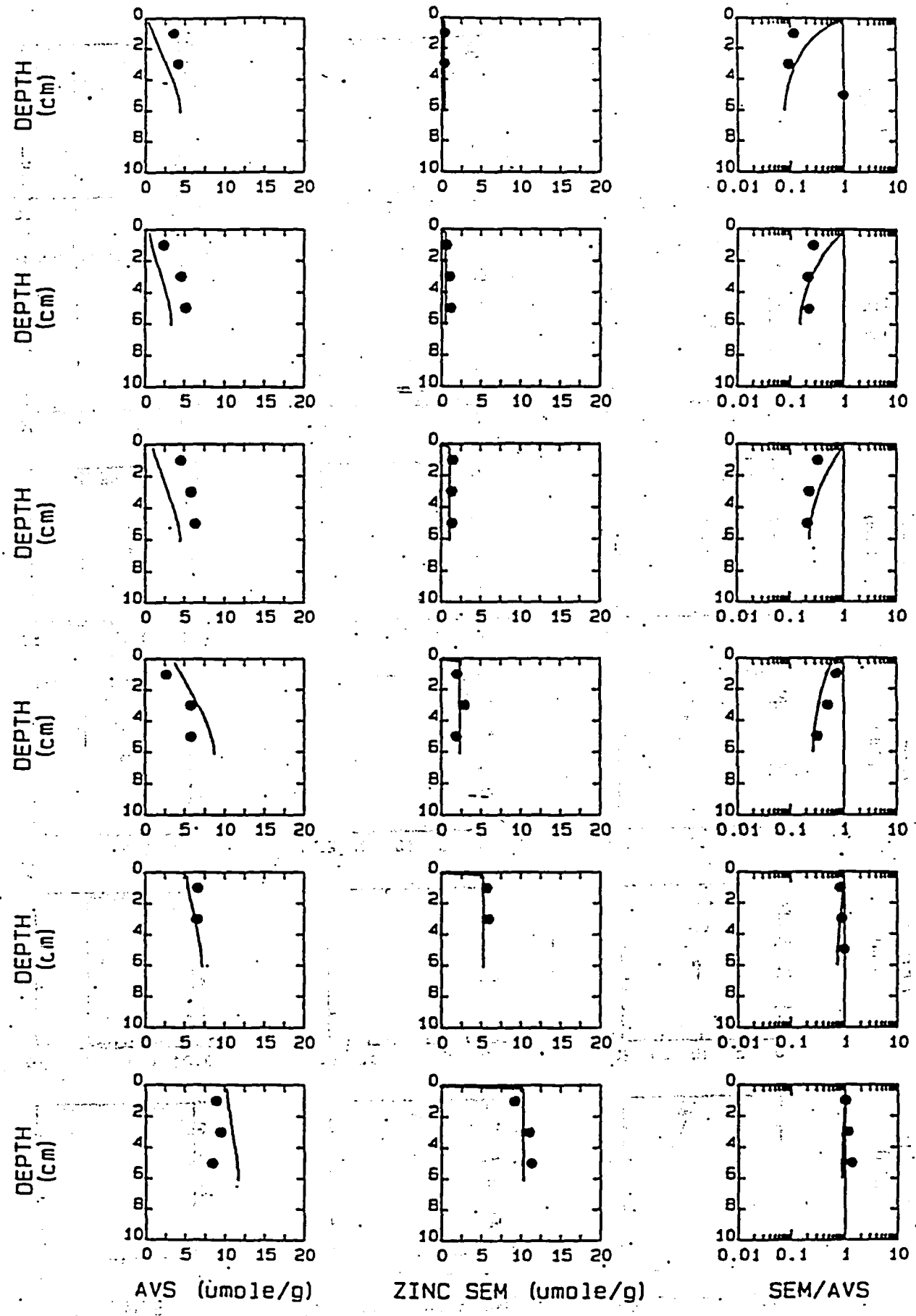


Figure 9-14. Vertical distributions of AVS, zinc SEM and SEM/AVS ratios at day 327 of the zinc field experiment for the control and five treatments.

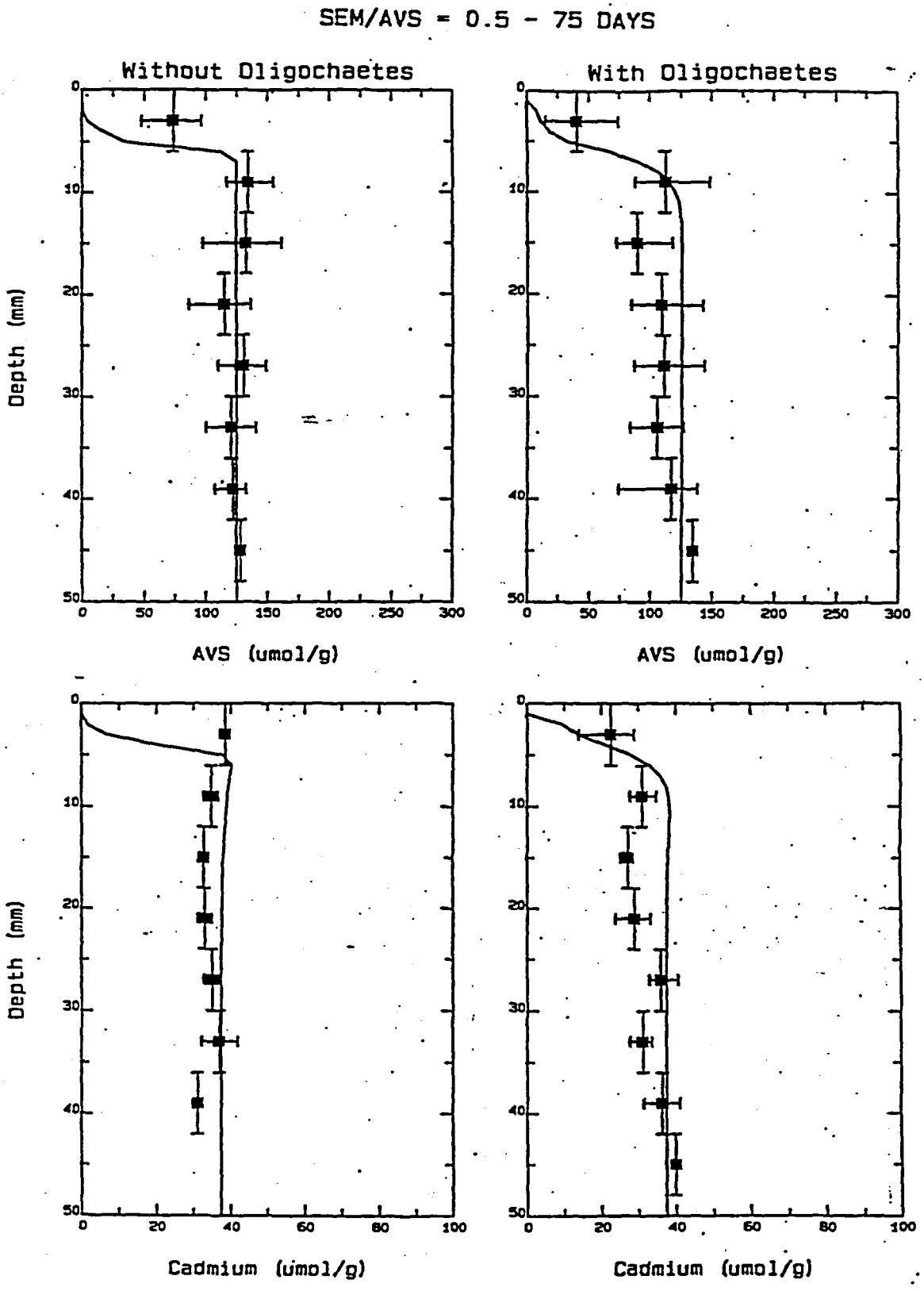


Figure 9-15. Vertical distributions of AVS (top panels) and cadmium (bottom panels) for with (left panels) and without (right panels) oligochaetes for cadmium oxidation experiment and benthic mixing model. Data are plotted as means (symbols) and ranges (vertical and horizontal bars) for plotting intervals. The model results are represented by the solid line.

lower benthic biomass. The model is in reasonable agreement with the observations. The result points out the need for an independent tracer for particle mixing so that the particle diffussion coefficient can be determined separately.

Conclusions

The oxidation of the metal sulfides is a critical mechanism that can liberate the metals from the anaerobic layer and cause the SEM/AVS ratio to exceed one and thereby possibly cause toxicity. The loss of FeS and the liberation of free metal from its metal sulfide both contribute to this phenomena. The kinetics of FeS oxidation are well understood. Application of the laboratory measured rates in models of the vertical distribution of sediments reproduce the observed decline in AVS.

The equivalent definitive laboratory data for the oxidation of the other metal sulfides of interest are not yet available. Initial results for cadmium suggest that the rate is much slower than for FeS but still large enough to liberate an amount of cadmium sufficient to change the SEM/AVS from less than to greater than one in the top layers of the sediment which would increase interstitial cadmium to amounts of toxicological significance and result in impacts in benthic biota (see Chapter 7). However a similar experiment for zinc failed to produce such a result, suggesting that the oxidation rate of zinc sulfide is much slower than cadmium sulfide.

Organic Carbon Binding

The binding of metals to other phases in sediments also can be important in determining toxicity when SEM exceeds AVS. This can be seen by considering the data presented previously (Chapters 5 through 7). If the SEM/AVS ratio is greater than one then, 56.8 percent of the sediments were toxic. If both SEM/AVS > 1 and the porewater metals toxic unit concentrations >0.5 then 79.1 percent of the sediments were toxic. Thus even if the SEM/AVS ratio is greater than one, implying that all the binding capacity of the AVS has been exhausted, there may be another sediment component that is

providing binding capacity for the metal and reducing its activity and, therefore, its toxicity (see Figure 6-15). If the binding capacity is sufficient, the pore water toxic unit concentration should be insignificant toxicologically. If, however, all the strong binding components are exhausted, then the sediment pore water toxic unit concentrations will exceed one and the sediment could be toxic. The data presented previously shows that this is indeed the case where 79.1 of the sediments tested were toxic when SEM/AVS > 1.0 and IWTU 70.5 (see Table 6-3). For the remaining 20.9 percent it is likely that dissolved ligands (probably dissolved organic carbon) and dissolved sulfide are providing additional binding capacity.

An experimental method has been developed to investigate the sediment chemistry associated with metal sorption under anaerobic conditions at equilibrium. It is named the Anoxic Sequential Batch Titration (ASBT) method (see Appendix 9A for a description). Sediment properties other than AVS were correlated to metals binding capacities in excess of AVS binding capacity (i.e., non-AVS sorptive capacity), and equivalently to metals porewater activity for copper, cadmium and lead at varying pHs. The results of partitioning behavior of these three metals to several freshwater sediments under anaerobic conditions are presented below.

Analysis Framework

The experimental protocol developed in this study was designed to investigate the sorption of copper, cadmium, or lead under anaerobic conditions at equilibrium. The experimental procedure allows (a) sediment samples to be contaminated with varying metal concentrations under anaerobic conditions, (b) direct measurement of aqueous metals activity, and (c) simultaneous sediment AVS determination on unspiked sediment samples from the same homogenates.

The pH of the solution phase was controlled using various buffers. Metal complexation by the buffer matrix was eliminated by using Goode buffers [18 through 20]. These buffers are designed to be non-reactive with metal species. The dissolved oxygen

in the system was eliminated by stripping with nitrogen, and confirmed by direct measurement. By controlling these two parameters, the water in the ASBT system provides a chemical environment that is similar to that found in anaerobic sediments. The exception to this is the dilution of porewater dissolved species.

The ASBT experimental procedure was evaluated with respect to several important factors impacting sorption processes and anaerobic sediment chemistry. The four parameters evaluated were (a) deoxygenation efficiency, (b) maintenance of a reducing chemical environment, (c) sorption kinetics, and (d) particle induced desorption mechanisms. The results of these evaluations are briefly summarized below and presented in more detail elsewhere [21].

The primary requirement that sediment AVS not be oxidized was confirmed during the sorption experiment. The kinetics of copper sorption onto various sediments was investigated to determine a time to equilibrium. The results of several experiments all confirmed a time to equilibrium of 1 to 2 hours. Lastly, the solids concentration was evaluated for its effects on copper partitioning. Sediment samples were spiked and stirred for one hour, representing a worse case with respect to particle interactions. Sediment sorption isotherms were obtained at two or three different solids concentrations for three different sediments. The sorption isotherms were not significantly different at solids concentrations differing by an order of magnitude, suggesting that partitioning of copper to anaerobic sediments is not dependent on solids concentration.

The metal in the ASBT system was in the form of (1) free metal, (2) hydrolysis products of metal, (3) metal complexed with dissolved organic carbon (DOC) released from the sediment sample and other ligands, and (4) sorbed metal partitioned onto sediment particles. Loss of metal by sorption onto glass surfaces and by complexation to buffer matrix was shown to be insignificant [17]. Thus metals sorbed onto the sediment particle (C_s) can be calculated by difference between the added metal (C_T) and the total aqueous metal (C_w):

$$C_s = C_T - C_w \tag{9-2}$$

Total sediment-bound metal can be divided into that precipitated as metal sulfide by AVS ($C_{s,AVS}$), and that bound to other sediment components ($C_{s,Non\text{-}AVS}$):

$$C_s = C_{s,AVS} + C_{s,Non\text{-}AVS} \tag{9-3}$$

Measurement of sediment AVS on an experiment-by-experiment basis provides the first term in this equation. Thus the magnitude of the Non-AVS sorbed metal fraction can be calculated by difference:

$$C_{s,Non\text{-}AVS} = C_s - C_{s,AVS} \tag{9-4}$$

This fraction of the sediment bound metal is analyzed below.

