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**CADMIUM, COPPER, LEAD, NICKEL, SILVER AND
ZINC:**

Proposed Sediment Guidelines

for the Protection

of Benthic Organisms:

Technical Basis and

Implementation

p. 56 - Water quality criteria

p. 73 - Interstitial water guidelines

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SECTION 1

INTRODUCTION

1.1 GENERAL INFORMATION

Under the Clean Water Act (CWA) the U.S. Environmental Protection Agency (U.S. EPA) is responsible for protecting the chemical, physical and biological integrity of the nation's waters. In keeping with this responsibility, the U.S. EPA published ambient water quality criteria (WQC) in 1980 for 64 of the 65 toxic pollutants or pollutant categories designated as toxic in the CWA. Additional water quality documents that update criteria for selected consent decree chemicals and new criteria have been published since 1980. These WQC are numerical concentration limits that are the U.S. EPA's best estimate of concentrations protective of human health and the presence and uses of aquatic life. While these WQC play an important role in assuring a healthy aquatic environment, they alone are not sufficient to ensure the protection of environmental or human health.

Toxic pollutants in bottom sediments of the nation's lakes, rivers, wetlands, estuaries and marine coastal waters create the potential for continued environmental degradation even where water-column concentrations comply with established human health and aquatic life WQC. In addition, contaminated sediments can be a significant pollutant source that may cause water quality degradation to persist, even when other pollutant sources are stopped (USEPA 1997a, b, c). The scarcity of defensible sediment guidelines and the single chemical nature of those available make it difficult to accurately assess the extent of the ecological risks of contaminated sediments, to establish pollution prevention strategies, and to identify, prioritize and implement appropriate clean up activities and source controls.

As a result of the need for a procedure to assist regulatory agencies in making decisions concerning contaminated sediment problems and their prevention, a U.S. EPA Office of Science and Technology and Office of Research and Development research team was established to review alternative approaches (Chapman, 1987). All of the approaches reviewed had both strengths and weaknesses and no single approach was found to be applicable for sediment guidelines derivation in all situations (U.S. EPA, 1989). The equilibrium partitioning (EqP) approach was selected for non-ionic organic chemicals because it presented

the greatest promise for generating defensible national chemical specific sediment guidelines applicable across a broad range of sediment types. The term EqP sediment guidelines (ESG) refers to numerical concentrations for individual chemicals that are applicable across the range of sediments encountered in practice. The three principal observations that established the EqP method of deriving sediment guidelines for non-ionic organic chemicals were:

1. The concentration of non-ionic organic chemicals in sediments, expressed on an organic carbon basis, and in interstitial water, correlate to observed biological effects on sediment dwelling organisms across a range of sediments.
2. Partitioning models can relate sediment concentrations for non-ionic organic chemicals on an organic carbon basis to freely dissolved concentrations in interstitial water.
3. The distribution of sensitivities of benthic and water column organisms to chemicals are similar, thus, the currently established WQC final chronic values (FCV) can be used to define the acceptable effects concentration of a chemical freely dissolved in interstitial water.

Due to their wide-spread release and persistent nature, metals such as cadmium, copper, lead, nickel, silver and zinc are commonly elevated in aquatic sediments. These metals are a potential aquatic environmental concern in addition to nonionic organic chemicals. Thus, there have been various proposals for deriving sediment guidelines or standards for protecting benthic communities from metal toxicity. Many such attempts have featured measurement of total sediment metals followed by comparison to background metal concentrations, or in some cases an effects-based endpoint (Ingersoll et al., 1996; Long and Morgan, 1991; MacDonald et al., 1996; Persaud et al., 1989; Sullivan et al., 1985). An important limitation to these types of approaches is that causality can not be established in part because of the procedures used to derive correlative values and because values derived are based on total rather than bioavailable metal concentrations; i.e., for any given total metal concentration, adverse toxicological effects may or may not occur, depending upon physico-chemical characteristics of the sediment of concern (Di Toro et al., 1990; Luoma et al., 1989; Tessier and Campbell, 1987).

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

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

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

The same three principals observed in applying the EqP approach to non-ionic organic chemicals listed above, also apply with only minor adjustments to deriving ESG for mixtures of the cationic metals cadmium, copper, lead, nickel, silver and zinc.

1. The concentrations of *these six metals in sediments, normalized to the concentration of acid volatile sulfide (AVS) and simultaneously extracted metals (SEM; the metals extracted with AVS) in sediments*, and in interstitial waters correlate to observed biological effects on sediment dwelling organisms across a range of sediments.
2. Partitioning models can relate sediment concentrations for *divalent cationic metals (and silver) on an AVS basis* to the absence of freely dissolved concentrations in interstitial water.
3. The distribution of sensitivities of benthic and water column organisms to organic chemicals and metals are similar (U.S. EPA, 1998a), thus, the currently established WQC final chronic values (FCV) can be used to define the acceptable effects concentration of *the metals* freely dissolved in interstitial water.

The EqP approach, therefore, assumes that: (1) the partitioning of the metal between sediment AVS (or any other binding factors controlling bioavailability) and interstitial water is at equilibrium; (2) organisms receive equivalent exposure from interstitial water-only exposure or from exposure to any other equilibrated sediment phase: either from interstitial water via respiration, sediment via ingestion, sediment-integument exchange, or from a mixtures of exposure routes; (3) for the cationic metals cadmium, copper, lead, nickel, silver and zinc, no-effects concentrations in sediments can be predicted using the difference between the total molar concentration of SEM for these metals and the total molar concentration of AVS. This difference is the amount of either excess metal or excess AVS. So long as the molar concentration of AVS equals or exceeds the sum of the molar concentrations of these metals, the sediment is not expected to cause acute or chronic toxicity in benthic organisms; and (4) the WQC FCV concentration is an appropriate effects concentration for freely dissolved metal in interstitial water and the toxicity of metals in interstitial water is no more than additive.

Two equally applicable ESG for metals, a solid phase and an interstitial water phase, are proposed. For the first time, the Agency is publishing ESG that account for bioavailability in sediments and potential for effects of a mixture in the aquatic environment. The mixtures approach for these six metals will provide an ecologically relevant benchmark by resolving the longstanding toxicological problem of their interdependent geochemistry. The solid phase ESG is defined as the $\Sigma[\text{SEM}] - [\text{AVS}] \leq 0$ (total molar concentration of simultaneously extracted metal - total molar concentration of acid volatile sulfide is less than or equal to zero). Note that cadmium, copper, lead and nickel are divalent metals so that one mole of each metal can bind with one mole of AVS. The molar concentrations of these metals are compared to AVS on a one to one basis. Silver however exists predominantly as a monovalent metal so that silver monosulfide (Ag_2S) binds two moles of silver for each mole of AVS. Therefore SEM_{Ag} by convention will be defined as the molar concentration of silver divided by two, $[\text{Ag}]/2$, which is compared to the molar AVS concentration. The interstitial water phase ESG is $\Sigma[\text{M}_{\text{i,d}}]/[\text{FCV}_{\text{i,d}}] \leq 1$ (the sum over all of the six metals of the concentration of each individual metal dissolved in the interstitial water/ the metal-specific Final Chronic Value based on dissolved metal is less than or equal to one). This latter value is termed interstitial water guidelines toxic units (IWGTUs). The IWGTUs approach by definition requires that the IW metals are additive. The data presented in this document supports additivity.

Importantly, both the solid phase ESG and interstitial water ESG are no-effect guidelines; i.e., they predict sediments that are acceptable for the protection of benthic organisms. These ESG when exceeded do not predict sediments that are unacceptable for the protection of benthic organisms. The solid phase (SEM-AVS) guideline avoids the methodological difficulties of interstitial water sampling that may lead to an overestimate of exposure and provides information on the potential for additional metal binding. The use of both the solid phase and interstitial water guidelines will improve estimates of risks of sediment-associated metals. For example, the absence of significant concentrations of metal in interstitial water in toxic sediments having $\text{SEM-AVS} > 0$ and in nontoxic sediments having $\text{SEM-AVS} \leq 0$ demonstrates that metals in these sediments are unavailable. Because of the known spatial and temporal cycling of the important metal-binding phases in sediments, Section 5 of this document provides implementation guidance on sediment collection, handling and analysis that will improve estimates of risk.

The ESG developed using the latest available scientific data are suitable for providing guidance to regulatory agencies because they are:

1. numeric values,
2. chemical specific,
3. causal,
4. applicable to most sediments and
5. protective of benthic organisms.

It should be emphasized that these guidelines are intended to protect benthic organisms from the direct effects of these six metals associated with sediments. ESG are intended to apply to sediments permanently inundated with water, intertidal sediment and to sediments inundated periodically for durations sufficient to permit development of benthic assemblages. They do not apply to occasionally inundated soils containing terrestrial organisms. These guidelines do not address the question of possible contamination of upper trophic level organisms or the synergistic, additive or antagonistic effects of other substances. The ESG presented in this document represent the U.S. EPA's best recommendation at this time of the concentration of a metals mixture (cadmium, copper, lead, nickel, silver and zinc) in sediment that will not adversely affect most benthic organisms. ESG values may be adjusted to account for future data or site specific considerations (U.S. EPA, 1998c).

This document presents the theoretical basis and the supporting data relevant to the derivation of the ESG for the metals cadmium, copper lead, nickel, silver and zinc. An understanding of the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" (Stephan et al., 1985), response to public comment (U.S. EPA, 1985a); "Ambient Water Quality Criteria for Cadmium" (U.S. EPA, 1985b); "Ambient Water Quality Criteria for Copper" (U.S. EPA, 1985c); "Ambient Water Quality Criteria-Saltwater Copper Addendum" (U.S. EPA, 1995c); "Ambient Water Quality Criteria for Lead" (U.S. EPA, 1985d); "Ambient Water Quality Criteria for Nickel" (U.S. EPA, 1986); "Ambient Water Quality Criteria for Zinc" (U.S. EPA, 1987); "Ambient Water Quality Criteria for Silver" (U.S. EPA, 1980) is necessary in order to understand the following text, tables and calculations. Guidance for the acceptable use of ESG values for metals mixtures is contained in "Users Guide for Multi-Program Implementation of Sediment Guidelines" (U.S. EPA, 1998b).

1.2 OVERVIEW OF DOCUMENT

Section 1: "Introduction" provides a brief review of the EqP methodology as it applies to the individual, and mixtures of, the divalent metals cadmium copper, lead, nickel and zinc and the monovalent form of silver. Section 2: "Partitioning of Metals in Sediments" reviews published experimental results that describe the partitioning and bioavailability of these metals in freshwater and marine sediments. The role of AVS, SEM and interstitial water concentrations of metals is described. Section 3: "Toxicity of Metals in Sediments" reviews the results of acute and chronic toxicity tests conducted with spiked and field sediments that demonstrate that the partitioning and bioavailability of metals in sediments can be used to accurately predict the toxicity of sediment-associated metals. Section 4: "Derivation of Sediment Guidelines for Metals" describes the SEM-AVS and interstitial water guidelines toxic unit approaches for the derivation of the ESG for individual metals and mixtures of metals. Published WQC values for dissolved metal for five of these six metals (the silver FCV for freshwater is not available) are summarized for use in the Interstitial Water Guidelines Approach. The ESG for metals is then compared to chemical monitoring data on the environmental occurrence of metals and AVS in sediments from Lake Michigan, the Virginian Province from EPA's Environmental Monitoring and Assessment Program (EMAP) and NOAA's National Status and Trends. Section 5: "Implementation" describes procedures for collection, handling, analysis of sediments and interpretation of data from sediment samples required if the assessments of the risks of sediment-associated metals are to be accurate. Section 6: "Guidelines Statement" concludes with EPA's guidelines statement for the metals cadmium, copper, nickel, lead, silver and zinc. The references cited in this document are listed in Section 7.

SECTION 2

PARTITIONING OF METALS IN SEDIMENTS

2.1 METAL TOXICITY IN WATER-ONLY AND IN INTERSTITIAL WATER OF SEDIMENT EXPOSURES

The equilibrium partitioning methodology for establishing sediment guidelines requires that the chemical concentration be measured in the bioavailable phase and that the chemical potential of the chemical be determined. This Section demonstrates that biological effects correlate to metal activity. Secondly it demonstrates that biological response is the same for water only exposures and for sediment exposures using the interstitial water concentrations. Therefore, for both metals and non-ionic chemicals this fundamental tenant of the Equilibrium Partitioning model is satisfied.

A direct approach to establishing sediment guidelines for metals would be to apply the water quality criteria final chronic values to measured interstitial water concentrations. The validity of this approach depends on the degree to which interstitial water concentration 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. Many metals readily bind to dissolved (actually colloidal) organic carbon (DOC), and DOC complexes do not appear to be bioavailable (Bergman and Dorward-King, 1997). Hence guidelines based on interstitial water concentrations of metals may be overly protective with the direct use of the concentration of metals in interstitial water.

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 metal species (Stumm and Morgan, 1996).

The sampling of sediment interstitial water for metals is not a routine procedure. The least invasive technique employs a diffusion sampler which has cavities covered with a filter

membrane (Allen et al., 1993; Bufflap and Allen, 1995; Carignan, 1984; Carignan et al., 1985; Hesslein, 1976). 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 interstitial water samples. Since the sampler is removed after equilibration, the concentrations of metals inside the sampler should be equal to the concentrations of freely dissolved metals in the interstitial water. The time required for equilibration depends on the interstitial size of the membrane and the geometry of the cavity and usually exceeds one day.

An alternate technique to separate the interstitial water is to obtain a sediment core, slice it, filter or centrifuge the slice and then filter the resultant interstitial water twice. 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 (Allen et al., 1993; Troup, 1974).

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 interstitial water metal activity could be deduced, it would obviate the need for interstitial water sampling and analysis, circumvent the need to deal with complexing ligands, and provide fundamental insight into metal binding phases in sediments needed to predict bioavailability.

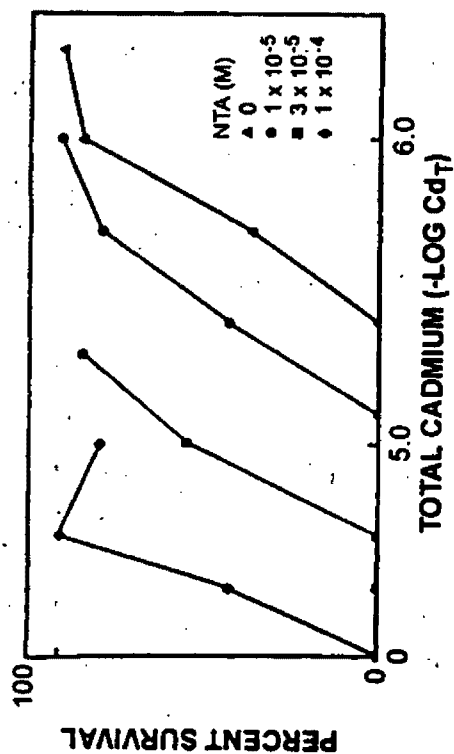
2.1.1 Toxicity correlates to metal activity

A substantial number of water only exposure experiments discussed 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 the complexing ligand NTA, both of which form cadmium complexes (Sunda et al., 1978). The concentration response curves as a function of total cadmium (Figure 2-1, top panels) are quite different at varying concentrations of chloride, indexed by salinity, and NTA. However, if the organism response is evaluated with respect to Cd^{2+} activity in the solution then the data become a single concentration-response relationship

ACUTE TOXICITY OF CADMIUM TO GRASS SHRIMP (*Palaemonetes*) EFFECT OF NTA COMPLEXATION

(AFTER W.G. SUNDA et al., 1978)



ACUTE TOXICITY OF CADMIUM TO GRASS SHRIMP (*Palaemonetes*) EFFECT OF SALINITY

(AFTER W.G. SUNDA et al., 1978)

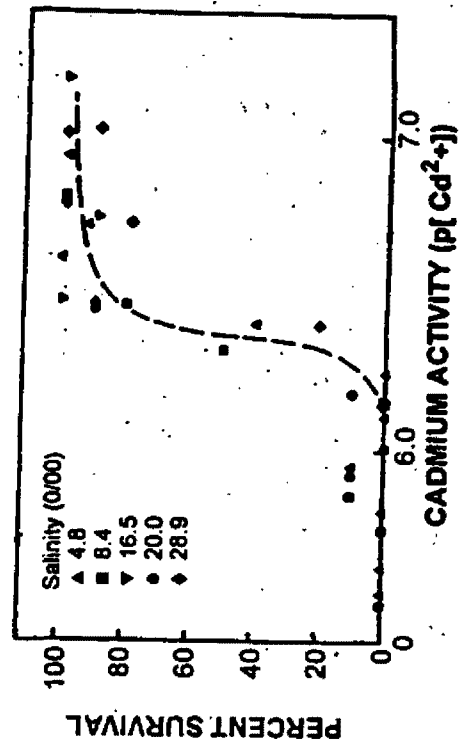
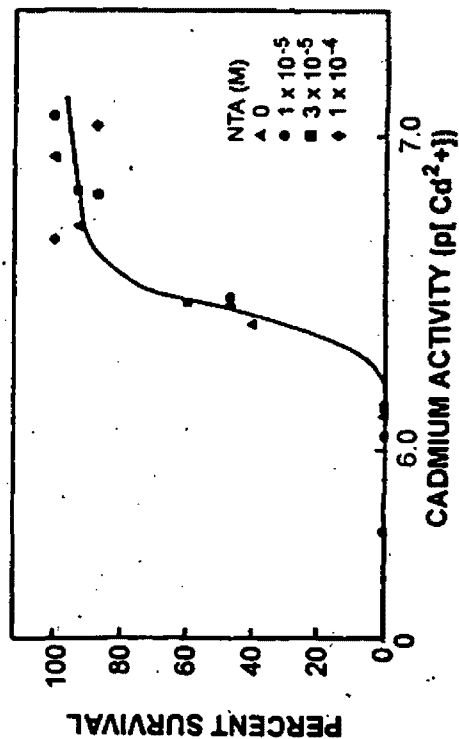
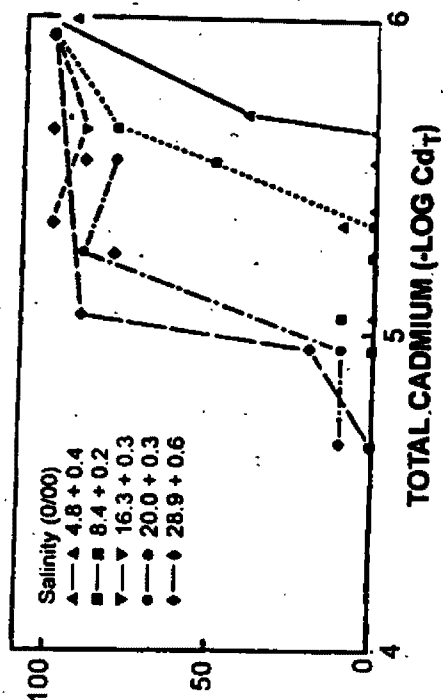


Figure 2-1. Acute toxicity to *Palaemonetes* of total cadmium (top) and cadmium activity (bottom) with different concentrations of the complexing ligands NTA (left) and chloride as salinity (right) (This figure is from Sunda et al., 1978).

(bottom panels). Comparable results have been reported for copper-EDTA complexes (Anderson and Morel, 1978) for which concentration-response correlates to Cu^{2+} activity (Figure 2-2, left top and bottom).

When the concentration of zinc is held constant and the concentration of the complexing ligand NTA is varied, the effect on growth of the phytoplankter *Microcystis* decreases as NTA added increases (Figure 2-2, right top and bottom; Allen et al., 1980). The cell density increases rather than decreases in time and reaches control levels at the highest NTA concentration (left top and bottom panels). The data can all be correlated to free zinc activity as shown (right top and bottom panels). Similar results for diatoms exposed to copper and the complexing ligand Tris (Figure 2-3, top; Sunda and Guillard, 1976). 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 (1978) with DOC from river water as the complexing ligand (Figure 2-3, right top and bottom).

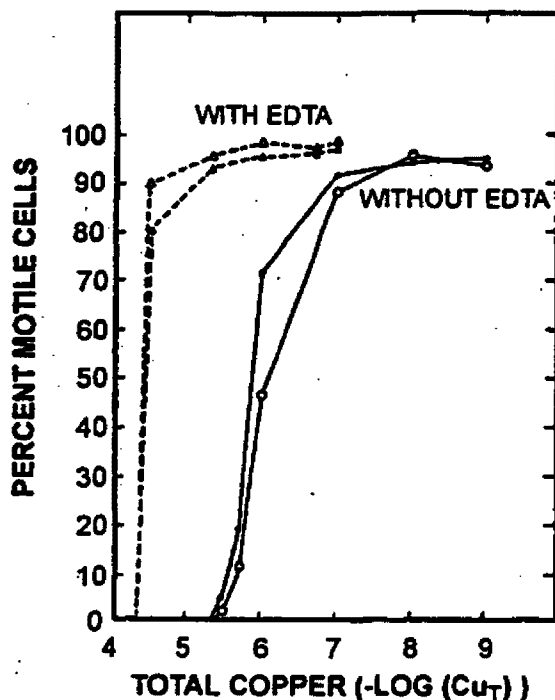
Metal bioavailability as measured by metal accumulation into tissues of organisms has also also been examined (Zamuda and Sunda, 1982). Uptake of copper by oysters is correlated not to total copper concentration (Figure 2-4, top) but to copper activity (bottom).

The implication to be drawn from these experiments is that the partitioning model required for establishing sediment guidelines should predict dissolved metal in interstitial water. The following subsection examines the utility of this idea.

2.1.2 Toxicity correlates to interstitial water concentration

This subsection presents some early data that first indicated the equivalence of interstitial water concentrations and water only exposures. Much more data of this sort are presented in Section III of this document. Swartz et al. (1985) tested the acute toxicity of 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. 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 (Figure 2-5).

ACUTE TOXICITY OF COPPER
TO A DINOFLAGELLATE
(FROM ANDERSON AND MOREL, 1978)



CHRONIC TOXICITY OF ZINC
ON *MICROCYSTIS AERUGINOSA*
(FROM ALLEN, et. al., 1980)

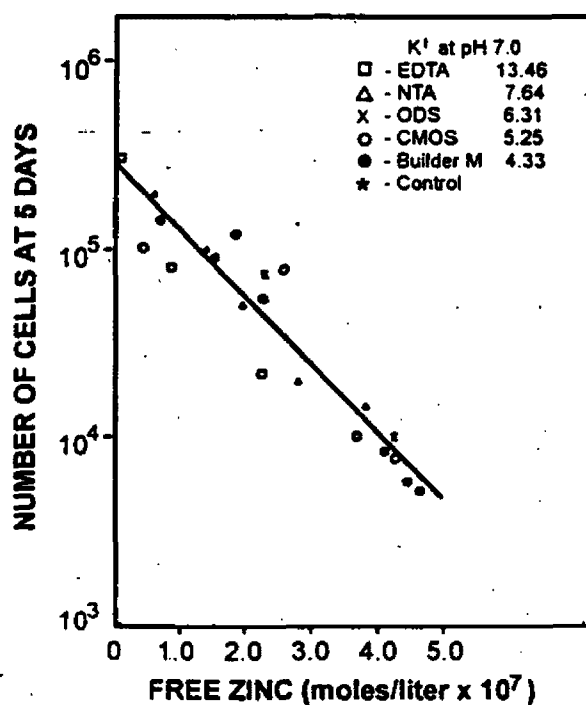
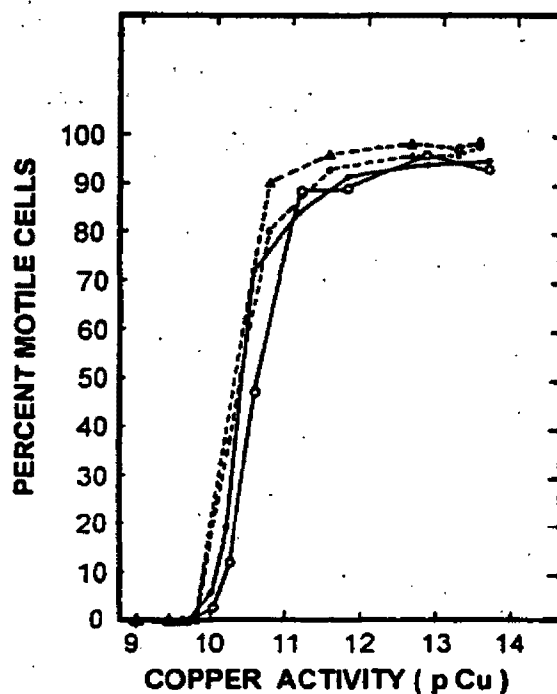
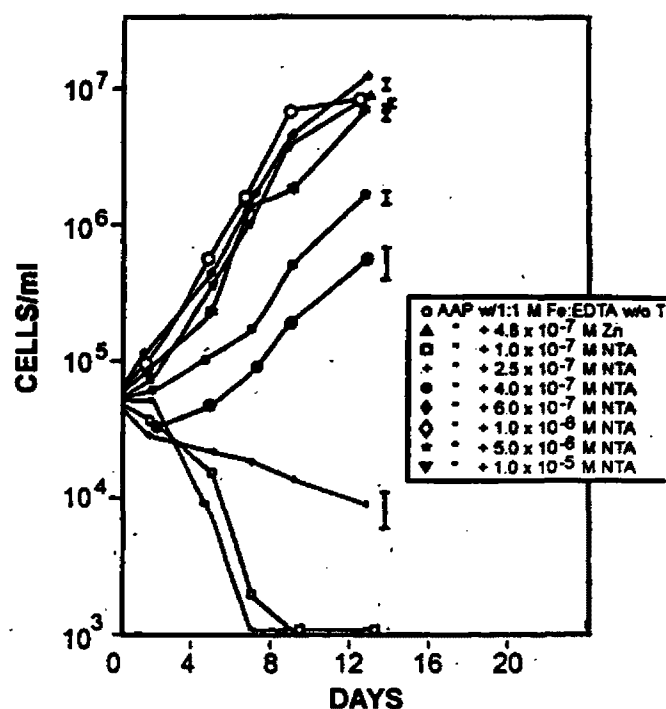
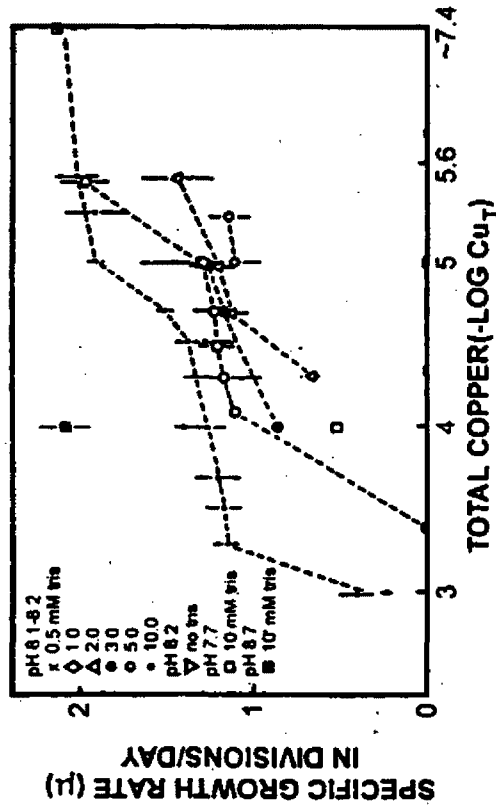


Figure 2-2. Acute toxicity to a dinoflagellate (left) of total copper (top) and copper activity (bottom), with and without the complexing ligand EDTA (this portion of the figure is from Anderson and Morel, 1978). Toxicity of zinc to *Microcystis aeruginosa* (right) showing growth as cells/ml versus time with different levels of the complexing ligands EDTA and NTA (top) and number of cells at five days as a function of free zinc concentration (bottom) (this portion of the figure is from Allen et al., 1980).

CHRONIC TOXICITY OF COPPER TO A DIATOM

(FROM SUNDA AND GUILLARD, 1976)



CHRONIC TOXICITY OF COPPER TO MONOCHRYSIS LUTHERI

(FROM SUNDA AND LEWIS, 1978)

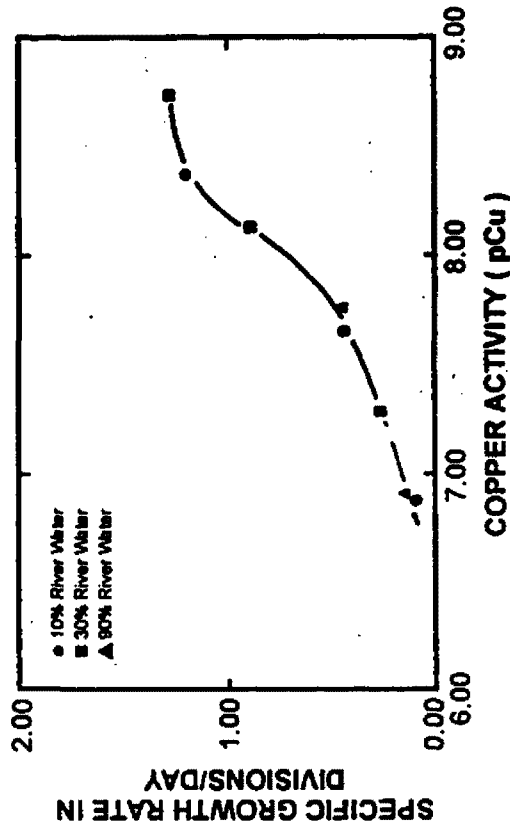
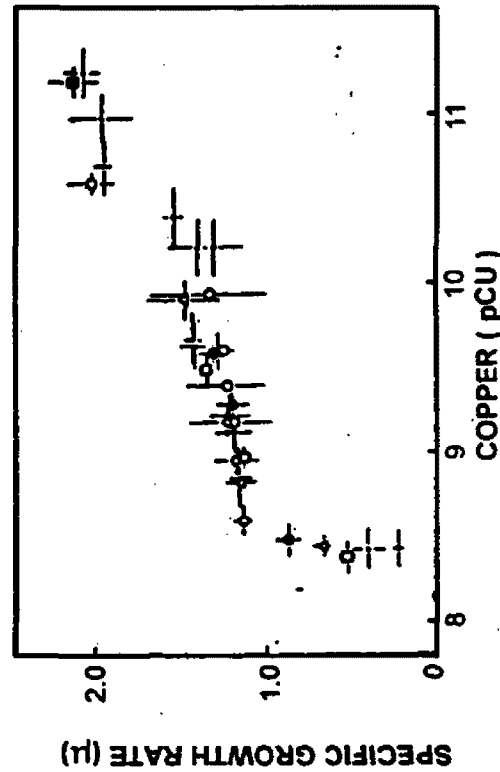
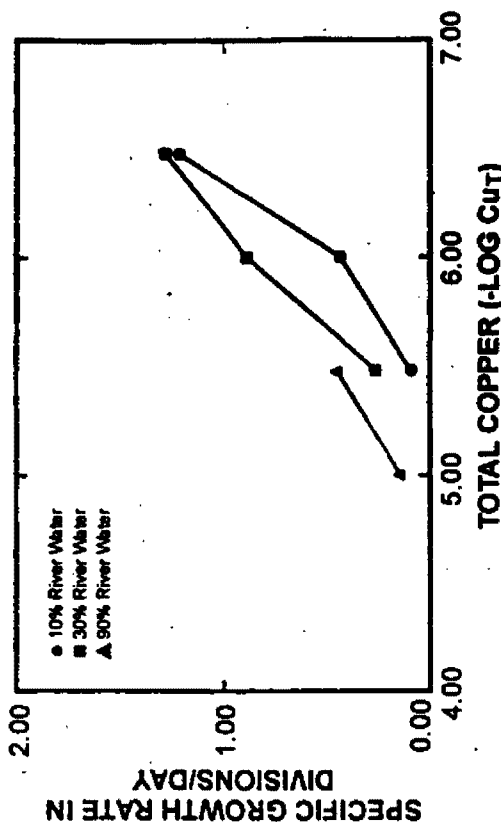


Figure 2-3. Specific growth rate of a diatom (left) (this portion of the figure is from Sunda and Guillard, 1976) and *Monochrysis lutheri* (right) versus total copper (top) and copper activity (bottom) for a range of concentrations of the complexing ligands Tris and natural DOC (this portion of the figure is from Sunda and Lewis, 1978).