Sorption Isotherm Results

The data analysis procedure for the sorption data is illustrated using the copper data at pH = 7 (Figure 9-16). The results from the various sediments are distinguished by the various letters used as plotting symbols. The top figure presents the conventional isotherm: the relationship of the total sorbed metal (C_s) to the metal activity in the solution phase as measured using a specific ion electrode (C_f). The middle plot presents the non-AVS sorbed metal concentration ($C_{s,Non\text{-}AVS}$) versus metal activity. The bottom plot presents the non-AVS sorbed metal concentration normalized by the organic carbon fraction of the sediment:

$$C_{s,Non\text{-}AVS,OC} = C_{s,Non\text{-}AVS}/f_{oc} \tag{9-5}$$

versus the aqueous metal activity of the sediment where f_{oc} is the weight fraction of organic carbon in the sediment. The extent to which the isotherms for the various carbon normalized sediments plot over each other is the extent to which the most important binding component of the sediment is organic carbon. The line fitted to the data is a Langmuir isotherm model which is discussed below.

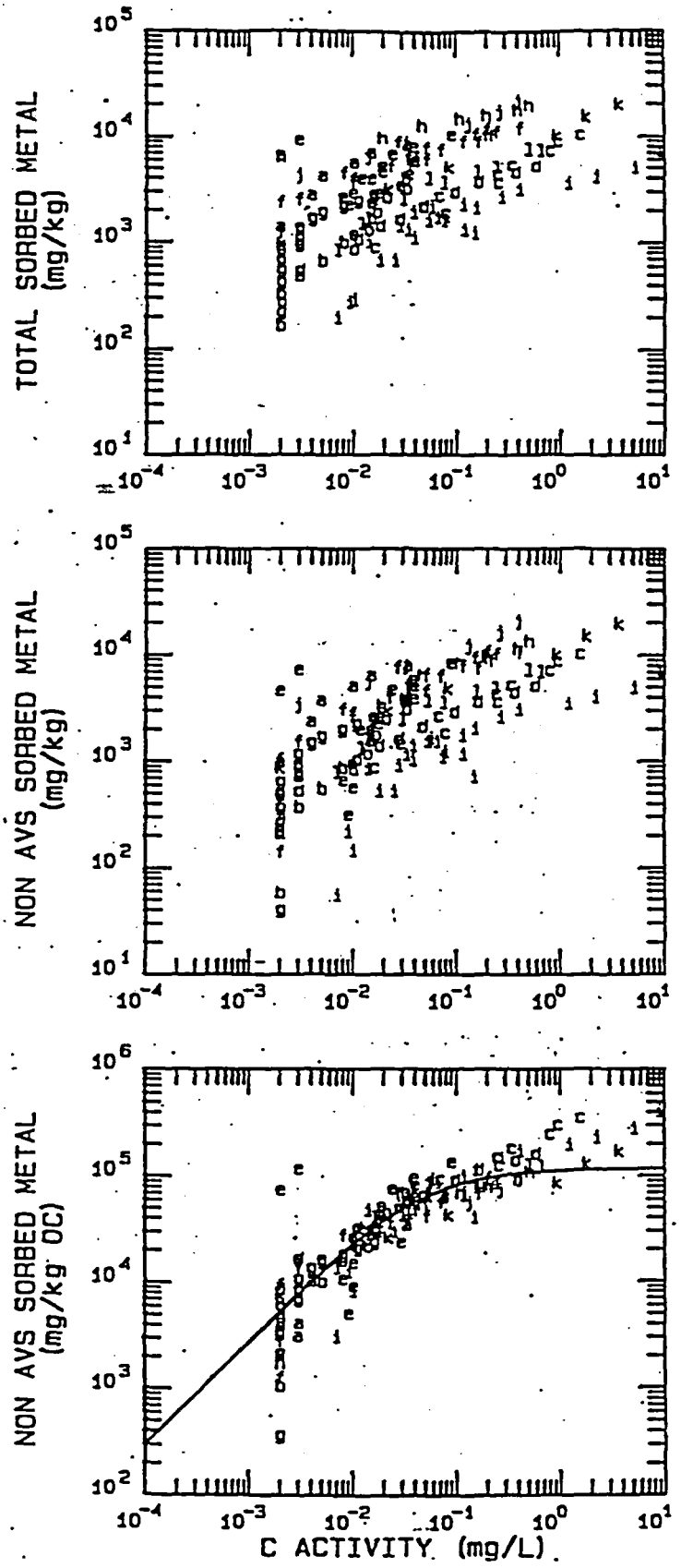


Figure 9-16. Copper activity versus total sorbed metal (top panel), non-AVS sorbed metal (center panel) and organic carbon normalized non-AVS sorbed metal (bottom panel) for pH 7.

Logarithmic isotherm plots revealed non-linear relationships between sorbed metal and metal activity. Logarithmic isotherm plots of all sediment systems at each pH are shown in the top panels of Figures 9-17 through 9-19. The sorbed metal concentrations represent total bound metal (as calculated by Equation 9-2) on a dry sediment weight basis. When the measured AVS component of the total sorbed concentration is subtracted out (Equation 9-4), the resulting isotherms at each pH are shown in the center panels. From these data it is clear that there is binding capacity for the three metals in these sediments in excess of AVS. More importantly, this excess binding capacity is not related to the dry sediment weight. The isotherms cover over a 10-fold range in partition coefficients.

When the non-AVS binding capacities (Equation 9-5) are normalized to sediment organic carbon fractions (f_{oc}), the isotherms represented in bottom panels of Figures 9-17 through 9-19 result. The isotherms collapse into a single isotherm with residual scatter (a factor of 2 to 3) with one exception due to binding to other sediment components and experimental error. The effect of sediment organic normalization is most dramatic at pH 7 although the normalization reduces the scatter at pH 6 also. At pH 8, however, the precipitation of metal hydroxides is present in addition to the sorption process and this complicates the analysis. The pH in sediments is typically 6.5 to 8.0. In support of organic carbon normalization, Allen et al. [22,23] showed that upon oxidation of sediments residual metal binding remained and that only a single phase was needed to explain this. In a later paper [24] he showed that the binding of Cd to such sediments was identical in nature to the binding by humic material extracted from the sediments.

The sorption isotherms can be fit using a number of models. The approximately straight line behavior for some of the data (e.g., cadmium at pH=6, Figure 9-18) suggests a Freundlich isotherm might be appropriate. However, the curvature that exists at higher concentration suggests that a limiting sorption capacity exists. The simplest model that includes an upper limit is the Langmuir isotherm. The Langmuir isotherm equation is:
where:

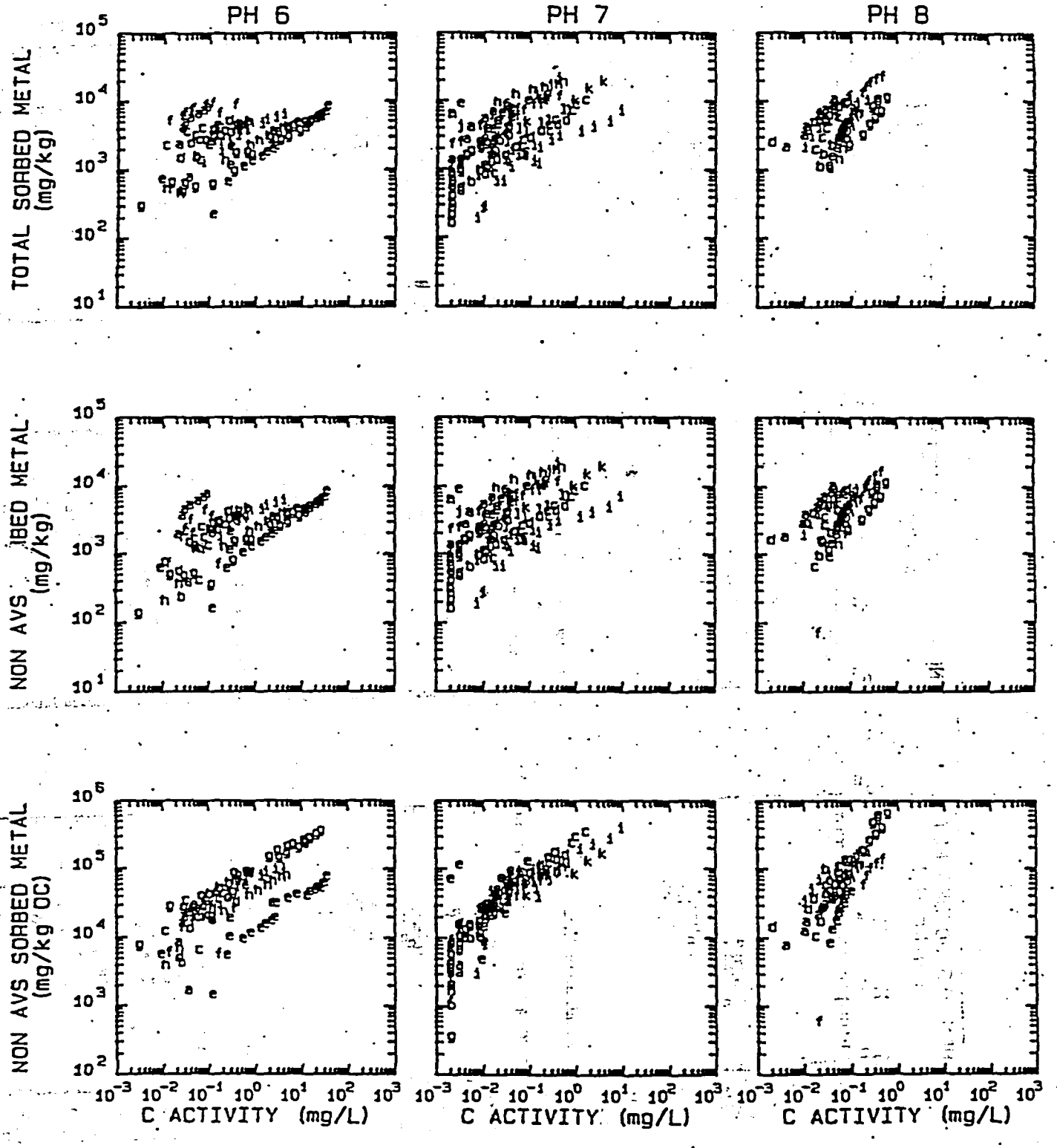


Figure 9-17. Copper activity versus total sorbed metal (top panels), non-AVS sorbed metal (center panels) and organic carbon normalized non-AVS sorbed metal (bottom panels) for pH 6, 7, and 8.

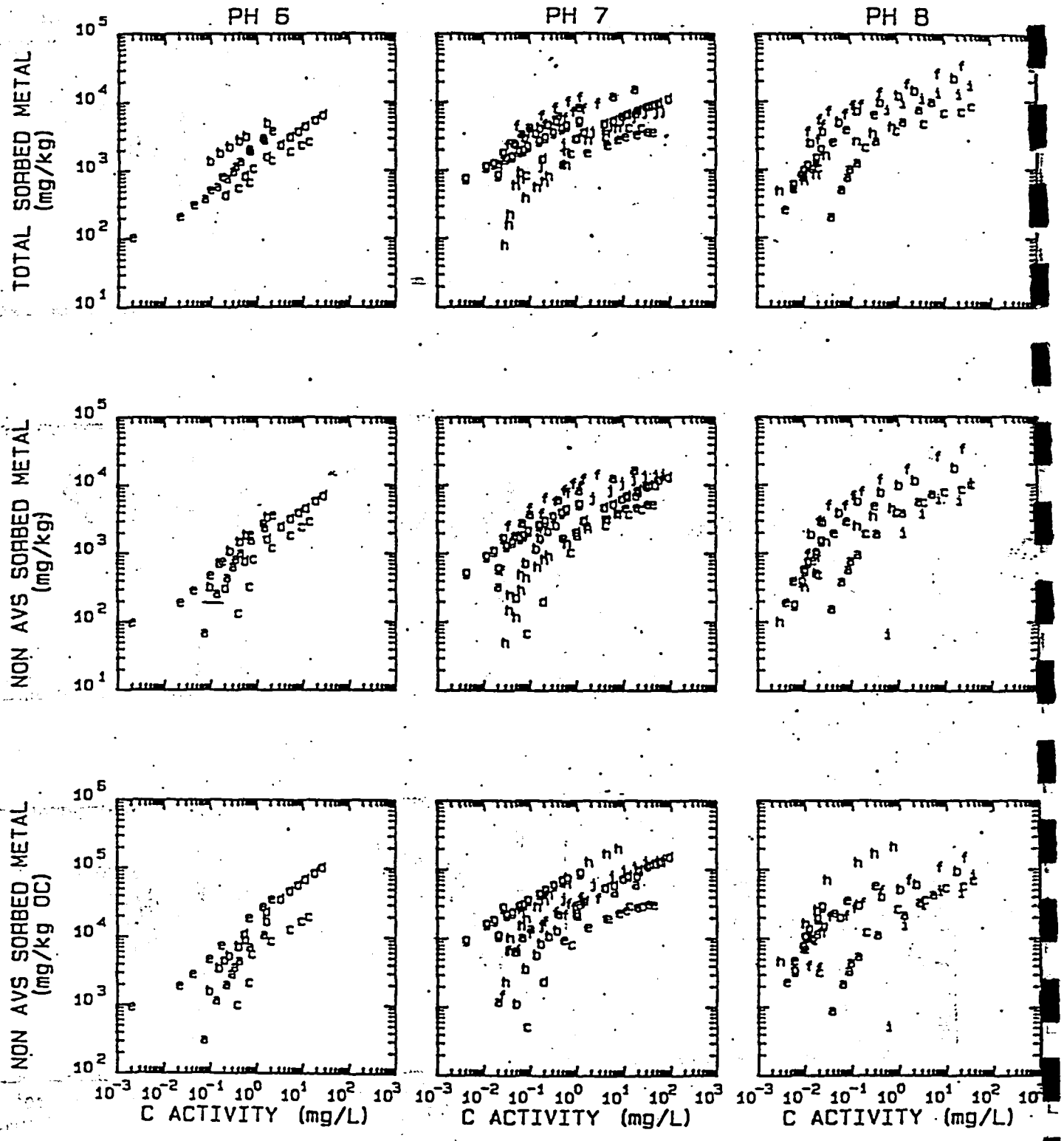


Figure 9-18. Cadmium activity versus total sorbed metal (top panels), non-AVS sorbed metal (center panels) and organic carbon normalized non AVS sorbed metal (bottom panels) for pH 6, 7, and 8.