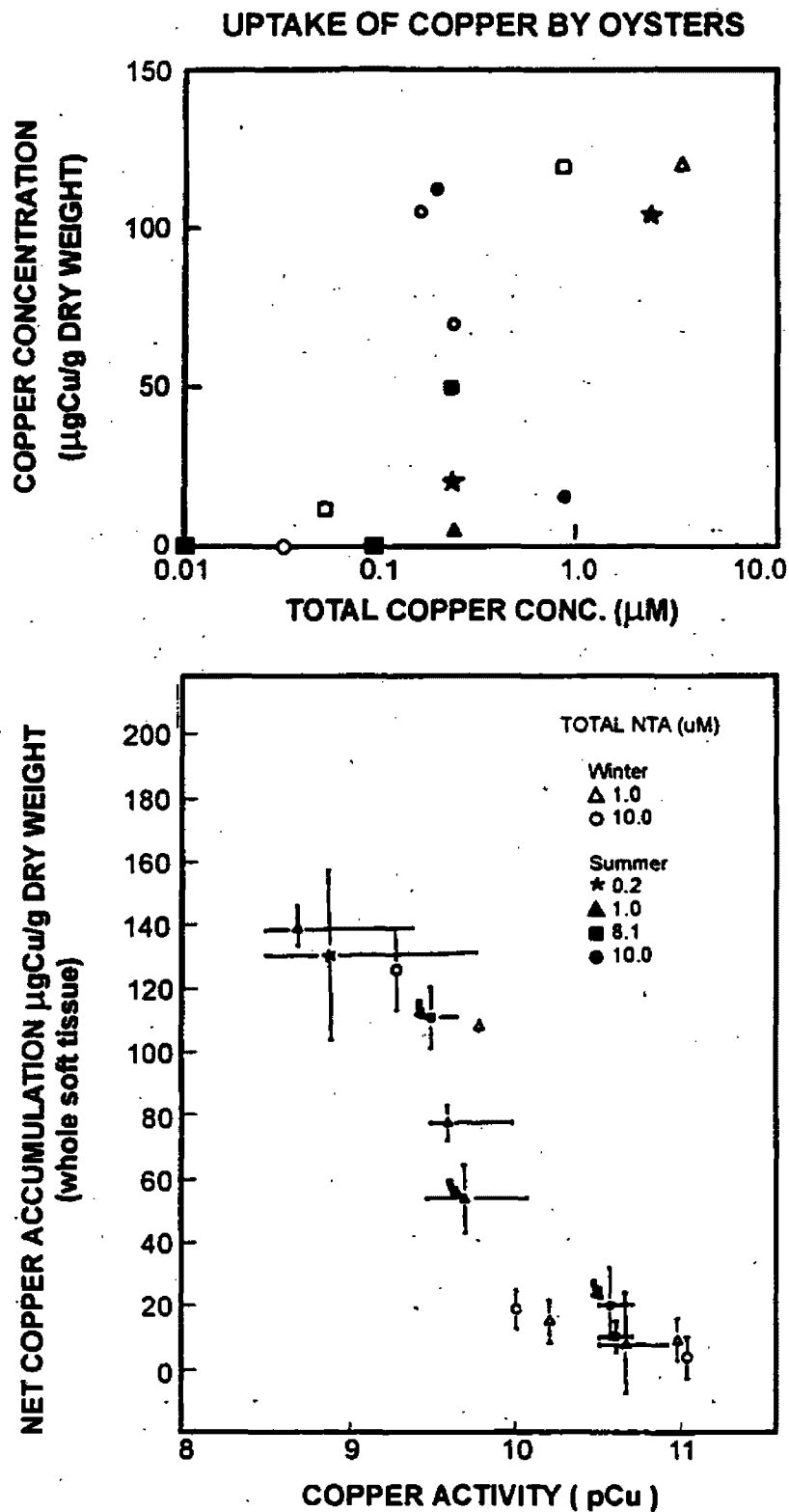


Figure 2-4. Body burdens of copper in oysters (*Crassostrea virginica*) versus total copper (top) and copper activity (bottom) with different levels of the complexing ligand NTA (this figure is from Zamuda and Sunda, 1982).

COMPARISON OF WATER AND SEDIMENT EXPOSURE

(AFTER R.C. SWARTZ et al., 1985)

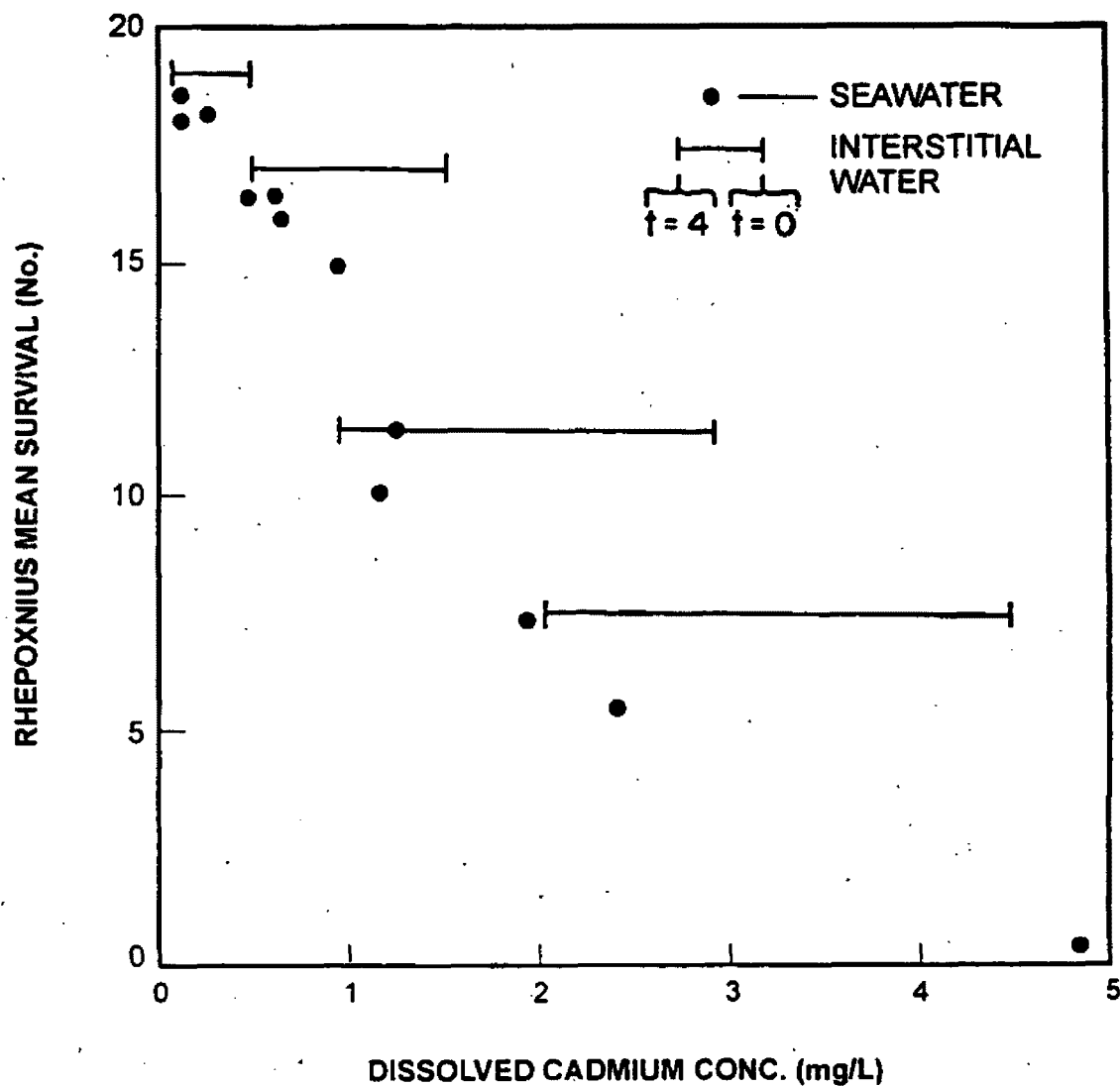


Figure 2-5. *Rhepoxynius abronis* mean survival versus dissolved cadmium for 4-day toxicity tests in seawater (symbols) and interstitial water at time 0 and 4 days (bars) (this figure is from Swartz et al., 1985).

Experiments were performed to determine the role of acid volatile sulfides in cadmium spiked sediments using the amphipods *Ampelisca abdita* and *Rhepoxynius hudsoni* (Di Toro et al., 1990). Three sediments were used, a Long Island Sound sediment with high AVS, a Ninigret Pond sediment with low AVS concentration and a 50/50 mixture of the two sediments. Figure 2-6 presents a comparison of the observed mortality in the three sediments to the interstitial water cadmium activity measured with a specific ion electrode. 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. These experiments also demonstrate the equivalence of organism response to metal concentrations in interstitial water and in water only exposures.

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

A series of 10-day toxicity tests using the amphipod *Hyaella 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 (Ankley et al., 1993). A water-only, 10-day copper toxicity test was also conducted with the same organism. The mortality resulting from the water-only test was strikingly similar to that from the Keweenaw sediment tests when related to interstitial water (Figure 2-7). The LC50s show strong agreement for the water-only (31 ug/L) and the Keweenaw sediment test (28 ug/L), using the average of day 0 and day 10 interstitial-water concentrations. Steilacoom Lake 10-day interstitial water concentrations were less than the 7 ug/L detection limit and were consistent with the observed lack of toxicity to *H. azteca* (Ankley et al, 1993).

The data presented in this subsection, and data to be presented in Section 3 of this document, demonstrate that in water-only exposures metal activity and concentration can be used to predict toxicity. The results of the four experiments above demonstrate that mortality

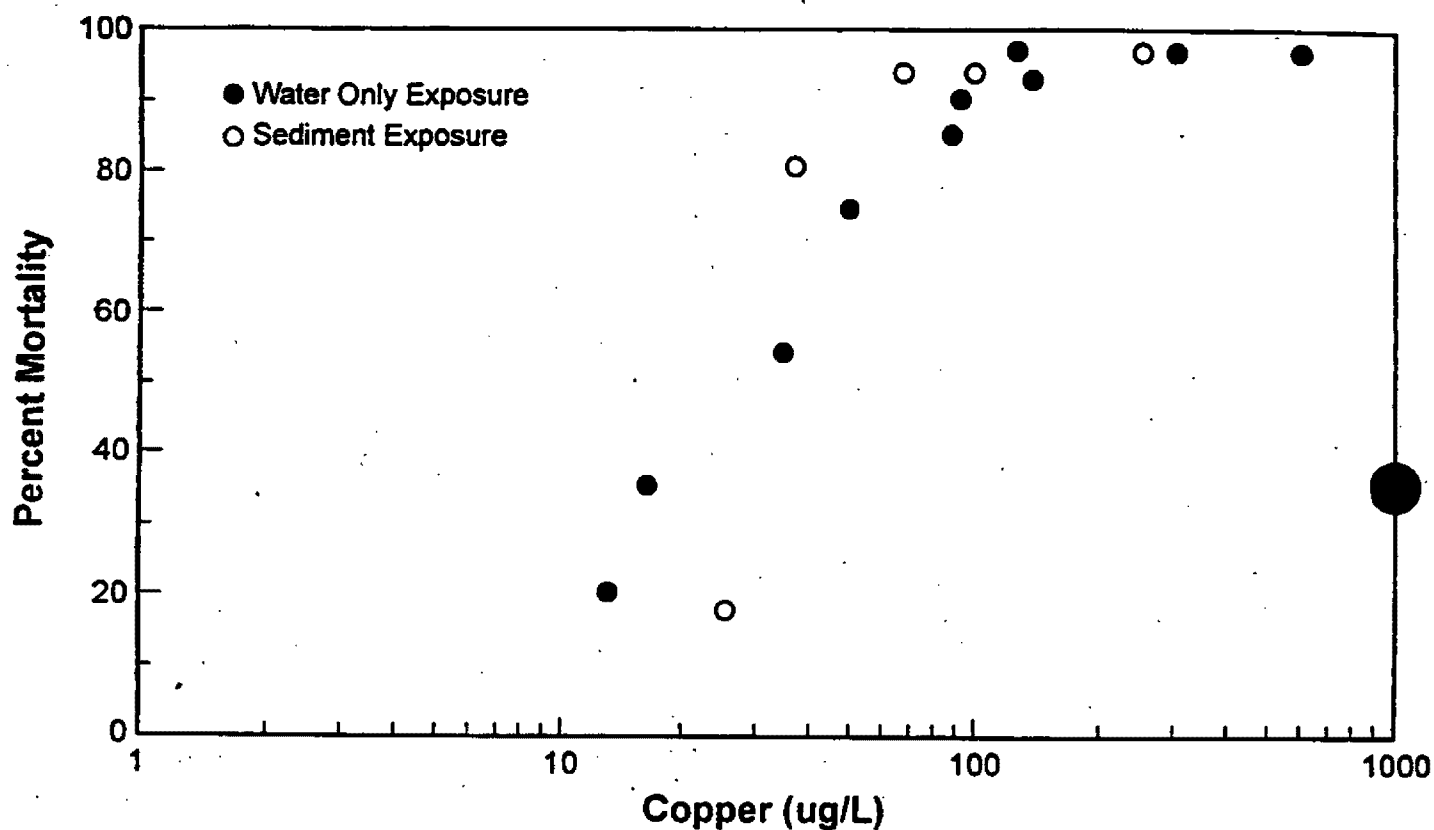


Figure 2-7. Toxicity of copper to *Hyalella azteca* versus copper concentrations in a water-only exposure (open symbols) and interstitial water copper concentrations in sediment exposures (closed symbols) using Keweenaw Waterway sediments (this figure is from Ankley et al., 1993).

data from water-only exposures can be used to predict sediment toxicity using interstitial water concentrations. Therefore, the metal activity or concentration in interstitial water would be an important component of a partitioning model needed to establish sediment guidelines. The solid metal-binding phases of this partitioning model need to be identified. The following subsection presents data that identifies solid phase sulfides as the important metal-binding phase.

2.2 SOLID PHASE SULFIDE AS THE IMPORTANT BINDING COMPONENT

Modeling metal sorption to oxides in laboratory systems is well developed, and detailed models are available for cation and anion sorption. [See the articles in Stumm, (1987) and Dzombak and Morel, (1990) 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 (Allen et al., 1980; Barrow and Ellis, 1986a,b,c; Sposito et al., 1988). Since the ability to predict partition coefficients is required if interstitial water metal concentration is to be inferred from the total concentration, some practical model is required. This subsection presents state of the science in the theoretical development of metals partitioning in sediments.

2.2.1 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 has been presented (Di Toro et al., 1987; Jenne et al., 1986). The basic idea was that instead of considering only one sorption phase as is assumed for non-ionic hydrophobic chemical sorption, multiple sorption phases must be considered. The conventional view of metals speciation in aerobic soils and sediments is that metals are associated with the exchangeable, carbonate and Fe and Mn oxide forms, as well as organic matter, stable metal sulfides, and a residual phase. In oxic soils and freshwater sediments

Iron and Manganese

sorption phases have been identified as particulate organic carbon (POC) and the oxides of iron and manganese (Jenne, 1968, 1977; Luoma and Bryan, 1981; Oakley et al., 1980). 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 metal sulfide interactions which dominate speciation in the anaerobic layers of the sediment.

2.2.2 Titration Experiments

The importance of sulfide in the control of metal concentrations in the interstitial water of marine sediments is well documented (Boulegue et al., 1982; Emerson et al., 1983; Davies-Colley et al., 1985; Morse et al., 1987). Metal sulfides are very insoluble and the equilibrium interstitial water metal concentrations in the presence of sulfides are small. If the interstitial water sulfide, S , concentration in sediments is large, then as metal, M , is added to the sediment, metal sulfide, MS , would precipitate following the reaction:



This appeared to be happening during a spiked cadmium sediment toxicity test (Di Toro et al., 1990) 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:



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

2.2.2.1 Amorphous FeS:

A direct test of the extent to which this reaction takes place was performed (Di Toro et al., 1990). A quantity of freshly precipitated iron sulfide was titrated by adding dissolved cadmium. The resulting aqueous cadmium activity, measured with the cadmium electrode versus the ratio of cadmium added, $[\text{Cd}]_A$, to the amount of FeS initially present, $[\text{FeS(s)}]_i$, is shown in Figure 2-8. The plot of dissolved cadmium versus cadmium added illustrates the increase in dissolved cadmium that occurs near $[\text{Cd}]_A / [\text{FeS(s)}]_i = 1$. 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 (Phillips and Kraus, 1965). The reaction was also postulated by Pankow (1979) to explain an experimental result involving copper and synthetic FeS.

These experiments plainly demonstrate that solid phase amorphous iron 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 2-9. 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 2-9) (DiToro et al., 1990).

2.2.2.2 Sediments

A similar titration procedure has been used to evaluate the behavior of sediments taken from four quite different marine environments: sediments from Black Rock Harbor, Hudson River and the sediments from Long Island Sound and Ninigret Pond used in the toxicity tests.

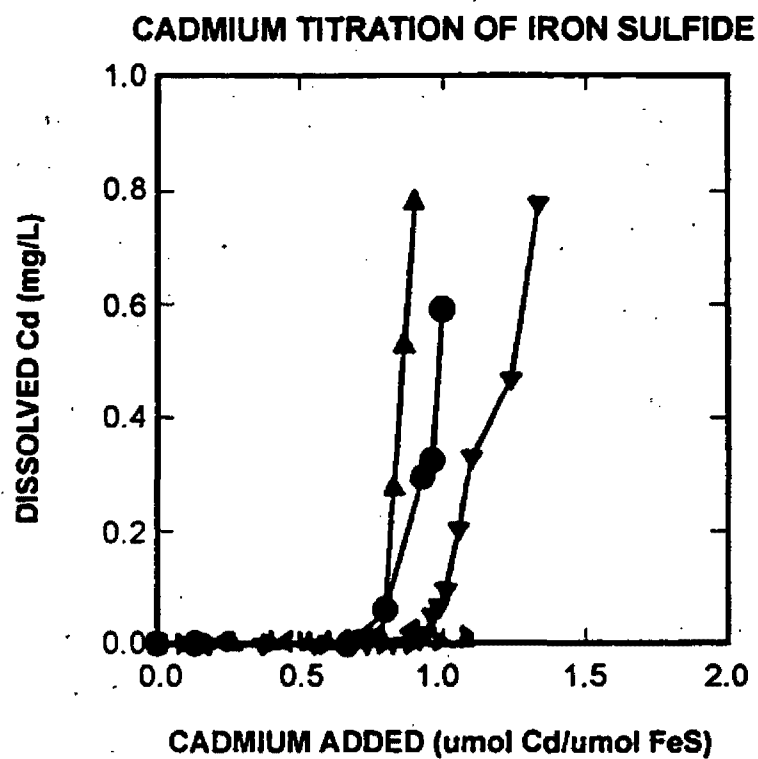


Figure 2-8. Cadmium titrations of amorphous FeS. X-axis is cadmium added normalized by FeS initially present (this figure is from Di Toro et al., 1990). Y-axis is total dissolved cadmium. The lines connecting the data points are an aid to visualizing the data.

RESULTS OF $\text{FeS} + \text{Cd}^{2+} = \text{CdS} + \text{Fe}^{2+}$

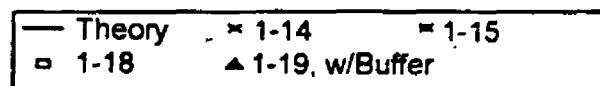
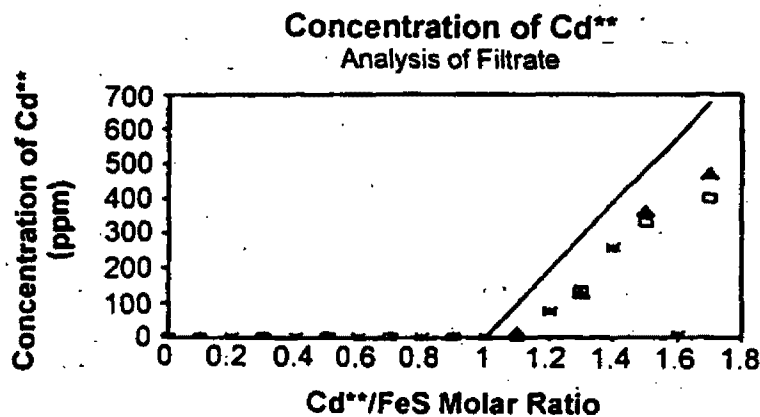
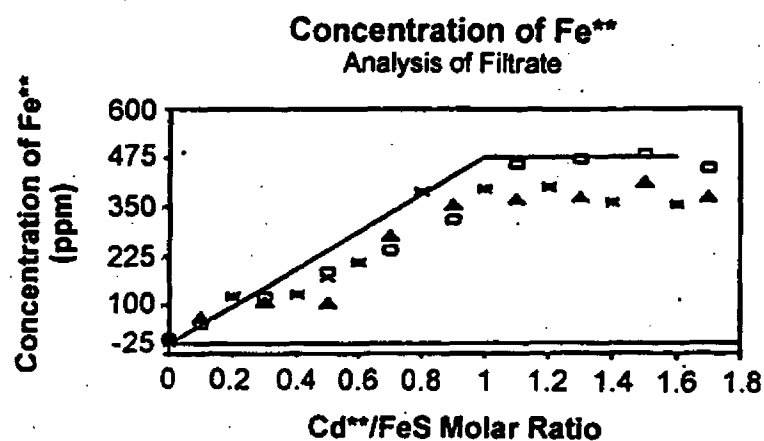


Figure 2-9. Concentrations of Fe^{2+} and Cd^{2+} in supernatant from titration of FeS by Cd^{2+} (personal communication with Di Toro 1992).

The binding capacity for cadmium is estimated by extrapolating a straight line fit to the dissolved cadmium data. The equation is:

$$[\Sigma\text{Cd}(\text{aq})] = \max\{0, m([\text{Cd}]_A - [\text{Cd}]_B)\} \quad (2-3)$$

where $[\Sigma\text{Cd}(\text{aq})]$ is the total dissolved cadmium, $[\text{Cd}]_A$ is the cadmium added, $[\text{Cd}]_B$ 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 2-1, ranging from approximately 1 $\mu\text{mol/gm}$ to more than 100 $\mu\text{mol/g}$. The question is whether this binding capacity is explained by the solid phase sulfide present in the samples.

Table 2-1. Cadmium binding capacity and AVS of sediments (from Di Toro et al., 1990).

Sediment	Initial AVS ($\mu\text{mol/g}$) ^(a)	Final AVS ($\mu\text{mol/g}$) ^(b)	Cd Binding Capacity ^(c) ($\mu\text{mol/g}$)
Black Rock Harbor	175.(41.)	-	114.(12.1)
Hudson River	12.6(2.8)	-	8.58 (2.95)
LI Sound ^(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 (Di Toro et al., 1990).
^(d)50/50 mixture of LI Sound and Ninigret Pond
^(e)From Equation (2-3)

2.2.3 Correlation to Sediment AVS

The majority of sulfide in sediments is in the form of iron monosulfides (mackinawite and greigite) and iron bisulfide (pyrite), of which the former are the most reactive. These sediment sulfides can be classified into three broad classes which reflect the techniques used for quantification (Morse et al., 1987; Berner, 1967; Goldhauber and Kaplan, 1974). 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 (Landers et al., 1983).

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

2.2.4 Solubility Relationships and Displacement Reactions

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



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



As the cadmium concentration increases, $[\text{Cd}^{2+}][\text{S}^{2-}]$ 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:



CADMIUM TITRATION OF SEDIMENTS

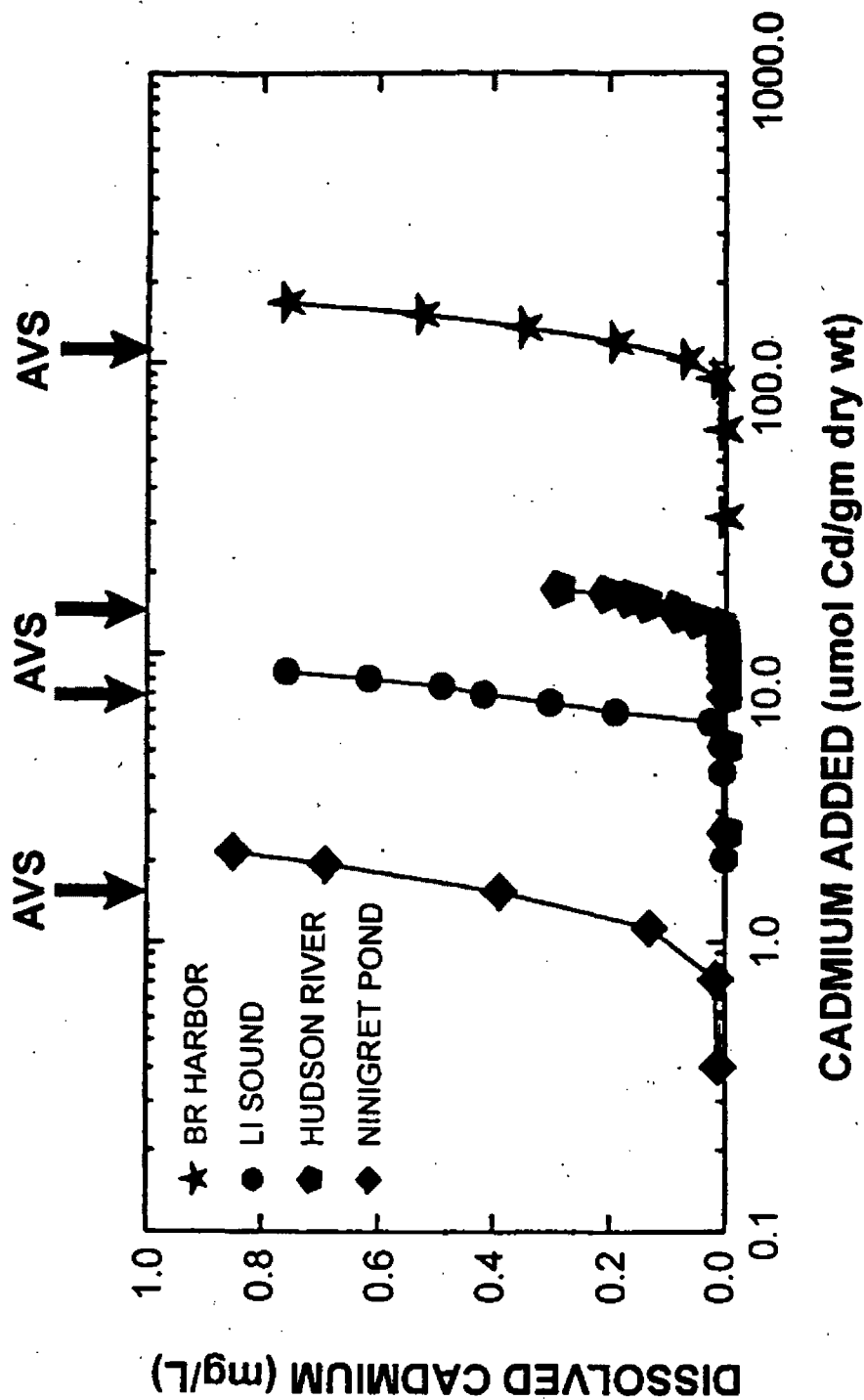


Figure 2-10. Cadmium titration of sediments from Black Rock Harbor, Long Island Sound, Hudson River and Ninigret Pond (this figure is from Di Toro et al., 1990). Cadmium added per unit dry weight of sediment versus dissolved cadmium.

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 B. 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:

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

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 2-6. However, the ratio is still less than the ratio of the sulfide solubility products.

This is an important finding since the data presented in Section 2.1 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 2-2. The ratio of cadmium activity to total cadmium is less than $10^{-10.46}$. For nickel the ratio is less than $10^{-5.59}$. By inference this reduction in metal activity will occur for any other metal that forms a sulfide that is significantly more insoluble than iron monosulfide. The ratios for the other metals in Table 2-2, Zn, Cd, Pb, Cu and Ag indicate that metal activity for these metals will be very small in the presence of excess AVS.

Table 2-2. Metal sulfide solubility products.

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
Ag ₂ S	-36.14	-54.71	-32.32

*Solubility products, $K_{sp,2}$, for the reaction $M^{2+} + HS^- \rightleftharpoons MS(s) + H^+$ for CdS (greenockite), FeS (mackinawite), and NiS (millerite) from Emerson et al., 1983. Solubility products for CuS (covellite), PbS (galena), ZnS (wurtzite), and Ag₂S (acanthite) and $pK_2 = 18.57$ for the reaction $HS^- \rightleftharpoons H^+ + S^{2-}$ from Schoonen, M.A.A. and H.L. Barnes, 1988. K_{sp} for the reaction $M^{2+} + S^{2-} \rightleftharpoons MS(s)$ is computed from $\log K_{sp,2}$ and pK_2 .

2.2.5 Application to Mixtures of Metals

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

$$\frac{\sum_i [M_T]_i}{[AVS]} < 1 \quad (2-8)$$

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

$$\frac{\sum_i [M_T]_i}{[AVS]} > 1 \quad (2-9)$$

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 1.0 discriminates between nontoxic and potentially toxic sediments. The additivity does not come from the nature of the mechanism that causes toxicity. Rather it results from the equal ability of the metals to form metal sulfides with the same stoichiometric ratio of M and S.

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, copper). 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 (Di Toro et al., 1992).

The above discussion is predicated on the assumption that all the metal sulfides behave similarly to cadmium sulfide. 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 were tested directly with benthic organisms using sediment toxicity tests. Results of these sediment spiking experiments with cadmium, copper, lead, nickel, silver, zinc and metals mixtures will be presented in Section III which follows.

SECTION 3

TOXICITY OF METALS IN SEDIMENTS

3.1 GENERAL INFORMATION

This Section of the guidelines document summarizes data from acute and chronic toxicity tests that demonstrate that the absence of sediment toxicity due to metals can be predicted by use of the interstitial water concentrations of metals or by comparison of the molar concentrations of AVS and SEM. This ability to predict the toxicity of metals in sediments, through a fundamental understanding of their bioavailability, is in sharp contrast with the absence of a causal correlation between metals induced sediment metal-induced toxicity and metals concentrations based on the dry weight of sediment (Berry et al., 1996a; Di Toro et al., 1990; 1992; Luoma, 1989, Berry et al., in review) and the use of sequential extractions (Ankley et al., 1996).

3.2 PREDICTING METAL TOXICITY: SHORT-TERM

3.2.1 Spiked sediments: Individual experiments

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

Di Toro et al. (1990) first investigated the significance of sulfide partitioning in controlling metal bioavailability and metal-induced toxicity in marine sediments spiked with cadmium. In these experiments, the operational definition of Cornwell and Morse (1987) was used to identify that fraction of amorphous sulfide, or AVS, available to interact with cadmium in the sediments. Specifically, the AVS was defined as the sulfide liberated from wet sediment

by treatment with 1N HCl acid. Di Toro et al. (1990) found that when the molar concentration of AVS in the test sediments was larger than that of the molar concentration of total cadmium, (i.e., when the cadmium:AVS ratio was less than 1, or the cadmium:AVS difference was less than 0), interstitial water concentrations of the metal were small and no toxicity was observed in 10-d tests with the amphipods *Rhepoxynius hudsoni* or *Ampelisca abdita*. Studies by Carlson et al. (1991) with cadmium-spiked freshwater sediments yielded similar results; when there was more AVS than total cadmium, significant toxicity was not observed in 10-d tests with oligochaetes (*Lumbriculus variegatus*) or snails (*Helisoma* sp). Based upon these initial studies, another study with nickel-spiked sediments using *A. abdita* and field sediments contaminated with cadmium and nickel using the freshwater amphipod *Hyaella azteca*, Di Toro et al. (1992) provided further support to the importance of AVS in controlling metal bioavailability in sediments. Based on these studies they suggested that it may be feasible to derive ESG for metals by direct comparison of molar AVS concentrations to the molar sum of the concentrations of cationic metals (specifically, cadmium, copper, nickel, lead and zinc) extracted with the AVS; i.e., $\sum \text{SEM}$. They observed that the expression of metals concentrations based on the $\sum \text{SEM}$ is required because a significant amount of nickel sulfide is not completely soluble in the AVS extraction. Hence, AVS must be used as the measure of reactive sulfide and $\sum \text{SEM}$ as the measure of total reactive metal.