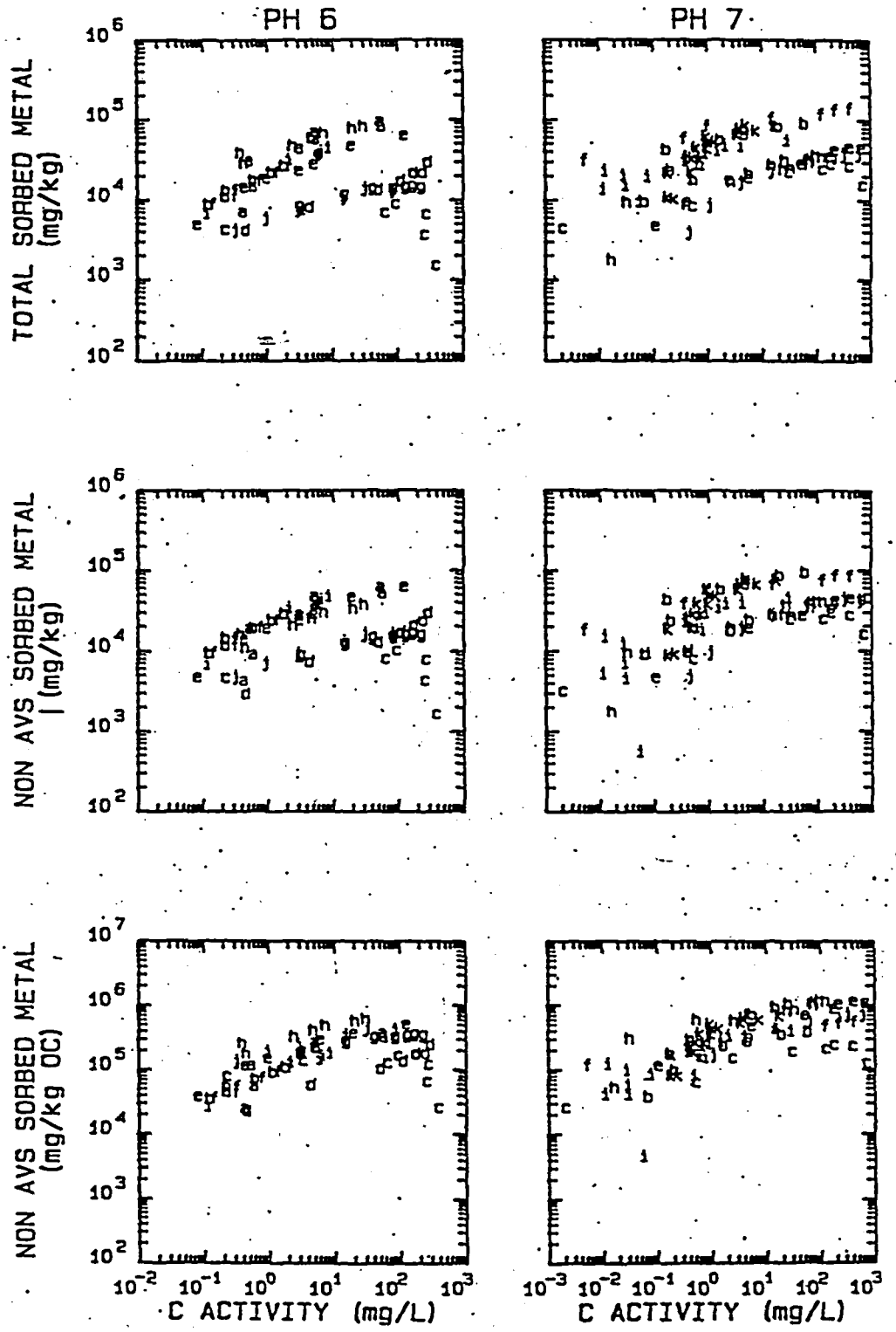


Figure 9-19. Lead activity versus total sorbed metal (top panels), non-AVS sorbed metal (center panels) and organic carbon normalized non-AVS sorbed metal (bottom panels) for pH 6 and 7.

$$C_{s,OC} = \frac{C^o_{s,OC}\ K_{d,OC}\ C_f}{C^o_{s,OC} + K_{d,OC}\ C_f} \qquad (9\text{-}6)$$

$C_{s,OC}$ = non-AVS sorbed metal per weight of sediment carbon (mg M/kg organic carbon) = C_s, non-AVS (Equation 9-5)

C_f = aqueous metal activity (mg $\{M^{2+}\}$/L), and

$K_{d,OC}$ = partition coefficient (L/kg organic carbon)

$C^o_{s,OC}$ = sorption capacity (mg M/kg organic carbon).

The properties of the Langmuir isotherm are shown in Figure 9-20A. The isotherm is linear (slope = 1) on a log-log scale and approaches a constant as the concentration exceeds $C^o_{s,OC}/K_{d,OC}$.

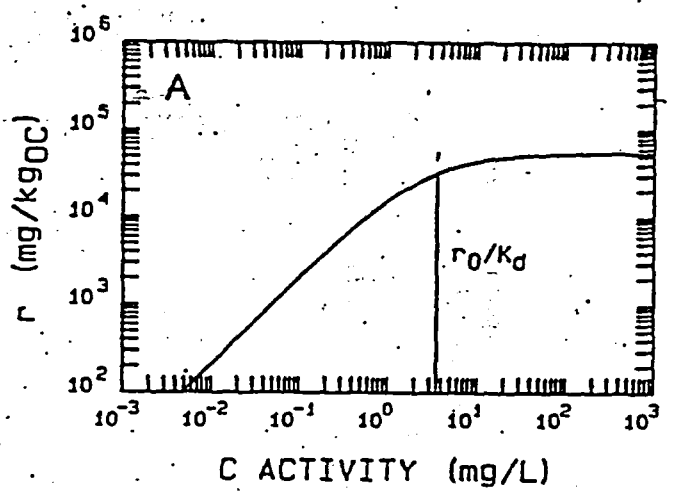
If organic carbon is the only significant sorption phase, then one would expect that the total sorption capacity of this phase is independent of pH within the narrow range tested. On the other hand, the partition coefficient for metal sorption to natural and synthetic particles is expected to vary with pH over a wider range. It arises because metal sorption is a competition between the metal ion and the hydrogen ion. As the pH is increases the concentration of hydrogen ion decreases, lowering the competition for sorption sites, so that the quantity of metals sorbing increases. The isotherms that result from this type of model are shown in Figure 9-20B. The increasing partition coefficient as pH increases results in an increased particulate concentration for a fixed metal activity.

The Langmuir parameters $K_{d,OC}$ for each pH, and the binding capacity ($C^o_{s,OC}$) can be obtained using a non-linear regression of the log-transformed sorption data for each metal. The resulting capacity and partition coefficients are listed in Table 9-4. Figures 9-21 through 9-23 present the Langmuir model and the data for copper, cadmium and lead at the various pH's. For each pH, the data are summarized and plotted in the following way. The sediment concentrations are sorted from low to high and divided into seven groups with an approximately equal number of concentrations in each group. Then the log mean of both the sediment concentration and aqueous activity are found. These mean

The Langmuir Isotherm:

$$C_{s,oc} = \frac{C^o_{s,oc} K_{d,oc} C_f}{C^o_{s,oc} + K_{d,oc} C_f} \rightarrow C^o_{s,oc} \qquad C_f > \frac{C^o_{s,oc}}{K_{d,oc}}$$

$$\rightarrow K_{d,oc} C_f \qquad C_f < \frac{C^o_{s,oc}}{K_{d,oc}}$$



Model:

$C^o_{s,oc}$ Independent of pH

$K_{d,oc}$ Depends on pH

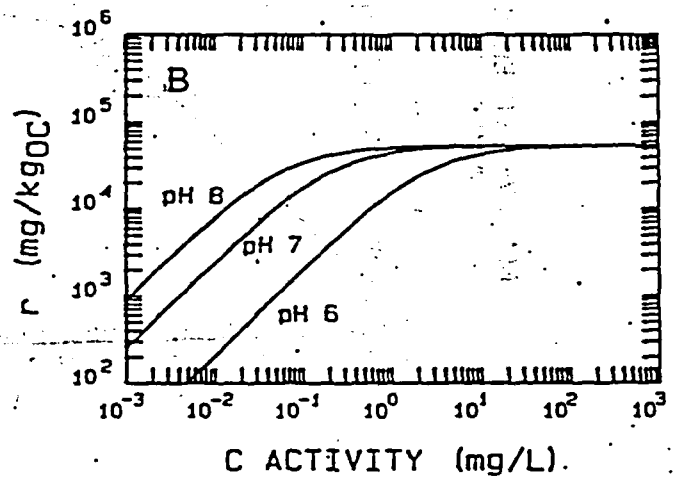


Figure 9-20. Properties of the Langmuir isotherm (top panel, A) and resulting isotherms at varying pHs (bottom panel, B).

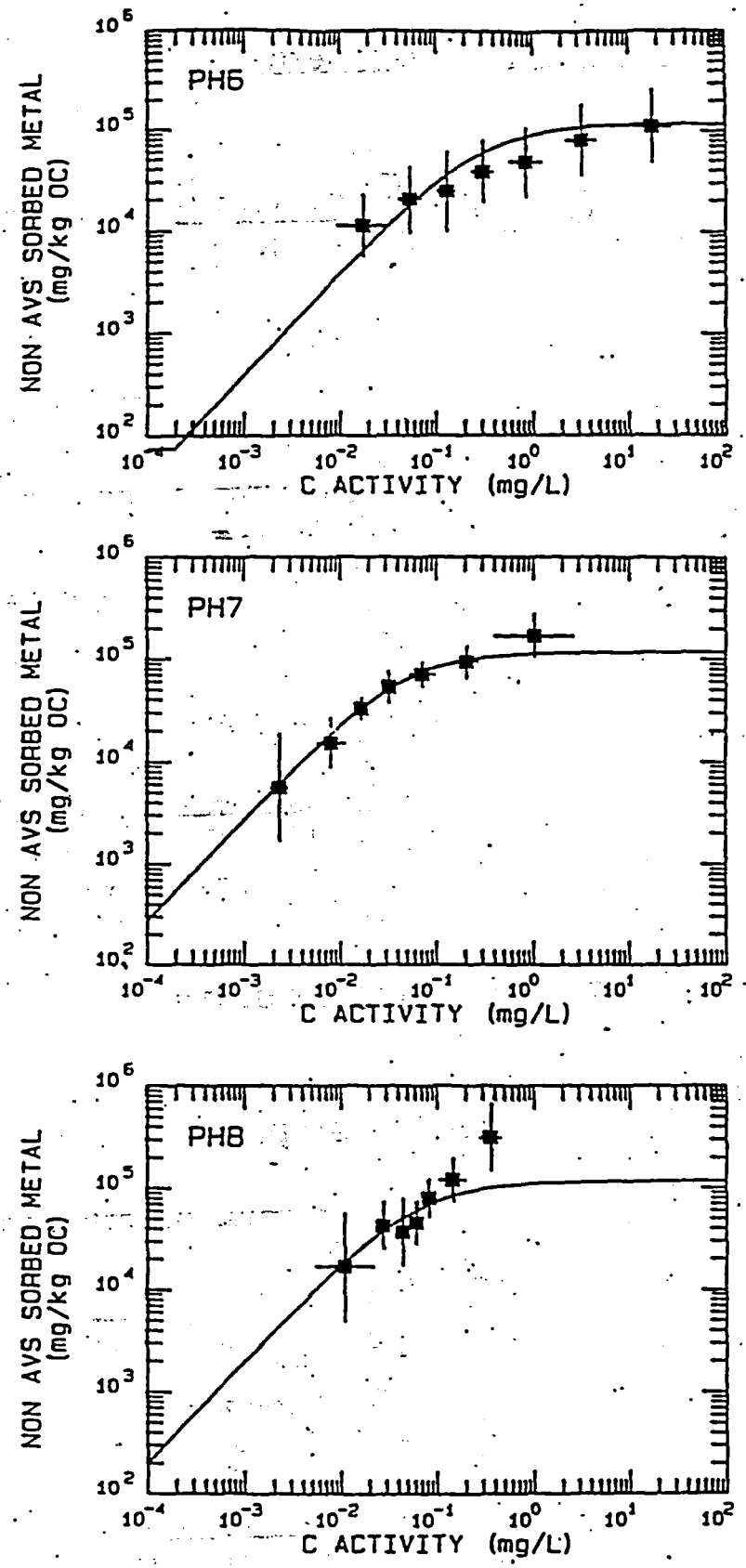


Figure 9-21. Copper sorption isotherms for pH 6, 7, and 8. Data for plotting intervals is represented by symbols (mean) and bars (standard deviation). The Langmuir isotherm model is represented by the solid line.