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

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

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

where

$[M_d]$ is the dissolved metal concentration in the interstitial water, and the LC50 is the concentration of the metal causing 50% mortality of the test species in a water-only test. If interstitial water exposure in a sediment test is indeed equivalent to that in a water-only test then 1.0 IWTU should result in 50% mortality of the test animals. Berry et al. (1996a) reported that significant (>24%) mortality of the saltwater amphipod occurred in only 3.0% of sediments with less than 0.5 IWTU, while samples with greater than 0.5 IWTU were toxic 94.4% of the time. Berry et al. (1996a) also made an important observation relative to interstitial water metal chemistry in their mixed-metals test. Chemical equilibrium calculations suggest that the relative affinity of metals for AVS should be silver > copper > lead > cadmium > zinc > nickel (Emerson et al., 1983; Di Toro et al., 1992). Hence, the appearance of the metals in interstitial water as AVS is "exhausted" should occur in an inverse order (e.g., zinc would replace nickel in a monosulfide complex and nickel would be liberated to the interstitial water, etc). Berry et al. (1996a) observed this trend in sediments spiked with cadmium, copper, nickel and zinc (Figure 3-1). Furthermore, an increase in the concentration in a sediment of a metal with a low sulfide solubility product constant (K_{sp}) theoretically would displace a previously unavailable and nontoxic metal, with a higher K_{sp} making that metal available to bind to other sediment phases or enter interstitial water to become toxic. Berry et al. (1996b) also exposed the saltwater amphipod *Ampelisca abdita* to sediments spiked with silver. When AVS was detected in the sediments they were not toxic and interstitial water contained no detectable silver. For sediment that contain no detectable AVS, any SEM silver that is detected is dissolved interstitial silver, because silver sulfide and silver chloride precipitate are not extracted using the standard AVS procedure.

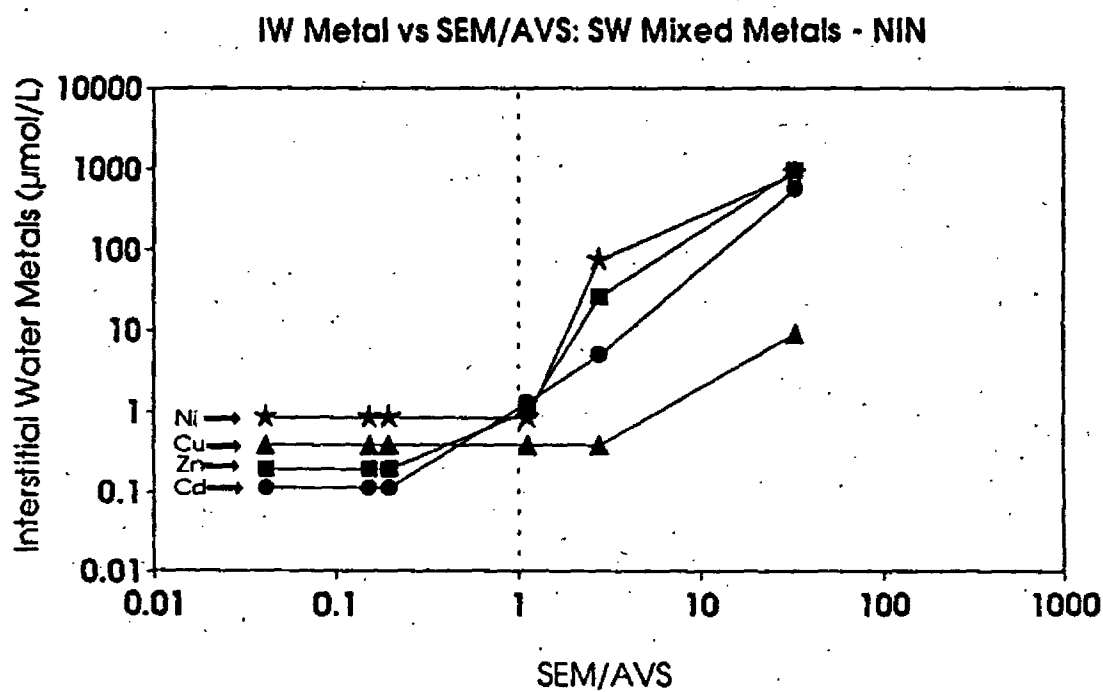
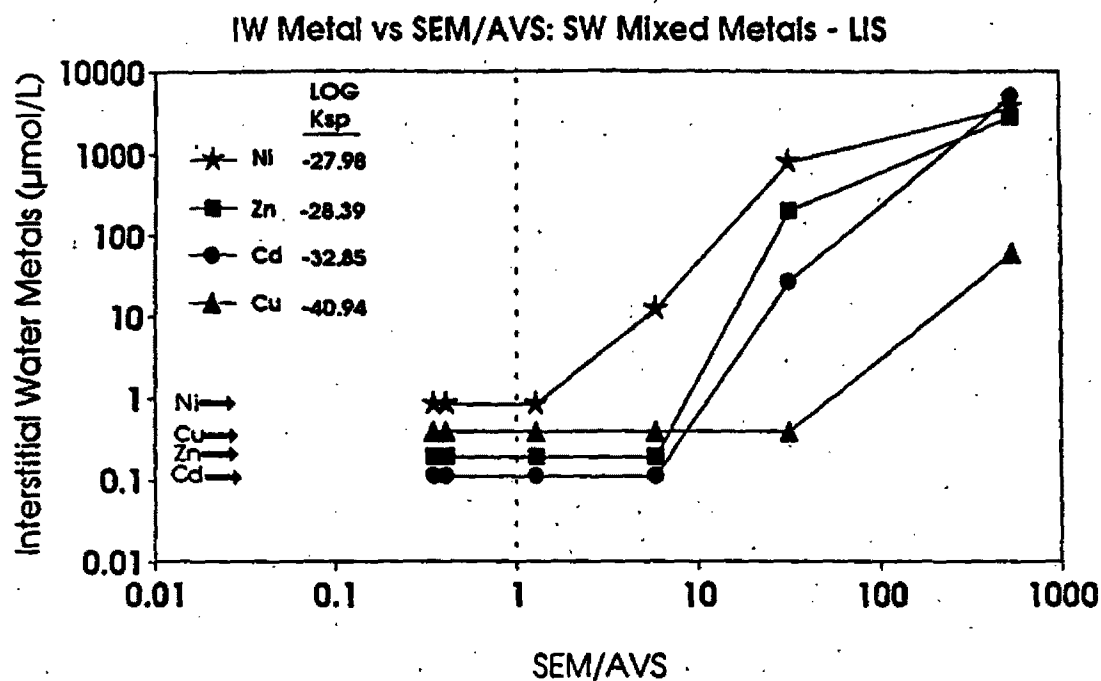


Figure 3-1. Concentrations of individual metals in interstitial water of sediments from Long Island Sound (top) and Ninigret Pond (bottom) in the mixed metals experiment as a function of SEM/AVS ratio (this figure is from Berry et al., 1996). Concentrations below the IW detection limits, indicated by arrows, are plotted at one half the detection limit. K_{sp} is the sulfide solubility product constant.

3.2.2 Spiked Sediments: All experimental results summarized

Berry et al. (1996a) summarized the results of all of the above studies using 10-day toxicity tests with saltwater sediments spiked with cadmium, copper, lead, nickel, silver or zinc and metal mixtures using amphipods (Di Toro et al., 1990; Berry et al., 1996a; 1996b), polychaetes exposed to sediments spiked with cadmium, copper, lead, nickel or zinc (Casas and Crecelius, 1994; Pesch et al., 1995) and copepods exposed to sediments spiked with cadmium (Green et al., 1993), and freshwater tests using oligochaetes and snails exposed to sediments spiked with cadmium (Carlson et al., 1991). These data describe tests with seven freshwater and saltwater species and sediments from seven locations, with AVS concentrations ranging from 1.9 to 65.7 $\mu\text{mol/g}$ dry wt and TOC ranging from 0.15 to 10.6% (Green et al., 1993 measured interstitial cadmium but not AVS). Similar results from 10-day tests with amphipods in two marine sediments are summarized in Berry et al., in review.

Overall, the results of these experiments demonstrate that it is not possible to predict the toxicity of sediments spiked with metals using the total metal concentration on a dry weight basis (Figure 3-2a). Sediments having $\leq 24\%$ mortality are considered nontoxic as defined by Berry et al., 1996a, and as indicated by the horizontal line in each panel of Figures 3-2 and 3-3. Much of this variability is caused by the fact that the relationship between mortality and total metal concentrations in tests was sediment specific as it was in the cadmium results shown in Figure 2-10. The dry weight metal concentrations required to cause acute mortality in these experiments are very high relative to those often suspected to be of toxicological significance in field sediments. This has sometimes been interpreted as a limitation of the use of SEM and AVS to predict metal-induced toxicity. However, the range in AVS in these sediments spiked with metals is similar to sediments commonly occurring in the field. The important point is that even a sediment with only a moderate concentration of AVS has a considerable capacity for sequestering metals as a metal sulfide, a form which is not bioavailable (Di Toro et al., 1990).

In contrast, the combined data from all available freshwater and saltwater spiked-sediment experiments supports the use of IWTU to predict mortality of benthic species in spiked sediment toxicity tests (Figure 3-2b). Mortality in these experiments was sediment independent when plotted against IWTU. Sediments with IWTUs of < 0.5 were generally not toxic. Of the 96 sediments with IWTU < 0.5 , 96.9% were not toxic, while 76.4% of the 89

Table 3-1. - 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 the difference between the molar concentrations of SEM and AVS (SEM-AVS), interstitial water toxic units (IWTUs) and both SEM-AVS and IWTUs (modified from Hansen et al., 1996a).

Study Type	Parameter	Value	n	Percent of Sediments	
				Nontoxic ¹	Toxic ¹
Lab-Spike (FW & SW)	SEM-AVS	$\leq 0^2$	101	98.0	2.0
		$> 0^3$	95	26.3	73.7
	IWTU	< 0.5	96	96.9	3.1
		≥ 0.5	89	23.6	76.4
	SEM-AVS, IWTU	$\leq 0^2, < 0.5$	83	97.6	2.4
		$> 0^3, \geq 0.5$	78	14.1	85.9
Field (FW & SW)	SEM-AVS	$\leq 0^2$	57	98.2	1.8
		$> 0^3$	79	59.5	40.5
	IWTU	< 0.5	79	98.7	1.3
		≥ 0.5	53	45.3	54.7
	SEM-AVS, IWTU	$\leq 0^2, < 0.5$	49	100.0	0.0
		$> 0^3, \geq 0.5$	45	33.3	66.7
All	SEM-AVS	$\leq 0^2$	158	98.1	1.9
		$> 0^3$	174	42.0	58.0
	IWTU	< 0.5	175	97.7	2.3
		≥ 0.5	142	31.7	68.3
	SEM-AVS, IWTU	$\leq 0^2, < 0.5$	132	98.5	1.5
		$> 0^3, \geq 0.5$	123	21.1	78.9

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

² SEM-AVS ≤ 0 is the same as an SEM/AVS ratio of ≤ 1.0 .

³ SEM-AVS > 0 is the same as an SEM/AVS ratio of > 1.0 .

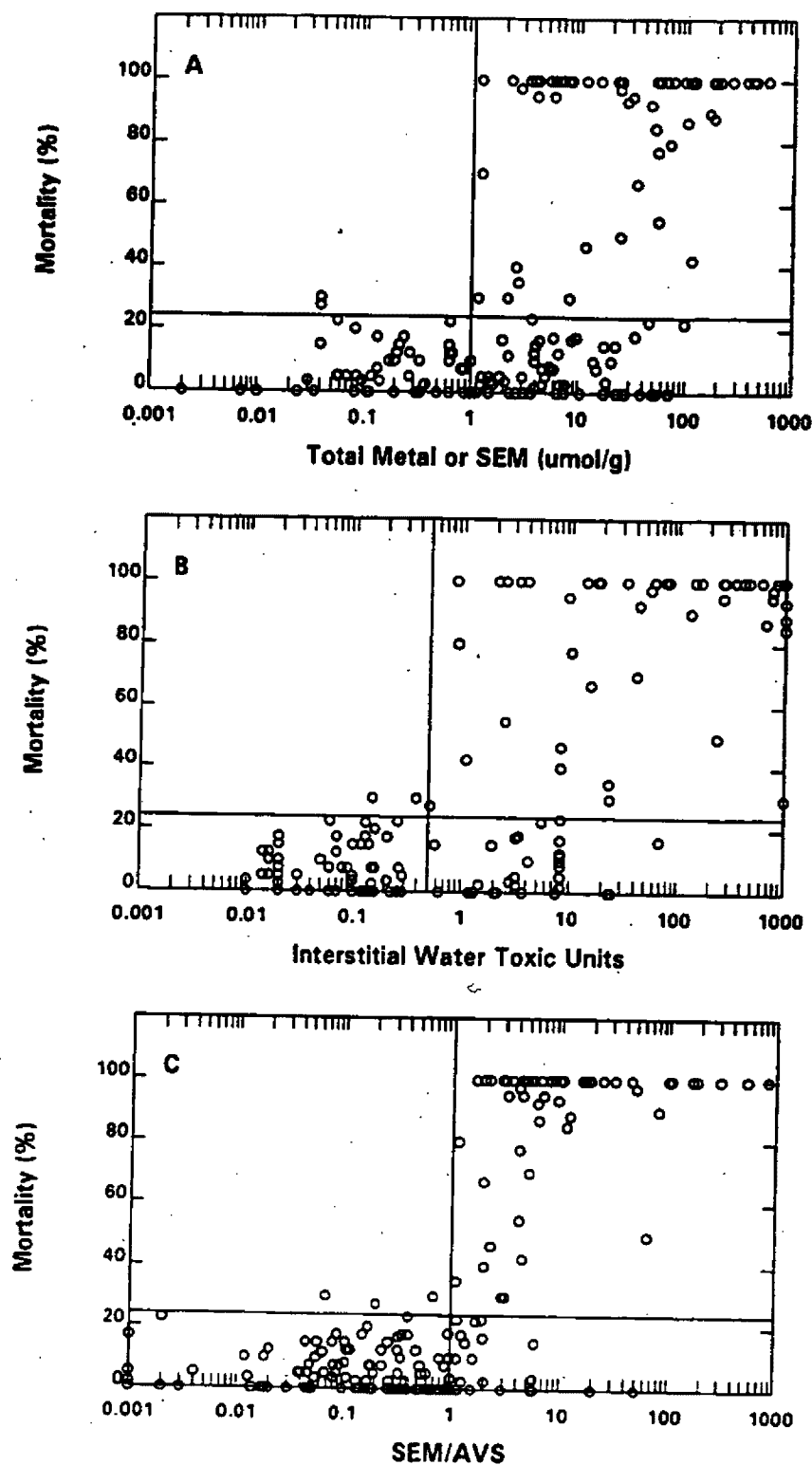


Figure 3-2. Percentage mortality of saltwater and freshwater benthic species in 10-day toxicity tests in sediments spiked with individual metals (Ag, Cd, Cu, Ni, Pb, or Zn) or a metal mixture (Cd, Cu, Ni and Zn). Mortality is plotted as a function of: (a) the sum of the concentrations of cadmium, copper, lead, nickel and zinc in μ moles metal per gram dry weight sediment; (b) SEM/AVS ratio; and (c) interstitial water toxic units (silver data from Berry et al., in review, all other data modified after Berry et al., 1996a). Species tested include: the oligochaete (*Lumbriculus variegatus*), polychaetes (*Capitella capitata* and *Neanthes arenaceodentata*), amphipods (*Ampelisca abdita* and *Hyalella azteca*), harpacticoid copepod (*Amphiascus tenuiremis*) and gastropod (*Helisoma* sp.). Data below the SEM detection limit are plotted at SEM/AVS = 0.01. Data below the detection limit of metals in interstitial water are plotted at IWTU = 0.01.

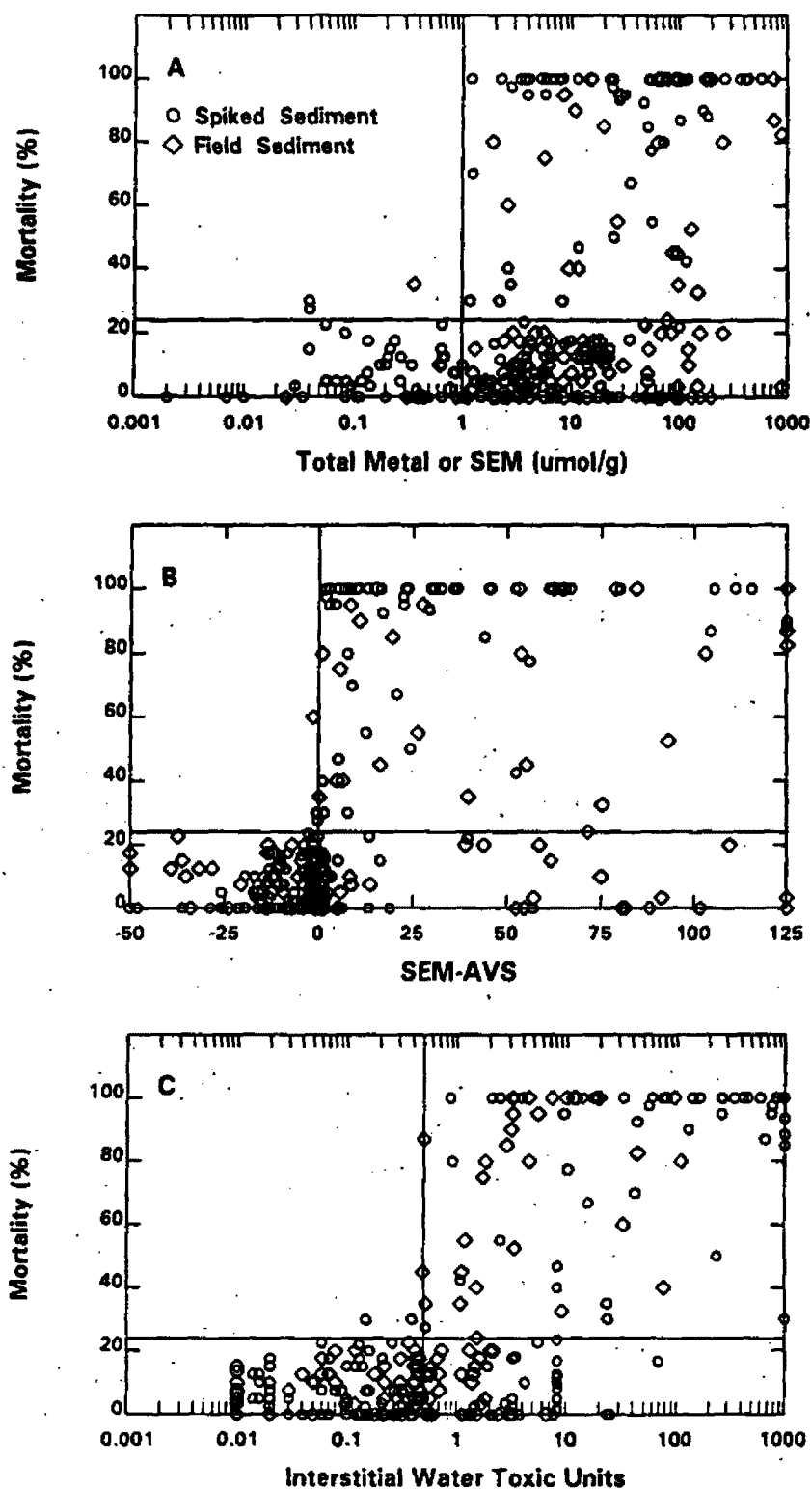


Figure 3-3. Percentage mortality of saltwater and freshwater benthic species in 10-day toxicity tests in spiked sediments (open symbols) and sediments from the field (closed symbols) (silver data from Berry et al., in review, all other data modified after Hansen et al., 1996a). Mortality is plotted as a function of (a) the sum of the concentrations of cadmium, copper, lead, nickel and zinc in μ moles metal per gram dry weight sediment; (b) SEM/AVS ratio; and (c) interstitial water toxic units. Species tested include: the oligochaete *Lumbriculus variegatus*, polychaetes (*Capitella capitata* and *Neanthes arenaceodentata*), the harpacticoid (*Amphiascus tenuiremis*), amphipods (*Ampelisca abdita* and *Hyaella azteca*) and the snail (*Helisoma* sp.). Data below the SEM detection limit are plotted at SEM/AVS = 0.01. Data below the detection limit of metals in interstitial water are plotted at IWTU = 0.01.

sediments with IWTU > 0.5 were toxic (Table 3-1). This close relationship between IWTU and sediment toxicity in sediments spiked with metals was also observed in studies with field sediments contaminated with metals (See Section 3-2-3 below), sediments spiked with non-ionic organic chemicals (Di Toro et al., 1991; Adams et al., 1985; Swartz et al., 1990) and field sediments contaminated with non-ionic organic chemicals (Hoke et al., 1994; Swartz et al., 1994).

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

The combined data from all available saltwater and freshwater spiked sediment experiments supports the use of SEM/AVS ratios to predict sediment toxicity to benthic species in spiked-sediment toxicity tests. All tests yield similar results when mortality is plotted against SEM/AVS ratio (Figure 3-2c). Mortality in these experiments was sediment independent when plotted on an SEM/AVS basis. With the combined data, 98.0% of the 101 metals-spiked sediments with SEM/AVS ratios ≤ 1.0 were not toxic, while 73.7% of the 95 sediments with SEM/AVS ratios > 1.0 were toxic (Table 3-1).

These overall data show that when both SEM/AVS ratio and IWTU are used, predictions of which sediments would be toxic were improved. Of the 83 sediments with SEM/AVS ratios ≤ 1.0 and IWTU < 0.5 , 97.6% were not toxic, while 85.9% of the 78 sediments with SEM/AVS ratios > 1.0 and IWTU ≥ 0.5 were toxic (Table 3-1). (Note: Table 3-1 uses SEM-AVS instead of SEM/AVS ratios. An SEM-AVS of ≤ 0 is the same as an SEM/AVS ratio of ≤ 1.0 . An SEM-AVS of > 0 is the same as an SEM/AVS ratio of > 1.0 .)

These results over all experiments show that SEM/AVS and IWTU are accurate predictors of the absence of mortality in sediment toxicity tests, however, predictions of which sediments might be toxic are less accurate. The fact that a significant number of sediments (26.3%) tested had SEM/AVS ratios of > 1.0 but were not toxic indicates that other binding phases, such as organic carbon (Mahony et al., 1996), may also control bioavailability in anaerobic sediments. While the SEM/AVS model of bioavailability accurately predicts which sediments will not be toxic, a model which utilizes SEM/AVS ratios or (SEM-AVS) (Hansen et al., 1996a) and incorporates other binding phases might more accurately predict which sediments will be toxic (Di Toro et al., 1987; Mahony et al., 1996).

Organism behavior may also explain why sediments with SEM/AVS ratios of > 1.0 were not toxic. Many of the sediments which had the highest SEM/AVS ratios in excess of 1.0 that produced little or no mortality were from experiments using the polychaete, *Neanthes arenaceodentata* (see Pesch et al., 1995, Figure 8). This appeared to be related, in part, to the ability of this polychaete to avoid burrowing into the test sediments, thereby limiting their exposure to the elevated concentrations of metals in the interstitial water and sediments. This same phenomenon may also explain the low mortality of snails, *Heliosoma* sp., in freshwater sediments with high SEM/AVS ratios. These snails are epibenthic and also have the ability to avoid contaminated sediments (G. Phipps, personal comm.). Increased mortality was always observed in sediments with SEM/AVS ratios > 5.9 in tests with the other five species.

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

exposure, and that the LC50 value for cadmium in IW associated with sediments was more than three times that in a water-only exposure.

3.2.3 Field sediments

In addition to short-term laboratory experiments with spiked sediments, there have been several published studies of laboratory toxicity tests with metal-contaminated sediments from the field. Ankley et al. (1991) exposed *L. variegatus* and the amphipod *Hyaella azteca* to 17 sediment samples along a gradient of cadmium and nickel contamination from a freshwater/estuarine site in Foundry Cove, NY. In 10-d toxicity tests, *H. azteca* mortality was absent in all sediments where SEM (cadmium plus nickel) was less than AVS. Mortality was greater than controls only in sediments with more SEM than AVS. *Lumbriculus variegatus* was far less sensitive to the sediments than *H. azteca*, which correlates with the differential sensitivity of the two species in water-only tests with cadmium and nickel.

In 10-day toxicity tests with the saltwater amphipod *A. abdita* in these same sediments from Foundry Cove, Di Toro et al. (1992) observed metals concentrations from 0.1 to 28 μ moles SEM/g sediment were not toxic in some sediments, whereas 0.2 to 1000 μ moles SEM/g were lethal in other sediments indicating that the bioavailable fraction of metals in sediments varies from sediment to sediment. In contrast, they observed a clearly discernable mortality-concentration relationship when mortality was related to the SEM/AVS molar ratio (i.e., there was no significant mortality where SEM/AVS ratios were < 1.0 , mortality increased in sediments having SEM/AVS ratios 1.0-3.0, and there was 100% mortality in sediments with ratios > 10). The sum of the interstitial water toxic units (IWTU) for cadmium and nickel ranged from 0.08 to 43.5. Sediments with ≤ 0.5 IWTUs were always nontoxic, those with > 2.2 IWTUs were always toxic and two of seven sediments with intermediate IWTUs (0.5 to 2.2) were toxic. Molar concentrations of cadmium and nickel in the interstitial water were similar. However, cadmium contributed over 95 percent to the sum of the toxic units because cadmium is 67 times more toxic to *A. abdita* than nickel illustrating the utility of interstitial water concentrations of individual metals in assigning the probable cause of mortality in benthic species (Hansen et al., 1996a).

In tests with the same sediments from this location, Pesch et al. (1995) observed that six of 17 sediments tested had SEM/AVS ratios < 1.0 , interstitial water toxic units < 0.5 ,

and none of the six were toxic to the polychaete *Neanthes arenaceodentata*. None of the 11 sediments that contained SEM/AVS ratios > 1.0 were toxic. This was not surprising because only one sediment had > 0.5 IWTUs and because this polychaete is not sensitive to cadmium and nickel and can avoid sediments containing toxic concentrations of these metals.

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

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

Hansen et al. (1996a) made an observation that is important to the interpretation of the toxicity of sediments from field locations, particularly those from industrial harbors. They observed that if these sediments are toxic and SEM/AVS ratios are < 1.0 non-metals associated toxicity should always be suspected even if metals concentrations are very high on a dry weight basis. Further, they stated that the use of such data to reach the conclusion that this EqP approach is not valid is incorrect. This is because when SEM/AVS ratios were less than 1.0 there was an almost complete absence of toxicity in spiked sediments, and field sediments where metals were the only known source of contamination and IWTUs for metals were < 0.5 . Metals concentrations, when expressed on a sum of the IWTU basis can, therefore,

provide insight that in part may explain apparent anomalies between SEM/AVS ratios and the observed toxicity of these sediments and sediments from other field sites. The joint use of both SEM/AVS ratios and interstitial water concentrations are powerful tools for explaining the presence of toxicity when SEM/AVS ratios are < 1.0 and the absence of toxicity when SEM/AVS ratios are > 1.0 . Over all saltwater and freshwater field sediments tested in the laboratory, 100% were not toxic when SEM-AVS was ≤ 0.0 and IWTUs were ≤ 0.5 and 66.7% were toxic when SEM-AVS was > 0.0 and IWTUs were > 0.5 (Table 3-1).

3.2.4 Field Sites and Spiked Sediments Combined

Figures 3-3, a,b, and c and Table 3-1 summarize available data from saltwater and freshwater sediments spiked with individual metals or metal mixtures, saltwater field sites and freshwater field sites on the utility of metals concentrations in sediments normalized by dry weight, interstitial water toxic units (IWTUs) or SEM/AVS ratios to explain the bioavailability and acute toxicity of metals in sediments. Data are from Hansen et al., 1996a and Berry et al., in review. This analysis contains 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. The relationship between benthic organism mortality and total dry weight metals concentrations in spiked and field sediments is not useful to causally relate metal concentrations to organism response (Figure 3-3a). The overlap among bulk metals concentrations which cause no toxicity and those which are 100 percent lethal is almost four orders of magnitude.

Data in Figure 3-3b show that over all tests, organism response in sediments whose concentrations are normalized on an SEM/AVS basis is consistent with metal-sulfide binding on a mole to mole basis as first described by Di Toro et al. (1990) and in recommendations for assessing the bioavailability of metals in sediments proposed by Ankley et al. (1994). Saltwater and freshwater sediments spiked with metals and from field locations with SEM/AVS ratios ≤ 1.0 were uniformly (98.1 percent of 158 sediments) nontoxic (Figure 3-3b; Table 3-1). The majority (58.0 percent) of 174 sediments having SEM/AVS ratios > 1.0 were toxic. Given the effect on toxicity or bioavailability of the presence of other sediment phases that also affect bioavailability (Di Toro et al., 1987; Mahony et al., 1996) it is not surprising that many sediments having SEM/AVS ratios > 1.0 are not toxic.

Data in Figure 3-3c show that over all tests, the toxicity of sediments whose concentrations are normalized on an IWTU basis are typically consistent with the interstitial water toxic unit concept; that is if IWTUs are ≤ 1.0 sediments should be lethal to ≤ 50 percent of the organisms exposed; significant mortality probably should be absent at < 0.5 IWTU (Figure 3-3c). Of the spiked and field sediments evaluated which had IWTUs < 0.5 , 97.7 percent of 175 sediments were nontoxic (Table 3-1). For the 142 sediments having IWTUs ≥ 0.5 , 68.3 percent were toxic (Table 3-1). Given the effect on toxicity or bioavailability of the presence of other binding phases (e.g., DOC) 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.

Over all tests, the data in Figure 3-3a, b, and c indicate that the use of both IWTUs and SEM/AVS ratios together did not improve the accuracy of predictions of sediments that were nontoxic (98.5 percent of 132 sediments; Table 3-1). However, it is noteworthy that 78.9 percent of the 123 sediments with both SEM/AVS > 1.0 and IWTUs ≥ 0.5 were toxic (Table 3-1). Therefore, the approach of using SEM/AVS ratios, IWTUs, and especially both indicators to identify sediments of concern is very useful.

The results of all available data demonstrate that using SEM, AVS and interstitial water metals concentrations to predict which sediments that contain cadmium, copper, lead, nickel, silver and zinc will not be toxic is quite certain. This is very useful, because the vast majority of sediments found in the environment in the U.S. have SEM/AVS ratios ≤ 1.0 suggesting that there should be little concern about metals in sediments (Wolfe et al., 1994; Hansen et al., 1996a; Leonard et al., 1996a; Section 4 of this document) on a national basis, even though localized areas of biologically significant metal contamination do exist. However, a very important consideration is that most of these data are from field sites where sediment samples were collected in the summer. This is the time of the year when the seasonal cycles of AVS produce the maximum metal-binding potentials (Boothman and Helmstetter, 1992; Leonard et al., 1993). Hence, sampling at seasons and conditions when AVS is at minimal values is a must in establishing the true level of overall concern about metals in sediments and in evaluations of specific sediments. Predicting which of the sediments with SEM/AVS > 1.0 will be toxic is presently less certain. Importantly, the correct classification rate seen in these experiments (accuracy of predicting which sediments were toxic was 58.0% using the SEM/AVS ratio alone, 68.3% using IWTUs and 78.9% using both indicators) is high. An SEM/AVS ratio > 1.0 , particularly at multiple adjacent sites, should trigger additional tiered assessments which might include characterization of the spatial (both vertical

and horizontal) and temporal distribution of chemical concentration (AVS and SEM) and toxicity, measurements of interstitial water metal and toxicity identification evaluations (TIE's). In this context, the SEM, AVS, IWTU approach should be viewed as only one of the many sediment evaluation methodologies.

Because AVS can bind divalent metals in proportion to their molar concentrations, Hansen et al. (1996a) proposed the use of the difference between the molar concentrations of SEM and AVS (SEM-AVS) rather than SEM/AVS ratios used previously. The molar difference provides important insight into the extent of additional available binding capacity and the magnitude by which AVS binding has been exceeded (Figure 3-4). Further, absence of organism response when AVS binding is exceeded can indicate the potential magnitude of importance of other binding phases in controlling bioavailability. Figure 3-4 shows that for most nontoxic saltwater and freshwater field sediments, one to 100 μ moles of additional metal would be required to exceed the sulfide binding capacity (i.e., SEM-AVS = -1 to -100 μ moles/g). In contrast, most toxic field sediments contained 1.0 to 1000 μ moles 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 μ moles/g) indicates that other sediment phases, in addition to AVS, have great significance in controlling metal bioavailability. In comparison to SEM/AVS ratios, the use of SEM-AVS differences is particularly informative where AVS concentrations are low, such as those from Steilacoom Lake and the Keweenaw Watershed, where the SEM-AVS difference is numerically low and SEM/AVS ratios are high (Ankley et al., 1993).