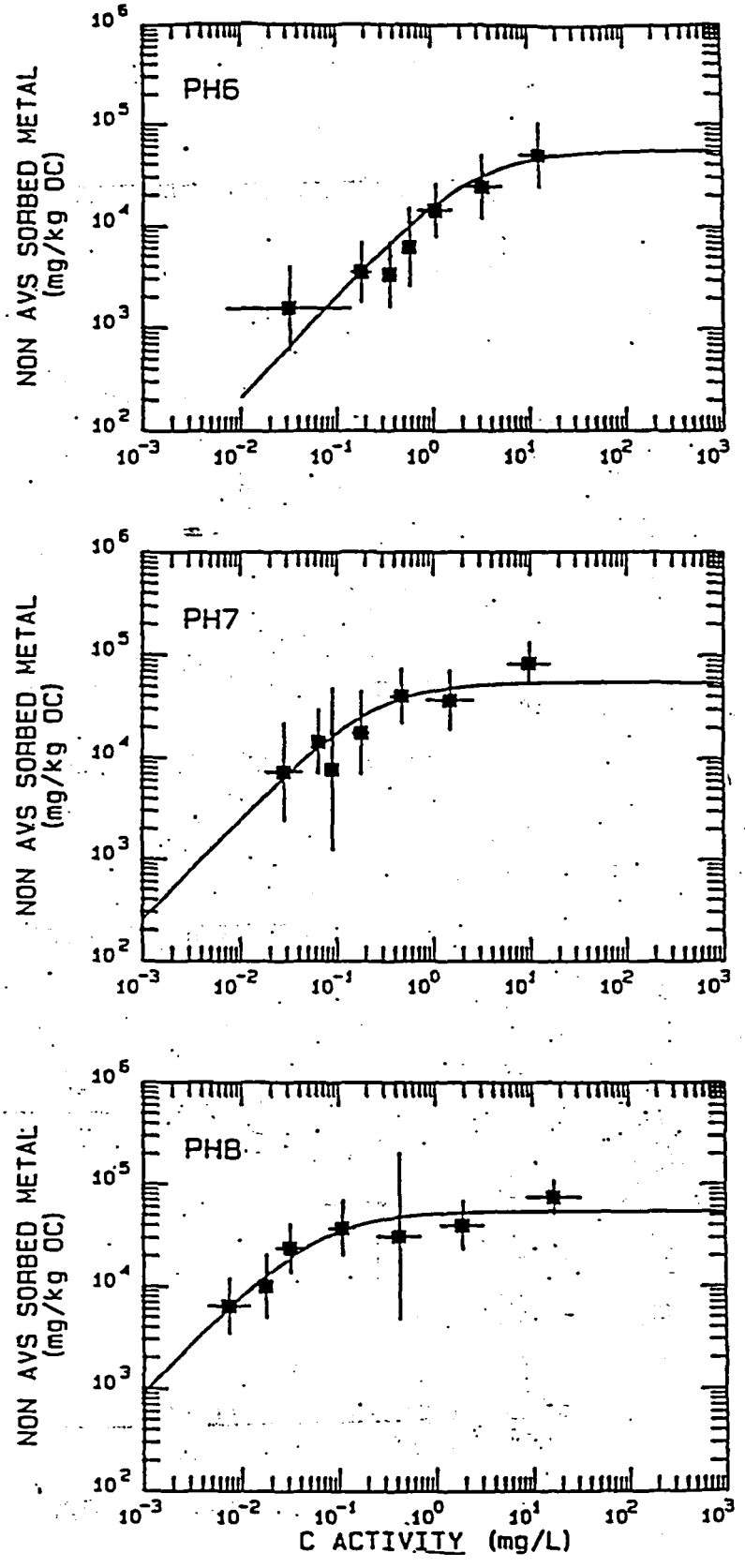
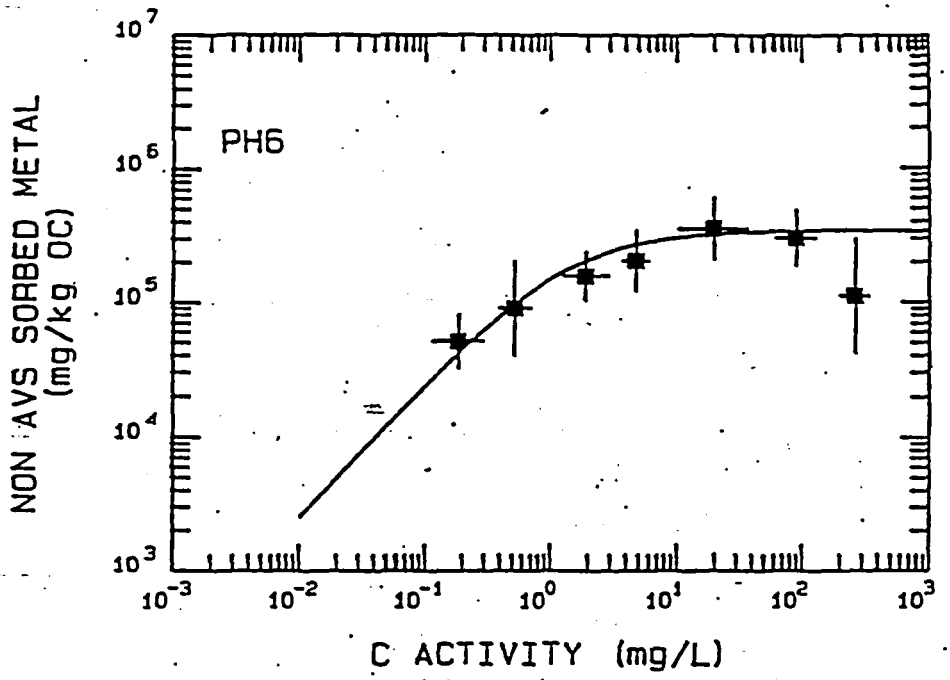


Figure 9-22. Cadmium sorption isotherms for pH 6, 7, and 8. Data for plotting intervals is represented by symbols (mean) and bars (standard deviation). The Langmuir isotherm model is represented by the solid line.



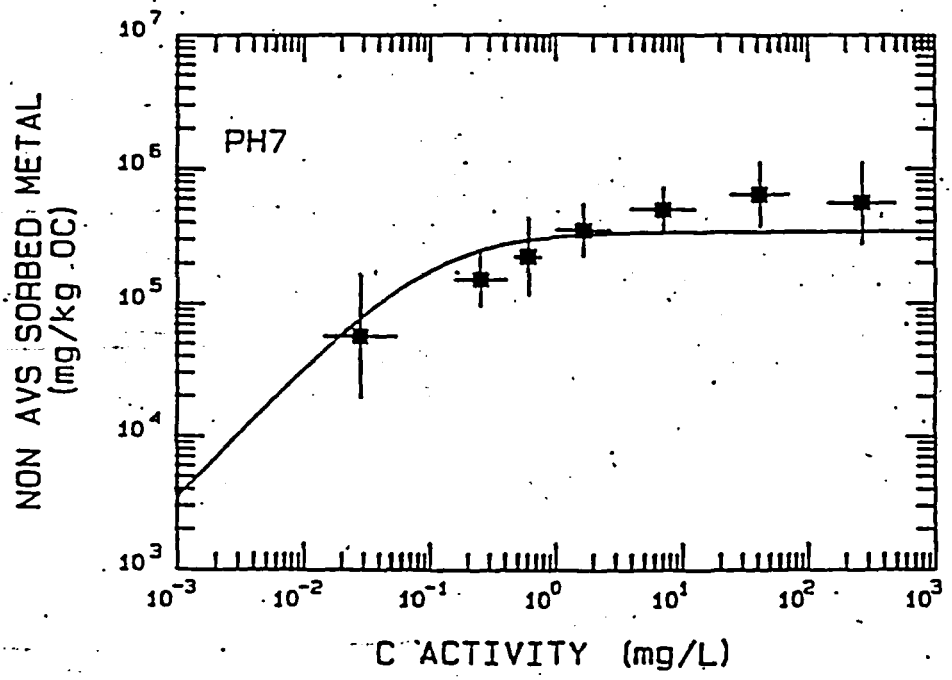


Figure 9-23. Lead sorption isotherms for pH 6 and 7. Data for plotting intervals is represented by symbols (mean) and bars (standard deviation). The Langmuir isotherm model is represented by the solid line.

concentrations are plotted as the filled symbol. The standard deviation of the data in each group is indicated by the lines in both the x and y axis directions. The model fits the data for each metal surprisingly well, especially at the low metals activity where the isothems will be used for setting Sediment Quality Criteria.

TABLE 9-4. ORGANIC CARBON BINDING CAPACITY AND PARTITION COEFFICIENTS FOR COPPER, CADMIUM, AND LEAD.

		K_d (L/kg OC)		
	Capacity (mg/kgOC)	pH6	pH7	pH8
Copper	117,500	390,400	2,731,000	2,003,000
Cadmium	54,450	20,740	250,700	914,400
Lead	339,400	248,700	346,400	-

The sorption capacities for copper, cadmium and lead are shown in the top panel of Figure 9-24. The capacities for copper and lead are similar whereas the capacity for cadmium is lower. The partition coefficients as a function of pH are shown in the bottom panel of Figure 9-24. They are almost equal for copper and lead but are an order of magnitude lower for cadmium. A line with slope = 1 is included in the figure for comparison. The relationship between log $K_{d,OC}$ and pH is essentially slope one between pH 6 and 7. This corresponds to a replacement of a single hydrogen ion with each metal ion sorbed, presumably as the metal hydroxide, MOH^+.

These results are used in deriving sediment quality criteria in Chapter 11. However, a simple case is examined in this chapter in order to assess the importance of sediment organic carbon binding. The sediment quality criteria for a single metal is:

$$SQC = AVS + K_d\ C_{FCV} \tag{9-7}$$

where K_d is the partition coefficient and C_{FCV} is the final chronic value for that metal. It should be pointed out that this equation is valid for a given metal *only if* the concentrations of other metals is small relative to the AVS. The partition coefficient can be expressed in

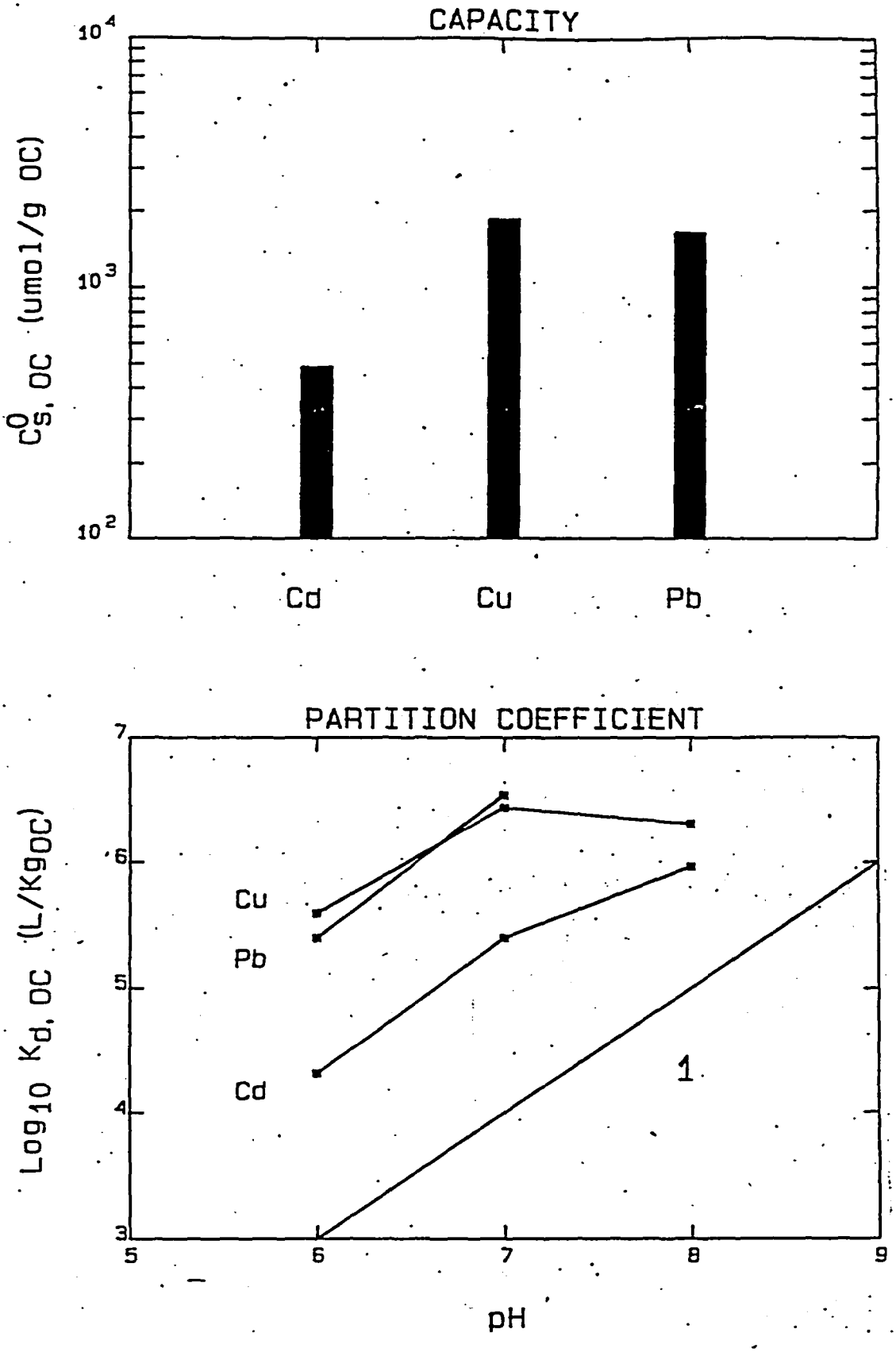


Figure 9-24. Calculated capacity (top panel) and organic carbon normalized partition coefficients (bottom panel) for cadmium, copper, and lead.

terms of the organic carbon partition coefficient and the fraction organic carbon in the sediment:

$$SQC = AVS + K_{d,OC} f_{OC} C_{FCV} \quad (9\text{-}8)$$

The importance of organic carbon binding can be assessed by comparing the magnitude of the term in the above Equation (9-8) that corresponds to organic carbon binding:

$$K_{d,OC} f_{OC} C_{FCV} \quad (9\text{-}9)$$

with typical AVS concentrations found in sediments. This is demonstrated in Figure 9-25 using the fresh water final chronic values (at hardness = 100 mg/L) and $K_{d,OC}$ for pH 7 for copper, cadmium and lead. The dashed horizontal lines show the typical range of AVS and the dashed vertical lines give a typical range of f_{oc}. As f_{oc} and AVS increase so does the allowable sediment metals concentration. Even with no AVS binding, sediment metals levels of up to 100 umol/g may be acceptable depending on the organic carbon content.

Least Sorptive Phase

The extent of partitioning between sediments and interstitial water is a critical component in establishing SQCs. Equation 9-8 points out the importance of the partition coefficient, K_d. In the absence of AVS and significant organic carbon in a sediment, the partitioning would be established between the mineralogical phases and the intersitital water.