EPA believes that results from tests using sediments spiked with metals and sediments from the field in locations where toxicity is metals-associated demonstrate the value in explaining the biological availability of metals concentrations normalized by SEM/AVS ratio and IWTUs instead of dry weight metals concentrations. Importantly, data from spiked sediment tests strongly indicate that metals are not the cause of most of the toxicity observed in field sediments when both SEM/AVS ratios are ≤ 1.0 and IWTU are < 0.5 . Expressing concentrations of metals in sediments on an SEM-AVS basis provides important insight into available additional binding capacity of sediments and the extent to which sulfide binding has been exceeded. It, along with measurement of interstitial water concentrations of metals, can potentially identify the specific metal causing toxicity. This can theoretically be accomplished by subtracting the metals-specific molar concentrations in order of their sulfide solubility product constants (K_{sp}). Predictions of sediments not likely to be toxic, based on use of SEM-AVS and IWTUs for all data from freshwater or saltwater field sediment and spiked sediment

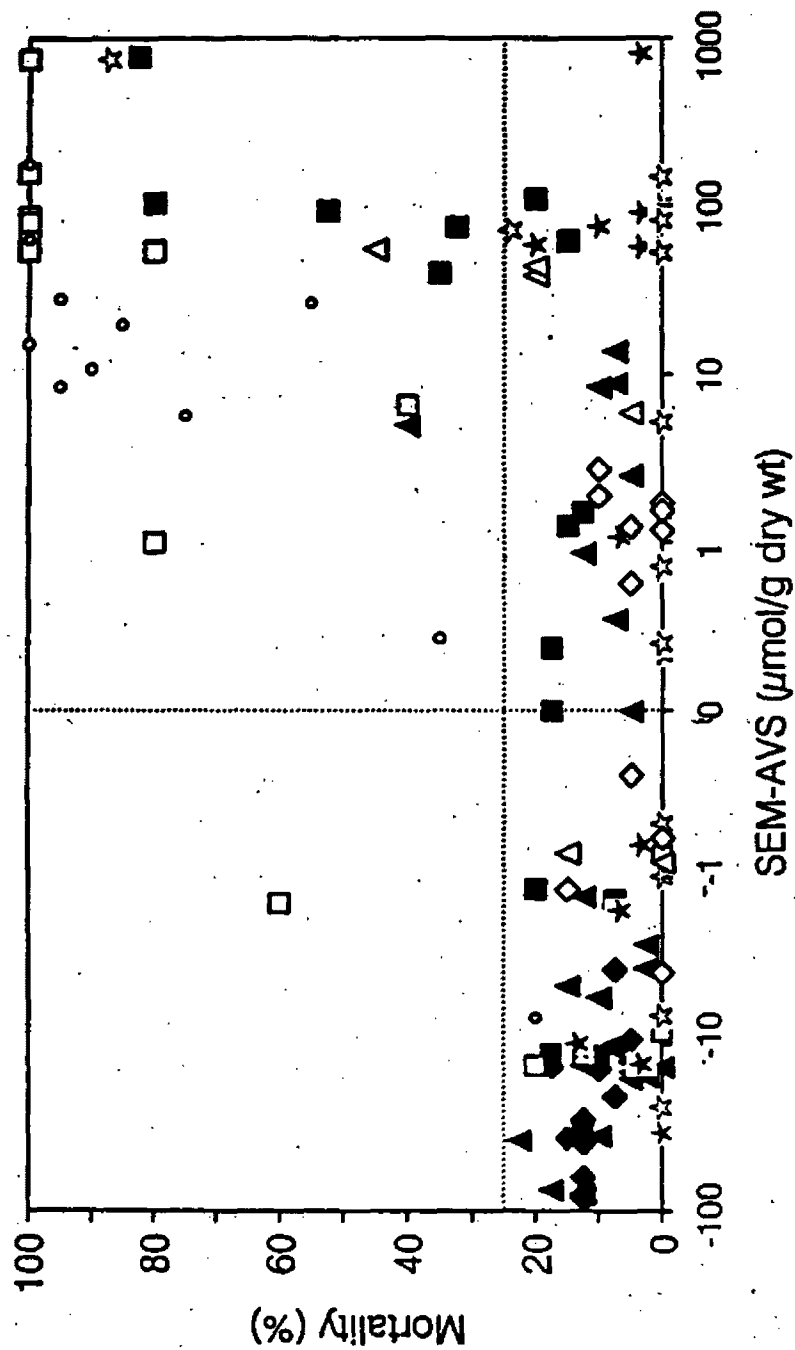


Figure 3-4. Percentage mortality of amphipods, oligochaetes and polychaetes exposed to sediments from three saltwater and four freshwater field locations as a function of the sum of the molar concentrations of SEM minus the molar concentration of AVS (SEM-AVS) (from Hansen et al., 1996a). The vertical dashed line at SEM-AVS = 0.0 indicates the boundary between sulfide-bound unavailable metal and potentially available metal.

tests are extremely accurate (98.5 percent) using both parameters (Table 3-1). While the predictions of sediments likely to be toxic are less accurate, the use of SEM-AVS is extremely useful in identifying sediments of potential concern (Table 3-1). Hansen (1995) summarized data from amphipod tests using freshwater and saltwater laboratory metals-spiked sediments and field sediments where metals were a known problem by comparing the percentage of sediments that were toxic to the SEM-AVS concentration. (Tests with polychaetes and gastropods were excluded because these organisms avoid exposure.) Seventy percent of the sediments in these amphipod studies with an SEM-AVS concentration of ≥ 0.76 μ moles of excess SEM/g were toxic. The corresponding values for 80, 90 and 100% of the sediments being toxic were 2.7, 16 and 115 μ moles of excess SEM/g, respectively.

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

3.3 PREDICTING METAL TOXICITY: LONG-TERM STUDIES

Taken as a whole, the short-term laboratory experiments with metal-spiked and field-collected sediments present a strong argument for the ability to predict an absence of metal toxicity based upon sediment SEM:AVS relationships and/or interstitial water metal concentrations. However, for this approach to serve as a valid basis for ESG derivation, comparable predictive success must be demonstrated in long-term laboratory and field experiments where chronic effects could be manifested (Luoma and Carter, 1993; Meyer et al.,

1994). This demonstration was the goal of experiments described by Hare et al. (1994), DeWitt et al. (1996), Hansen et al. (1996b), Liber et al. (1996) and Sibley et al. (1996). An important experimental modification to these long-term studies, as opposed to the short-term tests described in Section 3-2, was the collection of horizon-specific chemistry data. This is required because AVS concentrations often increase, and SEM/AVS ratios decrease, with increase in sediment depth (Howard and Evans, 1993; Leonard et al., 1996a); hence, chemistry performed on homogenized samples might not reflect the true exposure of benthic organisms dwelling in surficial sediments (Luoma and Carter, 1993; Hare et al., 1994; Peterson et al., 1996).

3.3.1 Life cycle toxicity tests

DeWitt et al. (1996) conducted an entire lifecycle toxicity test with the marine amphipod *Leptocheirus plumulosus* exposed for 28 d to cadmium-spiked estuarine sediments (Table 3-2). The test began with newborn amphipods and measured effects on survival, growth and reproduction relative to interstitial water and SEM/AVS normalization. Seven treatments of Cd were tested: 0 (control), 0.34, 0.74, 1.31, 1.55, 2.23 and 4.82 molar SEM_{Cd}/AVS ratios (measured concentrations). Gradients in AVS concentration as a function of sediment depth were greatest in the control treatment, decreased as the SEM_{Cd}/AVS ratio increased and became more pronounced over time. Depth gradients in SEM_{Cd}/AVS were primarily due to the spatial and temporal changes in AVS concentration, because SEM_{Cd} concentrations changed very little with time or depth. Thus, in most treatments SEM_{Cd}/AVS ratios were higher at the top of sediment cores than at the bottom. This is expected because the oxidation rate of iron sulfide in laboratory experiments is very rapid (100% in 60 to 90 minutes) and for cadmium sulfide is quite slow (10% in 300 hours) (Mahony et al., 1993). Interstitial cadmium concentrations increased in a dramatic step-function fashion in treatments having SEM/AVS ratios ≥ 2.23 ; and were below the 96-h LC50 for this amphipod in lesser treatments. There were no significant effects on survival, growth or reproduction in sediments containing more AVS than cadmium (SEM/AVS ratios 0.34, 0.74, 1.31 and 1.55), in spite of the fact that these samples contained from 183 to 1370 μg cadmium/g sediment. All amphipods died in sediments having SEM/AVS ratios 2.23. These results are consistent with predictions of metal bioavailability from acute tests with metal-spiked sediments (i.e., that sediments with SEM_{Cd}/AVS ratios ≤ 1 are not toxic, interstitial water metal concentrations are related to organism response and sediments with SEM_{Cd}/AVS ratios > 1 may be toxic).

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

Toxicity Test	Metal	Duration (days)	Measured SEM-AVS ^a		Effect	Reference
			NOECs	OECs		
<u>Life-cycle:</u>						
<i>Leptocheirus plumulosus</i>	Cadmium	28	-3.4, -2.0, 0.78, 1.9	8.9, 15.6	Mortality 100%	DeWitt et al., 1996
<i>Chironomus tentans</i>	Zinc	56	-4.3, -2.6, -1.4, 6.4	21.9, 32.2	Larval mortality 85-100%. Weight and emergence reduced.	Sibley et al., 1996
<u>Colonization:</u>						
Laboratory-saltwater	Cadmium	118	-13.4	8.0, 27.4	Fewer polychaetes, shifts in community composition, fewer species, bivalves absent, tunicates increased.	Hansen et al., 1996
Field-saltwater	Cadmium, copper, nickel, zinc	120	<0	-	No effects observed.	Boothman et al., 1996
Field-freshwater	Cadmium		-0.45, -0.25, 0.5 ^b	4.5 ^b	Reduced <i>Chironomus</i> numbers. Bioaccumulation.	Hare et al., 1994
Field-freshwater	Zinc	368	-3.6, -3.5, - 2.9, -2.0 ^c	1.0	Occasional minor reductions in Naididae oligochaetes.	Liber et al., 1996

^a SEM-AVS differences are used instead of SEM/AVS ratios to standardize across the studies referenced. An SEM-AVS difference of ≤ 0 is the same as an SEM/AVS ratio of ≤ 1.0 . An SEM-AVS difference of >0 is the same as an SEM/AVS ratio of >1.0 .

^b Nominal concentrations.

Sibley et al. (1996) reported similar results from a 56-d life-cycle test conducted with the freshwater midge *Chironomus tentans* exposed to zinc-spiked sediments (Table 3-2). The test was initiated with newly hatched larvae and lasted through one complete generation during which survival, growth, emergence and reproduction were monitored. In sediments where the molar difference between SEM and AVS was <0 , at dry wt zinc concentrations as high as 270 mg/kg, concentrations of zinc in the sediment interstitial water were low and no adverse effects were observed for any of the biological endpoints measured. Conversely, when SEM-AVS exceeded 0, AVS and interstitial water concentrations of zinc increased with increasing treatments (being highest in surficial sediments) and reductions in survival, growth, emergence and reproduction were observed. Over the course of the study, the absolute concentration of zinc in the interstitial water in these treatments decreased due to increase in sediment AVS and loss of zinc due to twice daily renewals of overlying water.

3.3.2 Colonization tests

Hansen et al. (1996b) conducted a 118-d benthic colonization experiment in which sediments were spiked to achieve nominal cadmium/AVS molar ratios of 0.0 (control), 0.1, 0.8 and 3.0 and held in the laboratory in a constant flow of unfiltered seawater (Table 3-2). Oxidation of AVS in the surficial 2.4 cm of the control treatment within two to four weeks resulted in sulfide profiles similar to those occurring in sediments in nearby Narragansett Bay, RI (Boothman and Helmstetter, 1992). In the nominal 0.1 cadmium/AVS treatment, measured SEM_{Cd} was always less than AVS, interstitial cadmium concentrations ($<3-10 \mu\text{g/L}$) were less than those likely to cause biological effects, and no significant biological effects were detected. In the nominal 0.8 cadmium/AVS treatment, measured SEM_{Cd} commonly exceeded AVS in the surficial 2.4 cm of sediment and interstitial cadmium concentrations ($24-157 \mu\text{g/L}$) were sufficient to be of toxicological significance to highly sensitive species. In this treatment, shifts in the presence or absence over all taxa, and fewer macrobenthic polychaetes (*Mediomastus ambiseta*, *Streblospio benedicti* and *Podarke obscura*) and unidentified meiofaunal nematodes, were observed. In the nominal 3.0 cadmium/AVS treatment, concentrations of SEM_{Cd} were always greater than AVS throughout the sediment column. Interstitial cadmium ranged from 28,000 to 174,000 $\mu\text{g/L}$. In addition to the effects observed in the nominal 0.8 cadmium/AVS treatment, sediments in the 3.0 cadmium/AVS treatment were colonized by fewer macrobenthic species, polychaete species and harpacticoids; had lower densities of diatoms; lacked bivalve molluscs; and exhibited other impacts. Over all

treatments, the observed biological responses were consistent with predicted possible adverse effects resulting from elevated SEM_{Cd}/AVS ratios in surficial sediments and interstitial water cadmium concentrations.

Boothman et al. (1996) conducted a field colonization experiment in which sediments from Narragansett Bay, RI were spiked with an equi-molar mixture of cadmium, copper, nickel and zinc at nominal $SEM:AVS$ ratios of 0.1, 0.8 and 3.0, placed in boxes, and replaced in Narragansett Bay (Table 3-2). AVS concentrations decreased with time in surface (0-3 cm) sediments in all treatments where $SEM < AVS$, but did not change in subsurface (6-10 cm) sediments or in the entire sediment column in the $SEM > AVS$ treatment. SEM decreased with time only where SEM exceeded AVS . The concentration of metals in interstitial water was below detection limits when SEM was less than AVS . When SEM exceeded AVS , significant concentrations of metals were present in interstitial water in order of their sulfide solubility product constants. Interstitial water concentrations in these sediments decreased with time exceeding the WQC in interstitial water for 60 days for all metals, 85 days for cadmium and zinc, and for the entire experiment (120 days) for zinc. Benthic faunal assemblages in the spiked sediment treatments were not different from the control treatment. Lack of biological response was consistent with the vertical profiles of SEM and AVS . AVS was greater than SEM , in all surface sediments, including the top 2 cm of the 3.0 $SEM:AVS$ treatment, due to the oxidation of AVS and loss of SEM . The authors speculate that interstitial metal was likely absent in the surficial sediments in spite of data demonstrating the presence of significant measured concentrations of interstitial metal. This is because the interstitial water in the nominal 3.0 SEM/AVS treatment was sampled from sediment depths where SEM was in excess. It is in surficial sediments where settlement by saltwater benthic organisms first occurs. Also, there was a storm event which allowed a thin layer of clean sediment to be deposited on top of the spiked sediment (Boothman, USEPA, personal communication). These data demonstrate the importance of sampling of sediments and interstitial water in sediment horizons where benthic organisms are active.

Hare et al. (1994) conducted an approximately 1-yr field colonization experiment in which uncontaminated freshwater sediments were spiked with cadmium, and replaced in the oligotrophic lake from which they originally had been collected (Table 3-2). Cadmium concentrations in interstitial waters were very low at cadmium: AVS molar ratios < 1.0 , but increased markedly at ratios > 1.0 . They reported reductions in the abundance of only the

chironomid *Chironomus salinarius* in the nominal 10.0 SEM/AVS treatment. Cadmium was accumulated by organisms from sediments with surficial SEM concentrations were greater than those of AVS. These sediments also contained elevated concentrations of cadmium in interstitial water.