A series of experiments have been initiated to determine the partition coefficients for metals using "clean" sediments which contain no AVS and no appreciable organic carbon. The idea is to measure partition coefficients that can be used as minimum values to determine the extent of partitioning. These partition coefficients would be used to compute lower bounds of the SQC. For sediments with metal concentrations below these values, the sediments would be judged to have satisfied the SQC.

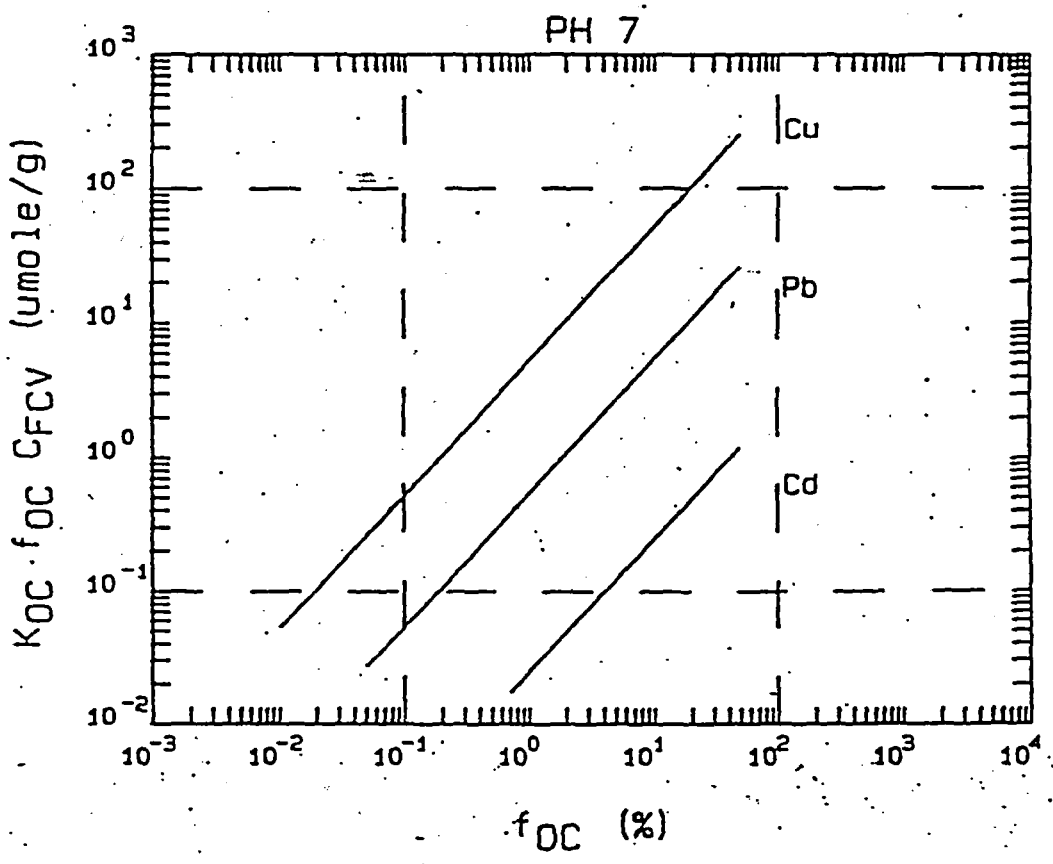


Figure 9-25. Magnitude of organic carbon binding (y axis) as f_{oc} (x axis) varies for cadmium, copper and lead, pH 7. Typical ranges of f_{oc} and AVS are represented by dashed lines. The freshwater FCVs at hardness of 100 mg/l are 1.1 ug/l for cadmium, 12.0 ug/l for copper and 3.2 ug/l for lead.

Determinations of the partiton coefficeint, K_d, for cadmium, copper, nickel, lead, and zinc were done using two adsorbents with very low organic carbon content. The analyses were done at the U.S. EPA Environmental Research Laboratory, Athens, Georgia [25]. The adsorbents were a commercially obtained washed sea sand and a sample of natural sand from Ona Beach, Oregon. The washed sea sand was used as provided. Most of the aqueous phase was removed from the Ona Beach sand samples. Remaining water content was 16.7 percent. Total organic carbon content was 0.006 percent, for the washed sea sand, and 0.019 percent for the Ona Beach sand.

About 5 g of sediment and 30 ml of a serial dilution of the five mixed metals were mixed and allowed to equlibrate. The samples were then centrifuged and the supernatants were analyzed for pH and remaining metals using the graphite furnace atomic adsorption spectrophotometer (GFAAS) [25]. The adsorbed amounts of each of the metals, on a gram weight basis were computed from the difference between the initial metals concentration and the remaining metals concentration in the supernatant divided by the initial volume of 30 ml. The amounts absorbed (gram) were then divided by the amount of sediment added (gram) to compute the adsorbed solid phase concentration, C_s. The partition coefficient, K_d was then computed as follows:

$$K_d = \frac{C_s}{C_w} \qquad (9\text{-}10)$$

where C_w is the remaining metals concentration in the supernatant. Table 9-5 presents the mean K_d and statndard error for each of the metals.

These initial results suggest that the partition coefficients are varying somewhat, but not by orders of magnitudes. Therefore, it is probable that minimum partition coefficients can be established which would provide a lower bound for the Sediment Quality Criteria on an SEM basis. The details of this formulation are discussed in Chapter 11.

TABLE 9-5. PARTITION COEFFICIENT, K_d, FOR LOW ORGANIC CARBON CONTENT SEDIMENTS

	K_d(L/Kg)				
	Copper	Nickel	Cadmium	Zinc	Lead
Sea Sand	163.05 (6.97,5)[a]	21.17 (4.15,5)	48.36 (7.34,5)	1,847.67 (137.95,6)	273.65 (24.1,5)
Ona Beach Sand	265.08 (16.1,6)	34.58 (1.87,6)	71.09 (5,44,7)	2,183.70 (260.53,5)	579.10 (33.5,4)

[a]Standard error, number of values

Pore Water and SEM/AVS Sampling

The sampling methods used for AVS and interstitial water have been studied and recommendations are available that appear to be the optimal choices at present.

Pore Water Sampling

Bufflap and Allen [26] reviewed the four commonly used methods for collection of pore water and potential artifacts from their use, particularly in the preparation of samples for trace metal analysis. Two of the methods, centrifugation and squeezing, are ex-situ, requiring the removal of sediment from the natural environment. The other two, dialysis and suction filtration, are used in-situ. Their work has been included in Volume II of this submission. In addition to each method having its own advantages and disadvantages, there are several general sources of error that can alter pore water chemical concentrations. A summary of their findings is presented below.

Several sources of error in sampling can lead to erroneuos porewater measurements. A primary source of error is the oxidation of anoxic pore waters. If a sample is allowed to oxidize the speciation of iron and other trace metals will be altered. Anoxic sediments should be handled in a glove box or glove bag when extracting pore water. Another source of error that can occur during sampling is pore water oxidation as

a result of the mixing of oxic and anoxic sediments during sampling. Also metal contamination should be avoided when sampling by avoiding contact with metal parts of the sampling device that may contaminate the sample. Some studies indicate that sample extractions at temperatures higher than in-situ may change the composition of the pore water however there is no direct evidence that extraction temperature plays a significant role in trace metal concentrations in pore water [26]. Pore water samples should be filtered during or after extraction to remove residual particles that can interfere with both analytical procedures or alter trace metal concentrations due to adsorbtion/desorbtion of the metal to the residual particles. Bufflap and Allen [26] discuss the three most common sampling techniques; dredging, grab sampling and coring, and give recommendations to minimize sampling errors.

The primary concern with analyzing sediment pore water is finding an extraction technique that will produce samples that best represent the natural environment. To accomplish this goal, the technique that is used should have the lowest potential for producing sampling artifacts. The ex-situ techniques, centrifugation and squeezing, require the removal of sediment samples from the natural environment. The squeezer method employs various apparatus to pressurize a sediment sample which forces the pore water through an exit port. The squeezer apparatus are known as core section or whole core squeezers. Core section squeezers employ either gas pressure or a mechanical means of pressurizing the sediment sample and forcing the pore water through an exit port. Core section squeezers are an inexpensive and simple means of extracting sediment pore water. They also offer immediate filtration of the water samples, thus eliminating a handling step which may introduce contamination to the samples. The disadvantage of core section squeezers is that their use requires handling the sediment which may introduce artifacts resulting from oxidation or temperature differences.

Whole core squeezers may help to remove the possibility of artifacts that may result when using the core section squeezers because the sediment remains in the core liner with which it was removed from the natural environment. These squeezers apply pressure to

the sediment by the use of plungers. A problem with the whole core squeezers is that solid phase pore water interactions may alter pore water concentrations during squeezing.

Centrifuging is another widely used ex-situ simple technique to obtain pore water. Centrifuging can be conducted at in-situ temperatures and handling the sediment samples can be done in an inert atmosphere to avoid artifacts that may change pore water concentrations. One problem with centrifuging is that some fine particulates may still remain in pore water. Fine particulates can be removed either by using a built-in filter at the top of the centrifuge cup or by displacement of the pore water in the sediment by an inert solvent placed in the centrifuge tube. The dense solvent replaces the pore water in the sediment forcing the less dense pore water to the top. Of the two existing techniques, squeezing has the lower potential for artifacts because all handling steps can be conducted in an inert atmosphere contained in a glove bag in order to avoid oxidation artifacts. In addition, pore water filtration can be conducted in-line, thus eliminating a handling step that is required in centrifugation, and lowering the potential for artifacts.

Squeezing and centrifuging are discussed by Bufflap and Allen [26] in more detail. In-situ techniques, such as dialysis and suction filtration, have less potential for producing sampling artifacts than ex-situ techniques because pore water samples are extracted directly from the natural environment. The general principle of dialysis sampling involves allowing a volume of deionized, distilled water to come to equilibrium with the sediment pore water in order to determine chemical concentrations. One problem with dialysis samplers is that the chamber water must be deaerated before insertion into anoxic sediemnts to avoid oxidation of the sample. Dialysis has limitations because equilibration times can last several weeks. In addition, the volume of sample is limited by the size of the sample chambers, not by the physical features of the sediment. Lastly dialysis samplers generally require placement and retrieval by SCUBA divers, thus increasing study costs.

Because there are different techniques available for extracting sediment pore water, it is often difficult to compare data from different laboratories. What is needed to limit

these discrepancies is to compare the existing techniques and to develop a sampling methodology that will produce pore water samples that best resemble the in-situ conditons and can be easily utilized by all researches. Studies done to compare the existing techniques are discussed by Bufflap and Allen [26]. However, more research is needed in this area.

AVS/SEM Sampling

A draft analytical method for the determination of AVS and SEM in sediment has been proposed [27,28]. This method describes procedures for the determination of acid volatile sulfides (AVS) and for metals that are solubilized during the acidification step (SEM). The conditions used have been reported to measure amorphous or moderately crystalline monosulfides. Because the relative amounts of AVS and SEM are important in the prediction of potential metal bioavailability, it is important to use the SEM procedure for sample preparation for metal analysis. This uses the same conditions for release of both sulfide and metal from the sediment and thus provides the most predictive means of assessing the amount of metal associated with sulfide. The method is included in Volume II and a summary is provided below.

The AVS in the sample is first converted to hydrogen sulfide (H_2S) by acidification with hydrochloric acid at room temperature. The H_2S is then purged from the sample and trapped. The amount of sulfide that has been trapped is then determined. The SEM are metals liberated from the sediment during the acidification. These are determined after filtration of the supernatant from the acidification step.

Two types of apparatus for sample purging and trapping of H_2S are described. One uses a series of Erlenmeyer flasks while the other uses flasks and traps with ground glass stoppers. The former is less costly. The latter is less prone to leakage that causes low recovery of AVS. The latter is recommended when higher degrees of precision are desired and for samples containing low levels of AVS (~ 0.1 μmol/g).

Three means of quantifying the H_2S released by acidifying the sample are provided. In the gravimetric procedure, the H_2S is trapped in silver nitrate. The silver sulfide that is formed is determined by weighing. This procedure is recommended for samples with moderate or high AVS concentrations. In an alternative procedure the H_2S is trapped in an antioxidant buffer before using an ion-selective electrode. After release of the H_2S, the acidified sediment sample is membrane filtered before determination of the SEM by atomic absorption or inductive coupled plasma spectrometric methods. In the colorimetric method, the H_2S is trapped in sodium hydroxide. The sulfide is converted to methylene blue that is measured. This procedure is recommended for samples that have low to moderate AVS concentrations.

Using the apparatus described by Allen et al. [27], the colorimetric method of analysis is capable of detecting AVS at concentrations normally encountered with a recovery of sulfide of at least 90 percent. High precision is possible if the Allen et al. [27] apparatus is used with a limit of detection of approximately 0.01 μmol/g dry sediment.

APPENDIX 9A

EXPERIMENTAL PROCEDURES

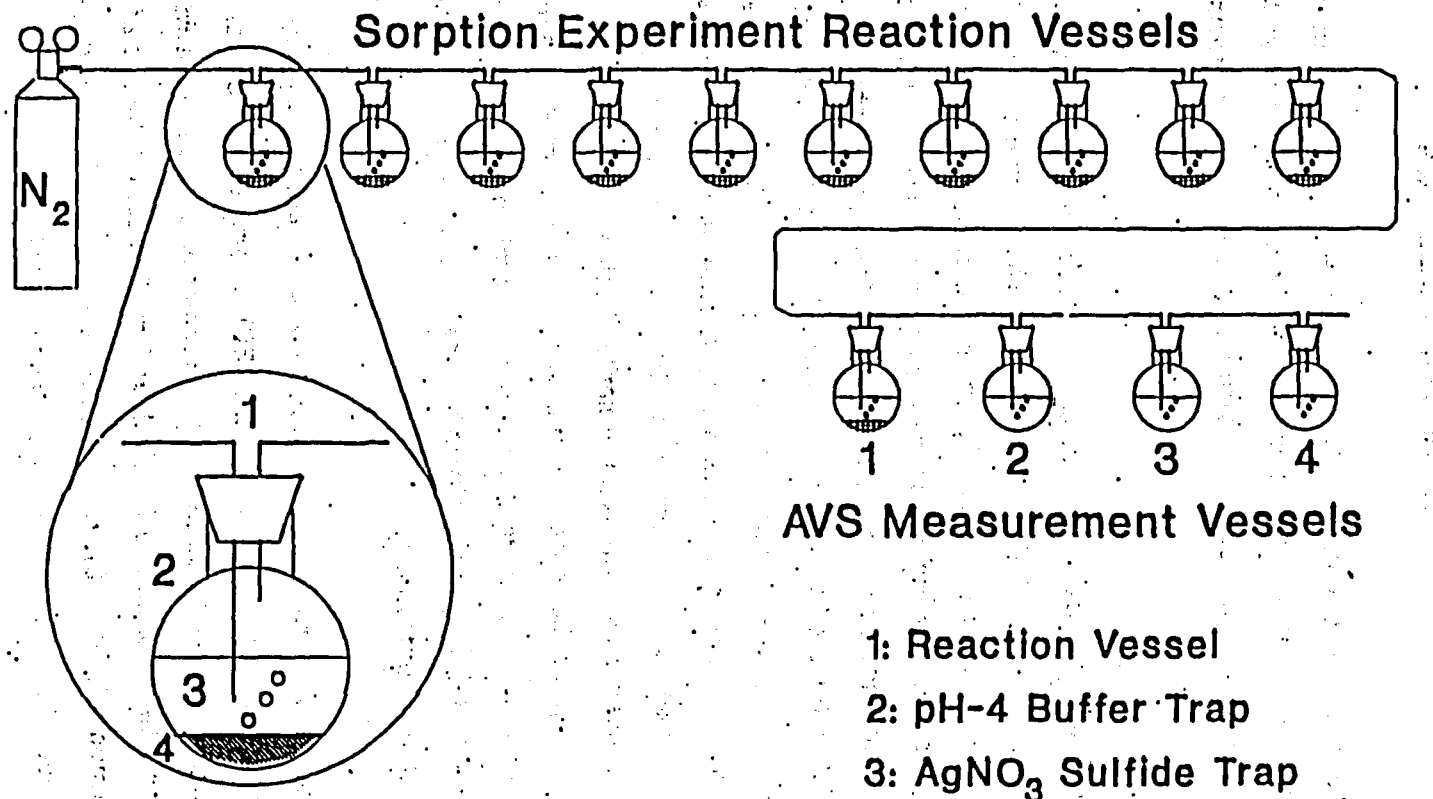
Sediment samples with overlying water were collected in one gallon plastic containers from various locations, transported under ice, and stored at 4°C throughout the study period. Subsampling procedures attempted to minimize exposure times to air and elevated temperatures.

Sorption isotherm data were obtained by titrating sediment with either copper, cadmium or lead in batch mode (Figure 9A-1). The Anoxic Sequential Batch Titration (ASBT) method consists of a series of 250ml, Florence flasks (typically 10) stoppered gas-tight with two-hole rubber stoppers fitted with glass tubing. The entire train of flasks is connected to a source of purified nitrogen gas (Matheson, Prepurified, 99.998 percent minimum) which is bubbled through a vanadate/HCl/amalgamated-zinc oxygen-stripping solution as a polishing de-oxygenation step. Into each flask, a wet sediment sample is introduced, a known volume of stock metal solution is added, and a known volume of deaerated buffer solution is added. Each flask is similarly prepared and sequentially attached to the flask train. An Acid Volatile Sulfide (AVS) determining apparatus is attached to the sorption flask train to measure the sediment AVS simultaneously. The sediment is then titrated by varying the copper, cadmium, or lead stock solution volume added to each flask and thereby obtaining a range of sediment-bound and aqueous copper, cadmium, or lead concentrations.

Total aqueous metal concentrations were determined by Atomic Absorption Spectroscopy (AAS; Perkin Elmer model PE-3030) in samples of the overlying water of the ASBT system which were filtered through glass fiber filter discs and acidified to 1 percent HNO_3 by volume. Metal concentrations below 1 mg/L required the use of AAS in Graphite furnace mode (model HGA-400). Concentrations greater than 1 mg/L were analyzed by AAS in Flame mode (air-acetylene flame; Perkin-Elmer lamps).

Metal activity in the overlying water of the ASBT system was measured directly by an ion-selective electrode (Orion, #90-29) in conjunction with a reference electrode (Orion,

Anoxic Sequential Batch Titration



1: Gas inlet & outlet
2: 250 mL Glass Flask
3: Buffer Matrix + Metal Spike
4: Sediment Sample

1: Reaction Vessel
2: pH-4 Buffer Trap
3: $AgNO_3$ Sulfide Trap
4: $AgNO_3$ Sulfide Trap

Figure 9A-1. Anoxic sequential batch titration (ABST) experimental set-up. Purified nitrogen gas is used to remove and exclude oxygen from the reaction flasks. Typically 10 flasks are used to expose sediment samples to pH buffer matrix and m[illegible]l contamination, as shown in the enlargement. A 4-fl[illegible] AVS measurement apparatus is included to determine [illegible] s[illegible]nent AVS of an unspiked sediment homogenate si[illegible]y.

#90-02) and a voltage meter (Orion SA-720). Daily metal activity standard curves generated at the appropriate pH were used to calculate a regression line on the linear portion of the curves. It was assumed that metal activity was linearly related to electrode response at all activities. This allowed a given day's standard curve regression equation to be used to calculate the metal activity of that day's ASBT overlying water samples, even though the millivolt reading of some samples fell below the lowest standard. Copper, cadmium or lead activities calculated in this way over-estimated the metal activity of samples below 0.01 mg $\{Me^{2+}\}$/L. The ionic strength of both samples and standards was adjusted to 0.005M $NaNO_3$ prior to determining metal activity.

The pertinent sediment characteristics relating to metal partitioning were determined as follows. Sediment dry solids were determined by weighing a sediment sample before and after drying at 103°C overnight. Sediment carbon (total, organic, and inorganic) was measured using a LECO model CHN-800 Carbon-Hydrogen-Nitrogen analyzer. Sediment dried at 103°C was analyzed for particulate total carbon (PTC). A subsample of this material was acidified with 0.05M HCl for one hour and dried at 103°C. This treated sediment was analyzed for particulate organic carbon (POC), and the difference between PTC and POC was attributed to particulate inorganic carbon (PIC; i.e., carbonates).

The pH of the overlying water was measured using a Beckman (ALTEX) ϕ60 pH meter with a Fisher Standard Polymer-Body Gel-filled combination pH electrode (#13-640-108). The pH of the ASBT systems were buffered using Goode buffers (0.005 to 0.01M solutions adjusted to desired pH with NaOH). At pH 6, MES (2-[n-morpholino]ethanesulfonic acid, sodium salt; pK_a = 6.1; Sigma M-3885) was used, at pH 7, MOPS (3-[Morpholino]propanesulfonic acid, sodium salt; pK_a = 7.2; SIGMA M-9381) was used, and at pH 8, HEPES (N-[2-Hydroxyethyl]piperazine-N'-[2-ethanesulfonic acid, Sodium salt; pK_a = 7.5; SIGMA H-2393) was used. These buffers are designed to be non-reactive with metal species [17,18,19].

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CHAPTER 10

CONSIDERATIONS FOR ASSESSING METAL BIOAVAILABILITY IN SEDIMENTS

Based on the studies described in the preceding chapters, it is apparent that evaluation of pore water metal concentrations and/or SEM:AVS ratios can provide significant insights concerning metal bioavailability in sediments. We feel that the two techniques are complementary and should be used in conjunction with one another as an approach to providing assessments of the potential ecological impacts of metals in sediments. However, when using these measures of metal bioavailability, it is important to recognize the limits of applicability of the techniques. These are discussed below.

Interstitial Water

Comparison of metal concentrations in pore water to water-only toxicity data can be used to predict not only the presence, but also the extent of, metal toxicity in sediments. The ability to actually quantify bioavailable metals in sediments is attractive for a number of reasons. For example, quantification of bioavailable metal facilitates the evaluation of differences in relative species sensitivity and thus, enables the identification of species at risk. This is not yet possible with SEM and AVS. When SEM and AVS, due to other possible binding phases, it is not yet possible to predict actual pore water concentrations of metals. Another advantage to monitoring pore water metal concentrations is that they should be useful for predicting the toxicity of metals, such as chromium, which do not form insoluble sulfides. Finally, because AVS is readily oxidized, it is not an important binding phase for metals in completely aerobic sediments, however, the bioavailable fraction of metals should still be approximated by using the pore water concentrations.

There also are disadvantages to solely using pore water concentrations to quantify metal bioavailablity. First, because pore water is operationally defined (i.e.,

there is no standard method for isolation although we recommend a procedure in Chapter 9), there is a valid concern that laboratory variations in preparation may result in significant differences in metal concentrations found in pore water. A second disadvantage to using pore water metal concentrations to predict toxicity is that, if one accepts the paradigm that pore water is indeed a major route of contaminant exposure for epibenthic and benthic invertebrates, it may be difficult to account for the effects of the pore water matrix (e.g., dissolved organic carbon, hardness, salinity) on metal complexation and bioavailability. This is, of course, also an issue of on-going concern in the area of WQC issued by the US Environmental Protection Agency. A final potential complication is that for species-specific assessments, it is necessary to have a water-only effects data base for comparative purposes for the metal and the species of concern. However, for the purpose of SQC derivation for metals in sediments, target values for pore water metals could be obtained from appropriate WQC documents in a fashion similar to that for nonionic organic chemicals.

Acid Volatile Sulfide and SEM

The studies described in previous chapters have clearly demonstrated that AVS can be a key factor influencing interstitial water concentrations and bioavailability of metals in sediments. In virtually no instance have we seen metal toxicity when SEM is less than AVS and SEM greater than AVS often has been predictive of the presence (but not extent) of metal toxicity. The use of SEM and AVS concentrations alleviates the need for water-only effects data in an assessment since no bioavailability is expected at SEM less than AVS. A further advantage to measuring sediment SEM and AVS in sediments is that it gives an indication as to the relative size of the pool of both components. This is not possible through monitoring pore water metal concentrations. Pore water metal concentrations should be low in sediments with SEM very much less than AVS to, theoretically, Sem equals AVS. Yet, sediments with SEM close to AVS would be of more potential concern than those with SEM << AVS. In the absence of other metal binding phases, slight increases in SEM or

decreases in AVS could cause the SEM to exceed the AVS and thereby result in toxicity.

There are a number of limitations inherent in using either pore water or SEM and AVS to predict bioavailability. First, because AVS varies seasonally in a system-specific manner, it is desirable that SEM and AVS and pore water metals be measured over time, or at least when AVS is expected to be minimal (e.g., late winter in our studies). A single sampling is only a snap-shot of what occurs through the course of the year.

At present, investigations are ongoing to assess the role of AVS in deeper sediments relative to metal partitioning at the sediment surface, where most biological acitvity and exposure occurs. This is significant because the AVS pool in deeper sediments appears to remain relatively constant, as opposed to AVS in surficial sediments. It may be, for example, that as surficial sediments are depleted of AVS, metals will subsequently bind to AVS in deeper sediments. Alternatively, as AVS concentrations are depleted in surface sediments, other binding phases for metals may become important in determining bioavailability. In any instance, it is important that pore water metal and SEM and AVS measurements be made at all relevant points over the vertical gradient of the sediment cores; for example, if concern is only for exposure of current benthic communities, the measurements can be made in the surficial sediment horizon. On the other hand, if the assessment is focused on possible impacts of deeper sediments (e.g., for dredging), appropriate measurements should be made throughout the core.

Neither pore water metal concentrations nor SEM and AVS can be used to assess potential metal bioavailability in situations where sediments are expected to be altered and become aerobic through physical disturbance (e.g., storms, boat traffic). In fact, in these cases, it may be possible in a worst case evaluation to "exhaust" sediment AVS (e.g., by aerating the sample) before attempting to determine

the presence of bioavailable metals, possibly through evaluation of pore water metal concentrations.

Field validation of sediment quality criteria is an important component of the establishing their validity. To date, the most exhaustive studies have been conducted using spiked sediments in the laboratory and field which focus on changes in benthic community structures and the bioaccumulation of metals by benthos (Chapters 7 and 8). These studies have been consistent with predictions based on SEM and AVS ratios, and /or a pore water exposure model [1,2]. However, further work in this area is needed, in particular with in situ sediments contaminated by point or nonpoint source anthropogenic inputs of metals.

Based on the technical considerations described above, we present the following recommendations/caveats for assessing the potential bioavailability of metals in sediments.

1. Both SEM and AVS and pore water metal concentrations should be measured in sediment assessments focused on defining bioavailability. A standard method for the extraction and measurement of SEM and AVS has been described [3]. For the studies described above, pore water was isolated using either of two different techniques: dialysis chambers (peepers) or centrifugation. Other pore water isolation techniques also may be useful; however, we have had little experience with them.

2. If AVS is used as a normalization phase, it should be used *only* for cadmium, nickel, lead, zinc, and copper, and only for these metals when simultaneously extracted with the AVS. Molar concentrations of the metals then can be summed to generate SEM and compared to AVS ratios. Theoretically, however, it is possible to utilize pore water measurements of metals, other than the five listed above, to evaluate their potential bioavailability.

3. It is strongly recommended that cadmium, nickel, copper, lead and zinc all be measured when evaluating SEM and AVS and pore water metal concentrations, at least in initial test samples. This is because although all five of these metals have a higher affinity than iron for sulfide in monosulfide complexes, individually they also have varying affinities (solubility products) for the sulfide. Thus, for example, cadmium will displace nickel from sulfide, and if excess sulfide is not available, nickel will be released to the pore water. If only pore water metals were measured, or only nickel was measured in the solid phase, the analyst would erroneously conclude that nickel was the only problem in the sediments, when in fact, elevated concentrations of cadmium also were present. In order to have a complete understanding as to why a specific metal is present at elevated concentrations in pore water, it is necessary to know the molar concentrations of all the SEM. This is particularly true when considering the fact that metal concentrations often covary in contaminated aquatic sediments, that is, rarely is only one metal of concern.

4. In fully aerobic sediments (e.g., sand), AVS concentrations should not be used to attempt to predict the bioavailability of metals in sediments. Theoretically, however, it should be possible to infer bioavailability based on pore water metal concentrations. Moreover, as described in Chapter 9, significant progress is being made in identifying alternative normalization phases, such as carbon, for metals in aerobic sediments.

5. Only a limited amount of research has been conducted to assess the utility of SEM and AVS or pore water concentrations for predicting metal bioavailability in long-term exposures. Given the uncertainties in kinetics of metal and AVS interactions in temporal cycles, and the lack of information on the importance of other metal binding phases relative to these cycles, extrapolations of the exposure model to long-term situations should be made with care. Further information also is needed concerning the nature of the microhabitat of

invertebrates relative to long-term changes in metal bioavailability in sediments. In any case, it is important that pore water metal concentrations and SEM and AVS be measured in sediment horizons appropriate for defining exposure to species of concern. Based on our research, it appears that exposure of benthic organisms to surficial sediments can be defined reasonably well by measurement in the 0-2 cm horizon.

6. As with any chemical-specific monitoring method, the analyst should be aware that: (a) not all chemicals of possible toxicological concern can be measured in environmental samples; and (b) in most instances, it is difficult to account for possible toxicological interactions among measured toxicants. For these reasons, we strongly recommend toxicity tests as an integral part of any assessment concerned with the effects of sediment contaminants.

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CHAPTER 11

PROPOSED SEDIMENT QUALITY CRITERIA

Introduction

Sediment quality criteria are intended to be the U.S. Environmental Protection Agency's best recommendation of the concentration of a metal in a sediment that will be protective of benthic organisms. The sediment quality criteria for the five metals: cadmium, copper, nickel, lead, and zinc, will be based on the Equilibrium Partitioning model of bioavailability. EqP asserts that the bioavailability of a chemical is related to the chemical activity of the sediment - interstitial water system. For these metals it has been shown that biological effects correlate with free metal activity in either water only exposures or in sediment - interstitial water exposures. Thus the SQC for these metals are based on insuring that the free metal activity is below levels that can cause undesirable biological effects.

SQC's for the five metals being considered can be derived using four procedures:

(1) By comparing the molar concentrations of cadmium, copper, lead, nickel, and zinc to the molar concentration of AVS in sediments;

(2) By comparing the measured interstitial water concentrations of metals to the water quality criteria final chronic values (FCVs) for the metals;

(3) By using organic carbon based partition coefficients in addition to the AVS to compute the interstitial water concentrations and compare them to the water quality criteria FCVs;

(4) By using minimum partition coefficients and AVS to compute lower bound sediment concentrations that are unlikely to cause toxicity.

These procedures are described in more detail below. No citations to the literature are included in the chapter since these have been provided in the previous chapters. We believe that the technical basis for implementing procedures (1) and (2) are presently supportable. Initial data for implementing procedures (3) and (4) have also been presented. However, additional research is required to complete the required data sets, as discussed below.

In the following sections we discuss the application of these methods to deriving an SQC for a single metal. Then we continue with the more common situation where appreciable concentrations of all the metals are present. The application of these principles to the derivation of a sediment quality criteria for a single metal is included for illustrative purposes only. It is instructive to present the logic for this case as a prelude to the derivation of the multiple metal criteria. However, as will become clear subsequently, single metal criteria are not usually applicable to field situations since there is always a significant quantity of more than one metal to be considered. In fact it is misleading to think of the criteria one metal at a time. As we shall see, single metal criteria are inherently underprotective because of the additive nature of AVS binding. Nevertheless the following sections are included because of their instructional value.

One final point should be made with respect to nomenclature. When we use the terms non-toxic or having no effect, we mean only with respect to the five metals considered in this document. The toxicity of field collected sediments can be caused by other chemicals. Therefore not violating the SQC for metals does not guarantee that the sediments are non-toxic, only that the five metals being considered will not have an undesirable biological effect.

Single Metal Sediment Quality Criteria

Sediment quality criteria for metals will be expressed in molar units. These are the natural units because of the one to one molar stoichiometry of metal binding to AVS. Thus solid phase constituents: AVS and simultaneously extracted metal, SEM, are in μmol/g units. The interstitial water concentrations are in μmol/L units as are the metal activities. To be consistent with the usual chemical notation, metal activities are denoted by curly brackets {} and metal concentrations are denoted by square brackets []. The partition coefficients have units L/g consistent with the above solid and aqueous phase concentration units. Table 11-1 summarizes these conventions:

TABLE 11-1.

Species	Phase	Notation	Units
AVS	Solid	[AVS]	μmol/g
SEM	Solid	[SEM]	μmol/g
Metal activity	Aqueous	$\{M^{2+}\}$	μmol/L
Dissolved Metal conc.	Aqueous	$[M_d]$	μmol/L
Total Metal conc.	Solid + Aqueous	$[SEM_T]$	μmol/L(bulk)

The subscripted notation, M_d, is used to distinguish aqueous phase molar concentrations from solid phase molar concentrations with no subscript. For the total concentration, $[SEM_T]$, the units are the moles of metal per volume of solid + liquid phase. Since metal activity is used below only relative to the aqueous phase no subscript is needed.

AVS Criteria

It has been demonstrated that if the SEM of a sediment is less than the AVS:

$$[SEM] \leq [AVS] \tag{11-1}$$

then no toxicity effects are seen. This is consistent with the results of a chemical equilibrium model for the sediment - interstitial water system. The resulting metal activity $\{M^{2+}\}$ can be related to the total SEM of the sediment and water, and the metal sulfide (K_{MS}) and iron sulfide (K_{FeS}) solubility products. In particular it is true that if [SEM] < [AVS] then:

$$\frac{\{M^{2+}\}}{[SEM_T]} \leq \frac{K_{MS}}{K_{FeS}} \tag{11-2}$$

Since the ratio of metal sulfide to iron sulfide solubility products (K_{MS}/K_{FeS}) is very small ($< 10^{-5}$) even for the most soluble of the sulfides (Table 4-2, Chapter 4), the metal activity of the sediment is at least five orders of magnitude smaller than the SEM. This guarantees that no biological effects would be seen if this sediment were tested. Therefore the condition [SEM] < [AVS] is a no effect sediment quality criteria.

The reason we use the term "no effect" criteria is that for the condition [SEM] < [AVS] we expect no biological impacts. For [SEM] > [AVS], which would normally be considered a criteria violation, there are cases where we would expect no biological impacts, for example, where significant organic carbon partitioning is occurring. The most dramatic examples are for sediments with low AVS concentrations (Fig.6-5).

Interstitial Water Criteria

The condition [SEM] < [AVS] guarantees that the metal activity of the sediment - interstitial water system is very low and therefore, below any effect level of concern. Another way of guaranteeing this is to place a condition on the interstitial water activity directly. Let us suppose that we knew the metal activity, denoted by

{FCV}, that corresponded to the Final Chronic Value of the Water Quality Criteria: [FCV]. Then the SQC corresponding to this effect level is:

$$\{M^{2+}\} \leq \{FCV\} \qquad (11\text{-}3)$$

It is quite difficult to measure and/or calculate the metal activity in a solution phase, $\{M^{2+}\}$, at the low concentrations required since it depends on the identities, concentrations and thermodynamic affinities of other chemically reactive species that are present. Also the WQC on an activity basis, {FCV}, is not known.

An approximation to this condition is:

$$[M_d] \leq [FCV_d] \qquad (11\text{-}4)$$

That is, we require that the total dissolved metal concentration in the interstitial water $[M_d]$ be less than the Final Chronic Value from the WQC applied as a dissolved criteria. Although this requirement ignores the effect of chemical speciation on both sides of the equation - compare Equation (11-4) to (11-3) - it is the approximation that is currently being suggested by the EPA for the WQC for metals. That is, the WQC should be applied to the total *dissolved* - rather than the total acid recoverable - metal concentration. Hence, if this second condition is satisfied it is consistent with the level of protection afforded by the water quality criteria.

In situations where the SEM exceeds the AVS ([SEM] > [AVS]) but the interstitial water total dissolved metal is less than the final chronic value ($[M_d] < [FCV_d]$), this sediment does not violate the criteria. These cases occur when significant binding is occurring to other phases. It should be noted that using the final chronic value for metals requires that the hardness of the interstitial water be known since the criteria vary as hardness varies.

AVS and Organic Carbon Criteria

For sediments with an appreciable AVS concentration relative to SEM, the SQC requirement that [SEM] < [AVS] is a useful result. However if the AVS of the sediment is small, then the condition is of little value. The reason is that other sorption phases are present that affect the activity of the system. Similarly, even in situations where significant AVS occurs in sediments, other sorption phases may significantly limit the metal activity even if the SEM exceeds the AVS.

Consider the organic carbon in the sediment. It is demonstrated in Chapter 9 that a relationship exists between the SEM that is in excess of the AVS and the interstitial water metal activity $\{M^{2+}\}$:

$$[SEM]-[AVS]=K^{*}_{d,OC}f_{OC}\{M^{2+}\} \qquad (11\text{-}5)$$

where $K^{*}_{d,OC}$ is the partition coefficient between the organic carbon of the sediment and f_{oc} is the weight fraction of organic carbon of the sediment. If we require that the metal activity be at the FCV metal activity, then the SQC for SEM would be:

$$[SEM]_{SQC}=[AVS]+K^{*}_{d,OC}f_{OC}\{FCV\} \qquad (11\text{-}6)$$

If the activity is replaced with the WQC total dissolved FCV, then the criteria becomes:

$$[SEM]_{SQC}=[AVS]+K_{d,OC}f_{OC}[FCV_d] \qquad (11\text{-}7)$$

where $K_{d,OC}$ is the partition coefficient between organic carbon and total dissolved interstitial water metal concentration. Note that the organic carbon based partition coefficients vary with respect to pH so that the pH of the interstitial water must be either measured or estimated. In addition, the FCV for the five metals is hardness dependent in freshwater so that the hardness is also required.

This is the third condition from which a sediment quality criteria can be derived. For sediments where organic carbon provides all the excess binding capacity, it is a criteria in the ordinary sense. That is, exceeding the criteria would imply that unacceptable biological impacts would occur. Since the analysis of sediment binding data and the estimation of the K_{OC}'s in Chapter 9 attributes all the binding to organic carbon thereby indexing the binding to organic carbon, using these constants would imply that the criteria (Equation 11-8) is the boundary between no effects and effects. There are situations, however, for which the assumption that organic carbon is the only important phase may not be correct. In these cases, the criteria becomes a no effect criteria. Of course, using this as an effect criteria also assumes that applying the FCV as a total dissolved criteria is appropriate. If, in fact, a significant fraction of the interstitial water metal is not bioavailable, then again this criteria would be a no effect criteria.

AVS and Minimum Partitioning Criteria

It would be useful to have a solid phase criteria that would effectively screen sediments for which the metals concentrations are low enough so that no problem is anticipated. The idea is to examine sediments for which the partition coefficients are likely to be quite low. From these sediments it would be possible to establish minimum partition coefficients ($K_{d,min}$) which could be applied to any sediment. Then the no effect SQC would be:

$$[SEM]_{SQC}=K_{d,min}[FCV] \qquad (11\text{-}8)$$

This would also ba a no effect criteria since it is established using a minimum partition coefficient. No AVS term is included unlike Equation (11-7), because it is assumed that these sediments have no appreciable AVS. If there was a significant AVS concentration, then the AVS criteria (Equation 11-1) would apply.

These single metal criteria are derived only for illustrative purposes. Single metal criteria are misleading and should not be applied. Only criteria based on the five metals taken together are valid. They reduce to the single metal criteria in the unlikely situation where only one metal is present to any significant degree.

Multiple Metals Criteria

The previous section presents the derivation of criteria if only one metal is present in significant quantities in a sediment. In the usual case, however, it is insufficient and inappropriate to consider each metal separately. This is of particular concern for the AVS criteria.

AVS Criteria

The results of calculations using equilibrium chemical models indicate that metals act in an additive fashion when binding to AVS. That is, each of the five metals: Cu, Pb, Cd, Zn, and Ni will bind to the AVS and be converted to CuS, PbS, CdS, ZnS, and NiS in this sequence; i.e., in the order of increasing solubility. The mixed metals experiment (Figure 5-3) and the Foundry Cove data (Chapter 6) confirm this behavior. Therefore, the five metals must be considered together. There cannot be a criteria for just nickel, for example, since 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 SEM, then the SEM will be misleadingly small, and it may appear that [SEM] < [AVS] when in fact that is not true if all the metals are considered together. We restrict the discussion below to the five metals listed above. In special situations where other sulfide forming metals (e.g., Co, Hg, Ag) are in high concentrations they also must be considered.

The equilibrium model prediction of the metals activity if a mixture of the metals are present is similar to the single metals case. If the sum of the SEM's for the five metals is less than the AVS; i.e.:

$$\sum_i [SEM_i] \leq [AVS] \tag{11-9}$$

then:

$$\frac{\{M_i\}}{[SEM_{i,T}]} < \frac{K_{M_iS}}{K_{FeS}} \tag{11-10}$$

where $[SEM_{i,T}]$ is the total SEM (μmol/L(bulk)) for the ith metal. Thus the activity of each metal, $\{M_i\}$, is unaffected by the presence of the other sulfides. This can be understood as follows. Imagine that the chemical system starts initially as iron and metal sulfide solids and that the system proceeds to equilibrium by each solid dissolving to some extent. The iron sulfide dissolves until the solubility product of FeS is satisfied. This sets the sulfide activity. Then each metal sulfide dissolves until it reaches its solubility. Since so little of each dissolve relative to the FeS, the interstitial water chemistry is not appreciably changed. Hence the sulfide activity remains the same and the metal activity adjusts to meet each solubility requirement. Therefore, each metal sulfide behaves independently of each other. The fact that they are only slightly soluble relative to FeS is the cause of this behavior. Hence the AVS criteria is easily extended to the case of multiple metals. It is only necessary to sum the molar concentration of each metal SEM and compare it to the AVS (Equation 11-9).

Interstitial Water Criteria

The application of the interstitial water criteria to multiple metals is complicated not by the interactions of the metals chemistry of the sediment - interstitial water system as in the case with the AVS criteria, but rather their possible toxic interactions. Even if the individual concentrations do not exceed the FCV of each

metal (FCV_i), their additive effect might be toxic. Therefore, to address this additivity, the interstitial water metal concentrations are converted to toxic units and these are summed. Since the effects concentration to be used are the final chronic values from the water quality criteria, we call these toxic units the Interstitial Water Criteria Toxic Units (IWCTU). For freshwater sediments, the FCV's are hardness dependent for all of the metals being considered and they need to be adjusted to the hardness of the interstitial water from the sediment being considered. For the ith metal with total dissolved concentration $[M_{i,d}]$ the IWCTU for the ith metal is:

$$IWCTU_i = \frac{[M_{i,d}]}{[FCV_{i,d}]} \tag{11-11}$$

The sediment quality criteria requires that the sum of the interstitial water criteria toxic unit concentration is less than one:

$$\sum_i \frac{[M_{i,d}]}{[FCV_{i,d}]} \leq 1 \tag{11-12}$$

Hence the multiple metals criteria is quite similar to the single metal case (Equation 11-4) except that the criteria is expressed as toxic units and summed.

AVS and Organic Carbon Criteria

The case for which the sediment organic carbon needs to be considered in addition to AVS is more complicated. Consider, first, a single metal. The relationship between interstitial water concentrations and sediment concentration for the ith metal is given by the equation:

$$[SEM_i] = [AVS] + K_{d,oc,i} f_{oc} [M_{i,d}] \tag{11-13}$$

where $K_{d,OC,i}$ is the metal specific partition coefficient between sediment organic carbon and interstitial water, and $[M_{i,d}]$ is the total dissolved interstitial water metal concentration. For this case the interstitial water concentration is predicted using the

SEM in excess of the AVS and the partition coefficient between the excess SEM and the interstitial water:

$$\frac{[SEM_i]-[AVS]}{K_{d,oc,i}f_{oc}}=[M_{i,d}] \qquad (11\text{-}14)$$

In order to apply this equation to the case of multiple metals, it is first necessary to identify and quantify the metals which are not entirely present as metal sulfides. The best way to do this is to establish which metals are present as the metal sulfides and in what quantity. The procedure is to assign the AVS to the metals in the sequence of their solubility products from the lowest to the highest: SEM_{Cu}, SEM_{Pb}, SEM_{Cd}, SEM_{Zn}, and SEM_{Ni}. That is, the AVS complexed metals would be Cu, followed by Pb, followed by Cd, etc. until the AVS is exhausted. The remaining SEMs are present in excess of the AVS.

To be specific, let $\Delta[SEM_i]$ be the excess SEM for each of the ith metals. The least soluble metal sulfide (of the five metals being considered in this document) is copper sulfide (CuS). Thus if the copper SEM is less than the AVS ($[SEM_{Cu}] < [AVS]$), then all of the copper SEM must be present as copper sulfide (CuS) and no additional SEM is present so that $\Delta[SEM_{Cu}] = 0$. The remaining AVS is $\Delta[AVS] = [AVS] - [SEM_{Cu}]$.

This computation is repeated next for lead because lead sulfide (PbS) is the next least soluble sulfide. Suppose, unlike copper, the lead SEM is not less than the remaining AVS ($[SEM_{Zn}] > \Delta[AVS]$). Hence only a portion of the lead SEM is present as PbS and the remaining SEM, which is denoted as $\Delta[SEM_{Pb}]$, is the difference between the remaining AVS, $\Delta[AVS]$ and the lead SEM: $\Delta[SEM_{Pb}] = [SEM_{Pb}] - \Delta[AVS]$. Thus a portion of the lead is present as lead sulfide, and a portion is excess SEM.

Since the AVS has been exhausted by the lead SEM, the remaining metals are all present as excess SEM so that: $\Delta[SEM]_{Cd} = [SEM_{Cd}]$; $\Delta[SEM_{Zn}] = [SEM_{Zn}]$; and $\Delta[SEM_{Ni}] = [SEM_{Zn}]$.

For each of these metals, the interstitial water concentrations can be determined from the appropriate partition coefficients:

$$[M_{i,d}] = \frac{\Delta[SEM_i]}{K_{d,oc,i} f_{oc}} \qquad (11\text{-}15)$$

This equation is analogous to Equation (11-13) for the single metal case. Note that if $\Delta[SEM_i] = 0$ then so also is the interstitial water metal concentration. The interstitial water criteria toxic units are computed using this equation for the interstitial water concentrations. That is:

$$\sum_i \frac{[M_{i,d}]}{[FCV_{i,d}]} = \sum_i \frac{\Delta[SEM_i]}{K_{d,oc,i} f_{oc} [FCV_{i,d}]} \qquad (11\text{-}16)$$

where Equation (11-14) is used to compute the interstitial water concentrations. Note that the organic carbon based partition coefficients vary with respect to pH so that the pH of the interstitial water must be either measured or estimated together with the hardness if necessary.

The sediment quality criteria requires that the computed total interstitial water criteria toxic unit concentration is less than one:

$$\sum_i \frac{\Delta[SEM_i]}{K_{d,oc,i} f_{oc} [FCV_{i,d}]} \leq 1 \qquad (11\text{-}17)$$

This criteria is simply the interstitial water toxic unit criteria, Equation (11-12), with the interstitial water concentrations calculated from the excess SEM for each metal and the appropriate partition coefficients.

AVS and Minimum Partition Coefficient Criteria

The no effect criteria that use the minimum partition coefficients ($K_{d,Min,i}$) is analogous to that using the organic carbon based coefficients:

$$\sum_i \frac{\Delta[SEM_i]}{K_{d,Min,i}[FCV_{i,d}]} \leq 1 \qquad (11\text{-}18)$$

Since the minimum partition coefficients are being used, this would correspond to the upper bound estimate of the interstitial water criteria toxic units.

Criteria Summary

The proposed Sediment Quality Criteria is as follows. The sediment passes the SQC if any one of these conditions is satisfied:

(1) AVS Criteria:

$$\sum_i [SEM_i] \leq [AVS] \qquad (11\text{-}19)$$

(2) Interstitial Water Criteria:

$$\sum_i \frac{[M_{i,d}]}{[FCV_{i,d}]} \leq 1 \qquad (11\text{-}20)$$

(3) AVS and Organic Carbon Criteria:

$$\sum_i \frac{\Delta[SEM_i]}{K_{d,oc,i} f_{oc} [FCV_{i,d}]} \leq 1 \qquad (11\text{-}21)$$

(4) AVS and Minimum Partition Coefficient Criteria:

$$\sum_i \frac{\Delta[SEM_i]}{K_{d,Min,i} [FCV_{i,d}]} \leq 1 \qquad (11\text{-}22)$$

If any one of these criteria are violated, this does not mean that the sediment is toxic. For example, if the AVS in a sediment is virtually zero, then Condition (1) will be violated. However, if there is sufficient organic carbon sorption so that either Condition (3) or Condition (4) is satisfied then the sediment is non-toxic.

If all - *not any but all* - of these conditions are violated then there is reason to think that the sediment may be unacceptably contaminated by these metals. Further testing and evaluations are therefore required in order to assess the actual level of toxicity and its causal relationship to the five metals. These may include acute and chronic tests on species that are sensitive to the metals suspected to be in excess of the AVS and causing the toxicity. Also in situ community assessments and seasonal characterizations of the SEM's, AVS, and interstitial water concentrations would be appropriate.

Sediment Quality Criteria Uncertainty

The methodology for obtaining sediment quality criteria relies on certain simplifications and, for conditions 3-4, empirical partitioning models to insure that the metal activity of the sediment - interstitial water system is below effects levels. As

a consequence, there are uncertainties associated with their use. It is anticipated that when final SQC are generated, confidence limits will be generated as well. This was the case for the non-ionic organic chemical SQCs. It is anticipated that the derivation of the uncertainty limits will be derived in the same way, namely by quantifying the predictive power of the methods.

For the condition (1) criteria relating total SEM and AVS, and for the condition (2) using measured interstitial-water concentrations, sufficient data currently exists to derive the confidence limits. Since these are both no effect criteria, the confidence limits are set so that the predictive power of no effect has a high probability of being the case. That is the criteria requirement would be:

$$\sum_i [SEM_i]-[AVS] \leq [SEM]_{SQC,95} \qquad (11\text{-}23)$$

where $[SEM]_{SQC,95}$ is computed so that 95 percent of the tested sediments are correctly classified as non toxic. Based on the results in chapters 5-7, $[SEM]_{SQC,95} \approx 0$, the theoretical value based on one to one stoichiometric binding of the divalent metals by AVS.

A similar analysis will be applied to the measured interstitial water toxic unit condition. The condition:

$$\sum_i \frac{[M_{i,d}]}{[FCV_{i,d}]} \leq IWCTU_{SQC,95} \qquad (11\text{-}24)$$

where $IWCTU_{SQC,95}$ is set so that 95 percent of the cases are correctly predicted. Since we have no chronic data that would show effects at the criteria level, the acute data base would be analyzed instead:

$$\sum_i \frac{[M_{i,d}]}{[LC50_{i,d}]} \leq IWCTU_{SQC,95} \qquad (11\text{-}25)$$

using the water only LC50's. The criteria $IWCTU_{SQC,95}$ that predicted correctly with 95 percent confidence that less then 50 percent mortality was observed would be the criteria that would be applied to the FCV criteria, Equation (11-24).

For condition 3, the criteria depends additionally on partition coefficients which are also uncertain to some extent. We would derive the uncertainty bounds based on the predictive ability of the criteria. That is, the acute data base would be analyzed, not from the point of view of predicting no effect, but rather from the point of view of predicting the LC50s observed in the sediment tests. That is, the equations to be analyzed are:

$$\sum_i \frac{\Delta[SEM_i]}{K_{d,oc,i} f_{oc} [LC50_{i,d}]} < IWCTU_{SQC,5} \qquad (11\text{-}26)$$

and

$$\sum_i \frac{\Delta[SEM_i]}{K_{d,oc,i} f_{oc} [LC50_{i,d}]} > IWCTU_{SQC,95} \qquad (11\text{-}27)$$

where the 5 and 95 percent confidence limits, $IWCTU_{SQC,5}$ and $IWCTU_{SQC,95}$ are calculated such that 90 percent of the predictions are correct. For example if these methods are reliable within a factor of two 90 percent of the time, then $IWCTU_{SQC,5} = 0.5$ and $IWCTU_{SQC,95} = 2.0$

For condition 4, the criteria is a no effect criteria. For this case, the uncertainty analysis would correspond to a probability analysis of the minimum partitioning coefficients, $K_{d,min,i}$. A number of sediments would be analyzed and the 5th percentile would be estimated. This would be the recommended partition coefficient that would correctly classify 95 percent of the minimum partitioning sediments.

The experimental data is available to compute the confidence limits for the no effect conditions (1) and (2). However, the experiments required to compare predicted and observed LC50's are not available. The spiked experiments presented in Chapters 5 to 7 were all dosed with too wide a spacing of concentrations (0.1, 0.3, 1.0, 3.0, and 10.0 multiples of the AVS) to permit calculating a reliable LC50. Therefore, a selected number of sediments, with widely varying carbon concentrations, would need to be tested with a much more narrow range of concentrations. And the spacing would be computed using the predicted LC50 from the AVS and the organic carbon concentration.

For condition (4), more sandy low carbon sediments need to be evaluated and the metal partition coefficients measured, from which a probability distribution analysis could be made. From the small amount of data already available, it is interesting to note that even these low carbon sediments have $K_{d,OC}$'s that are in the same order of magnitude as found in the high carbon sediments.

Research Recommendations

There are a number of unfinished areas of research that need to be completed.

1. The organic carbon partition coefficients have been developed for three metals in freshwater: Cu, Cd, and Pb. The remaining metals need to be completed. A similar set of experiments are needed for saltwater.

2. Additional experiments need to be conducted, as outlined above, for the uncertainty analysis of condition 3. These are analogous to the set of experiments performed for the non-ionic organic chemicals.

3. Additional partition coefficients are needed for the low carbon sediments.

4. An explicit procedure is needed to handle the cases for which the no effect criteria are exceeded. Both field and laboratory testing methods need to be elaborated into a staged investigation.

There are the other metals for which criteria a needed. These include chromium, arsenic, and selenium. Some initial work has been done for chromium and arsenic. It appears that AVS can reduce Cr(VI) to Cr(III), and it may be able to do the same for the other redox sensitive metals. Further work is necessary to identify the controlling phases for these metals.

Conclusions

A proposal for establishing sediment quality criteria for cadmium, copper, nickel, lead, and zinc has been presented. It is based on the Equilibrium Partitioning Model. The criteria are based on keeping the activity of the sediment - interstitial water equilibrium system below effects levels. The criteria presented in this report are all lower bound criteria. That is, if the criteria are satisfied then no effects are expected. If the criteria are exceeded then further study is required. The difficulties are related to the presence of multiple binding species in both the solid phase and in the interstitial water.

The initial solid phase criteria is based on the strongest binding phase, namely the AVS. If sufficient AVS is present then no effects are expected. If the simultaneously extractable metal exceeds the AVS, then other binding phases become important. The next most important phase is organic carbon. A partitioning model has been suggested that can be used to develop criteria. It is analogous to the organic carbon normalized model used for the non-ionic organic chemical SQCs. It is uncertain at present whether any other solid phases need to be considered.

The interstitial water criteria are based on total dissolved interstitial water metals concentrations. Therefore, they are analogous to the water quality criteria. They do not take explicit account of metal speciation and so they are not regulating the metal activity. Therefore, these are also lower bound criteria. An exceedence of the water quality criteria in the interstitial water may or may not signal a toxicity problem. However, if the concentrations are below the WQC then no effects are expected.

It must be stressed that the sediment quality criteria are aquatic life criteria that apply only to benthic organisms. They do not address the water column consequences of contaminated sediments. Water column concentrations are determined by the transport of metals from the sediment to the overlying water. The resulting concentrations would be compared to the water quality criteria for metals. This is a separate evaluation that needs to be made if water column effects are suspected.