Liber et al. (1996) performed a field colonization experiment using sediments having 4.46 μmole sulfide/gram from a freshwater mesotrophic pond (Table 3-2). Sediments were spiked with 0.8, 1.5, 3.0, 6.0 and 12.0 μmole zinc/gram, replaced in the field and chemically and biologically sampled over 16 mo. There was a pronounced increase in AVS concentrations with increasing zinc concentration, AVS was lowest in the surficial 0-2 cm of sediment with minor seasonal variations. With the exception of the highest spiking concentration (ca., 700 mg/kg, dry wt), AVS concentrations remained larger than those of SEM. Interstitial water zinc concentrations were rarely detected in any treatment, and were never at concentrations that might pose a hazard to benthic macroinvertebrates. The only observed difference in benthic community structure across the treatments was a slight decrease in the abundance of Naididae oligochaetes at the highest spiking concentration. This absence of any noteworthy biological response was consistent with the absence of interstitial water concentrations of biological concern. This was attributed to the increase in concentrations of iron and manganese sulfides, produced during periods of diagenesis, which were replaced by the more stable zinc sulfide which is less readily oxidized during winter months. In this experiment, and theoretically in nature, excesses of sediment metal might be overcome over time due to the diagenesis of organic material. In periods of minimal diagenesis, the oxidation rates of metal sulfides, if sufficiently great, could release biologically significant concentrations of the metal into interstitial waters. This phenomenon should occur metal-by-metal in order of their sulfide solubility product constants.

SECTION 4

DERIVATION OF SEDIMENT GUIDELINES FOR METALS

4.1 GENERAL INFORMATION

Section 4 of this document presents the technical basis for establishing ESG for copper, cadmium, nickel, lead, silver and zinc. The basis of the overall approach is the use of EqP theory linked to the concept of maintaining metal activity for the sediment interstitial water system below effects levels. Extensive toxicological data from short-term and long-term laboratory and field experiments, with both marine and freshwater sediments and a variety of species indicates that it is possible to reliably predict an absence of metal toxicity based upon EqP theory. ESG for all six metals collectively can be derived using two procedures: (a) by comparing the sum of their molar concentrations, measured as SEM, to the molar concentration of AVS in sediments (AVS Guideline); or (b) by comparing the measured interstitial water concentrations of the metals to WQC final chronic values (FCVs) (Interstitial Water Guidelines). These approaches are described in more detail below. A lack of exceedence of ESG based upon any one of the two procedures indicates that metal toxicity should not occur. Exceedence of either the AVS or Interstitial Water Guidelines is indicative of a potential problem that would entail further evaluation.

At present, EPA believes that the technical basis for implementing these two approaches is supportable. The Organic Carbon and Minimum Partitioning Approaches as proposed to the SAB and in Ankley et al.(1996) require additional research prior to their implementation. Research issues for these latter two approaches include the development of robust partitioning datasets for the six metals, as well as investigation of factors such as the importance of other binding phases. The four approaches have been presented to and reviewed by the Science Advisory Board of EPA (U.S EPA, 1994a; 1995a).

Additional research required to fully implement other approaches for deriving ESG for these metals and to derive ESG for other metals includes the development of uncertainty estimates associated with any approach; part of this would include their application to a variety of field settings and sediment types. Research also is needed to establish the technical basis for ESG for metals other than the six described herein, such as mercury, arsenic and chromium.

Finally, the ESG approaches are intended to protect benthic organisms from direct toxicity associated with exposure to metal-contaminated sediments. They are not designed to protect aquatic systems from metal release associated, for example, with sediment suspension, or the transport of metals into the food web either from sediment ingestion or the ingestion of contaminated benthos. This latter issue, in particular, should be the focus of future research given existing uncertainty in the prediction of bioaccumulation of metals by benthos (Ankley, 1996).

The following nomenclature is used in subsequent discussion of ESG derivation for metals. The ESG for the metals are expressed in molar units because of the molar stoichiometry of metal binding to AVS. Thus, solid phase constituents (AVS, SEM) are in moles/g dry wt. The interstitial water metal concentrations are expressed in $\mu\text{moles/L}$, either as dissolved concentrations $[M_d]$ or activities $\{M^{2+}\}$ (Stumm and Morgan, 1981). The subscripted notation, M_d , is used to distinguish dissolved aqueous phase molar concentrations from solid phase molar concentrations with no subscript. For the combined concentration, $[\text{SEM}_T]$, the units are moles of metal per volume of solid plus liquid phase (i.e., bulk). Note also that when $[\text{SEM}_{Ag}]$ is summed and/or compared to AVS $1/2$ the molar Ag concentration is applied.

One final point should be made with respect to nomenclature. Use of the terms *non-toxic* and *having no effect*, mean only with respect to the six metals considered in this paper. The toxicity of field collected sediments can be caused by other chemicals. Therefore, avoiding exceedences of ESG for metals does not mean that the sediments are non-toxic. It only ensures that the six metals being considered should not have an undesirable biological effect. Moreover, as discussed in detail below, exceedence of the guidelines for the six metals does not necessarily indicate that metals will cause toxicity. For these reasons, we strongly recommend the use of toxicity tests, TIEs, chemical monitoring in vertical, horizontal and temporal scales, and other assessment methodologies as integral parts of any assessment concerned with the effects of sediment-associated contaminants (Ankley et al., 1994).

4.2 SINGLE METAL SEDIMENT GUIDELINES

Except in rare instances, single metal guidelines are not usually applicable to field situations since there is almost always more than one metal to be considered. As will become

subsequently clear, it would be technically indefensible to derive guidelines for one metal at a time because of the competitive nature of AVS binding. Nevertheless, it is illustrative to present the logic for single metals as a prelude to the derivation of the multiple metal guidelines.

4.2.1 AVS Guidelines

It has been demonstrated that if the SEM of a sediment is less than or equal to the

$$[\text{SEM}] \leq [\text{AVS}] \quad (4-1)$$

AVS then no toxic effects are seen. This is consistent with the results of a chemical equilibrium model for the sediment - interstitial water system (Di Toro et al., 1992). The resulting metal activity $\{M^{2+}\}$ can be related to the total SEM of the sediment and water, and to the solubility products of the metal sulfide (K_{MS}) and iron sulfide (K_{FeS}). In particular, it is true that at $[\text{SEM}] \leq [\text{AVS}]$ then:

$$\frac{\{M^{2+}\}}{[\text{SEM}_T]} \leq \frac{K_{MS}}{K_{FeS}} \quad (4-2)$$

Because 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, the metal activity of the sediment is at least five orders of magnitude smaller than the SEM (see Di Toro et al. (1992) for data sources and references). This indicates that no biological effects would be expected. Therefore, the condition $[\text{SEM}] < [\text{AVS}]$ is a "no effect" ESG.

The reason we use the term "no effect" is that for the condition $[\text{SEM}] < [\text{AVS}]$ no biological impacts are expected. However, for $[\text{SEM}] > [\text{AVS}]$, which might seemingly be considered a ESG violation, there are many documented instances where no biological impacts occur (e.g., because organic carbon partitioning controls metal bioavailability in the interstitial water, or the species of concern avoid or are insensitive to metals).

4.2.2 Interstitial Water Guidelines

The condition $[SEM] \leq [AVS]$ indicates that the metal activity of the sediment - interstitial water system is low and, therefore, below toxicologically-significant concentrations. Another way of ensuring this is to place a condition on the interstitial water activity directly. Suppose that we knew the metal activity, denoted by $\{FCV\}$, that corresponded to the $[FCV]$. Then the ESG corresponding to this effect level is:

$$\{M^{2+}\} \leq \{FCV\} \quad (4-3)$$

It is quite difficult, however, to measure and/or calculate metal activity in a solution phase, 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 are not expressed on an activity basis. An approximation to this condition is:

$$[M_d] \leq [FCV_d] \quad (4-4)$$

where $[FCV_d]$ is the FCV applied to total dissolved metal concentrations. That is, we require that the total dissolved metal concentration in the interstitial water $[M_d]$ be less than the FCV applied as a dissolved guideline. Although this requirement ignores the effect of chemical speciation on both sides of the equation - compare Equations (4-3) and (4-4) - it is the approximation that is currently being suggested by EPA for the WQC for metals (Prothro, 1993). That is, the WQC should be applied to the total dissolved - rather than the total acid recoverable - metal concentration (Table 4-1; U.S. EPA, 1995b). Hence, if this second condition is satisfied it is consistent with the level of protection afforded by the WQC.

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 would not violate the guidelines. These cases occur when significant binding to other phases occurs. It should be noted that using the FCV for metals in freshwater samples requires that the hardness of the interstitial water be measured since the WQC vary with hardness.

4.3 MULTIPLE METALS GUIDELINES

As described in the previous subsection, from a practical standpoint it is insufficient and inappropriate to consider each metal separately. Because of the interactive nature of metal-sulfide binding, this is of particular concern for the AVS guidelines.

Table 4-1: Water quality criteria (WQC) criteria continuous concentrations (CCC) based on the dissolved concentration of metal^{ab}. These WQC CCC values are for use in the Interstitial Water Criteria Toxic Unit (IWCTU) approach for deriving sediment guidelines based on the dissolved metal concentrations in interstitial water.

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

^a (U.S.EPA, 1995b).

^b Rounded all criteria to two significant figures.

^c For example the freshwater CCC at a hardness of 50, 100, and 200 $\text{mg CaCO}_3/\text{L}$ are 0.56, 0.94, and 1.6 μg cadmium/L, 6.2, 12, and 20 μg copper/L, 1.0, 2.5, and 6.1 μg lead/L, 88, 160, and 280 μg nickel/L, and 58, 108, and 187 μg zinc/L.

^d CF = Conversion factor to calculate the dissolved CCC for cadmium from the total CCC for cadmium: $\text{CF} = 1.101672 - [(\ln \text{hardness})(0.041838)]$

^e The saltwater CCC for copper is from the "Ambient Water Quality Criteria- Saltwater Copper Addendum" (U.S. EPA, 1995c).

^f The silver criteria are currently under revision to reflect water quality factors that influence the criteria such as hardness, and pH and any other factors. Since silver has the smallest solubility product (see Table 2-2) and the greatest affinity for AVS, it would be the last metal to be released from the AVS or the first metal to bind to the AVS so it is unlikely that silver would occur in the interstitial water. However in sediments contaminated with silver the user should be aware of the limitations in the above criteria for silver. AVS Guidelines can be applied, however, the Interstitial Water Guidelines can not. If the AVS Guideline is exceeded ($\Sigma \text{SEM} > \text{AVS}$) and the sediment is contaminated with silver, further testing and evaluations would be warranted to assess toxicity.

4.3.1 AVS Guidelines

The results of calculations using chemical equilibrium models indicate that metals act in a competitive manner when binding to AVS. That is, the six metals: silver, copper, lead, cadmium, zinc and nickel will bind to AVS and be converted to their respective sulfides in this sequence (i.e., in the order of increasing solubility). Therefore, they must be considered together. There cannot be a guideline 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 $\sum \text{SEM}$ will be misleadingly small, and it may appear that $[\sum \text{SEM}] < [\text{AVS}]$ when in fact this would not be true if all the metals are considered together. It should be noted that EPA currently restricts this discussion to the six metals listed above; however, in situations where other sulfide forming metals (e.g., mercury) are present at high concentrations, they also must be considered.

The equilibrium model prediction of the metal activity is similar to the single metal example when a mixture of the metals is present. If the molar sum of SEM for the six metals is less than or equal to the AVS, that is:

$$\sum_i [\text{SEM}_i] \leq [\text{AVS}] \quad (4-5)$$

then:

$$\frac{\{M_i\}}{[\text{SEM}_{i,T}]} < \frac{K_{M,S}}{K_{FeS}} \quad (4-6)$$

where $[\text{SEM}_{i,T}]$ is the total SEM ($\mu\text{mol/L(bulk)}$) for the i^{th} metal. Thus the activity of each metal, $\{M_i\}$, is unaffected by the presence of the other sulfides. This can be understood as follows. Suppose 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 iron sulfide is satisfied. This sets the sulfide activity. Then each metal sulfide dissolves until reaching its solubility. Since so little of each dissolve relative to the iron sulfide, 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 one another.

The fact that they are only slightly soluble relative to iron sulfide is the cause of this behavior. Thus, the AVS Guidelines are easily extended to the case of multiple metals.

4.3.2 Interstitial Water Guidelines

The application of the Interstitial Water Guideline to multiple metals is complicated, not by the chemical interactions of the metals in the sediment - interstitial water system (as in the case with the AVS Guideline), but rather because of their possible toxic interactions. Even if the individual concentrations do not exceed the FCV of each metal (FCV_i), the metals could exert additive effects that might result in toxicity (Biesinger et al., 1986; Spehar and Fiandt, 1986; Enserink et al., 1991; Kraak et al., 1994). Therefore, to address this potential additivity, the interstitial water metal concentrations are converted to toxic units (TUs) and these are summed. Since FCVs are used as the no effects concentrations these TUs are referred to as interstitial water guidelines toxic units (IWGTUs). For freshwater sediments, the FCVs are hardness dependent for all of the divalent metals under consideration and, thus, need to be adjusted to the hardness of the interstitial water of the sediment being considered. Because there are no FCVs for silver in freshwater or saltwater, this approach is not applicable to sediments containing significant concentrations of silver (i.e., $\Sigma SEM > AVS$). Since silver has the smallest solubility product (see Table 2-2) and the greatest affinity for AVS, it would be the last metal to be released from the AVS or the first metal to bind with AVS so it is unlikely that silver would occur in the interstitial water. For the i^{th} metal with a total dissolved concentration $[M_{i,d}]$, the IWGTU is:

$$IWGTU_i = \frac{[M_{i,d}]}{[FCV_{i,d}]} \quad (4-7)$$

A lack of exceedence of the ESG requires that the sum of the IWGTUs be less than or equal to one:

$$\sum_i \frac{[M_{i,d}]}{[FCV_{i,d}]} \leq 1 \quad (4-8)$$

Hence, the multiple metals guideline is quite similar to the single metal case (Equation 4-4) except that it is expressed as summed IWGTUs.

To summarize, the proposed ESG are as follows. The sediment passes the ESG for the six metals if either of these conditions is satisfied:

(a) AVS Guideline:

$$\sum_i [SEM_i] \leq [AVS] \quad (4-5)$$

where

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

(b) Interstitial Water Guideline:

$$\sum_i \frac{[M_{i,d}]}{[FCV_{i,d}]} \leq 1 \quad (4-8)$$

where

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

If either of these two conditions are violated, this does not mean that the sediment is toxic. For example, if the AVS in a sediment is non-detectable, then condition (a) will be violated. However, if there is sufficient organic carbon sorption so that condition (b) is satisfied, then the sediment would be deemed acceptable.

If both of these conditions are violated, or if the AVS guideline is violated and the sediment is contaminated with silver, then there is reason to believe that the sediment may be unacceptably contaminated by these metals. Further testing and evaluations would therefore be useful in order to assess actual toxicity and its causal relationship to the six metals. These may include acute and chronic tests with species that are sensitive to the metals suspected to be causing the toxicity. Also, *in situ* community assessments, sediment TIEs and seasonal

characterizations of the SEM, AVS and interstitial water concentrations would be appropriate (Ankley et al., 1994).

4.4 ESG FOR METALS VS. ENVIRONMENTAL MONITORING DATABASES

The purpose of this Section is to compare ESG based on SEM-AVS or IWGTUs to chemical monitoring data from freshwater and saltwater sediments in the United States. This comparison of AVS-SEM and interstitial water concentrations can indicate the extent of metals contamination in the United States. When toxicity or benthic organism community health data are available in conjunction with these concentrations it is possible to speculate as to potential causes of the observed effects.

4.4.1 Data Analysis

Three sources were identified which contain both AVS and SEM databases; one also had data on concentrations of metals in interstitial water. Toxicity tests were also conducted on all sediments from these sources. The databases are from the Environmental Monitoring and Assessment Program (EMAP) (Leonard et al., 1996a), National Oceanic and Atmospheric Administration, National Status and Trends Program (NOAA NS&T) (Wolf et al., 1994; Long et al., 1995; 1996) and from the Regional Environmental Monitoring and Assessment Program (REMAP) (Adams et al., 1996).

Freshwater sediments:

The AVS and SEM concentrations in the 1994 EMAP database from the Great Lakes were analyzed by Leonard et al. (1996a). Forty-six sediment grab samples and nine core samples were collected in the summer from forty-two locations in Lake Michigan. SEM, AVS, TOC, interstitial water metals (when sufficient volumes were present) and 10 day sediment toxicity to the midge *Chironomus tentans* and the amphipod *Hyallela azteca* were measured in sediments collected by the grab (Appendix C).

The AVS concentrations vs. SEM-AVS differences from Appendix C are plotted in Figure 4-1. Grab sediment samples containing AVS concentrations below the detection limit of 0.05 $\mu\text{mol/g}$ AVS are plotted at that concentration. Forty-two of the 46 (91 percent) samples had

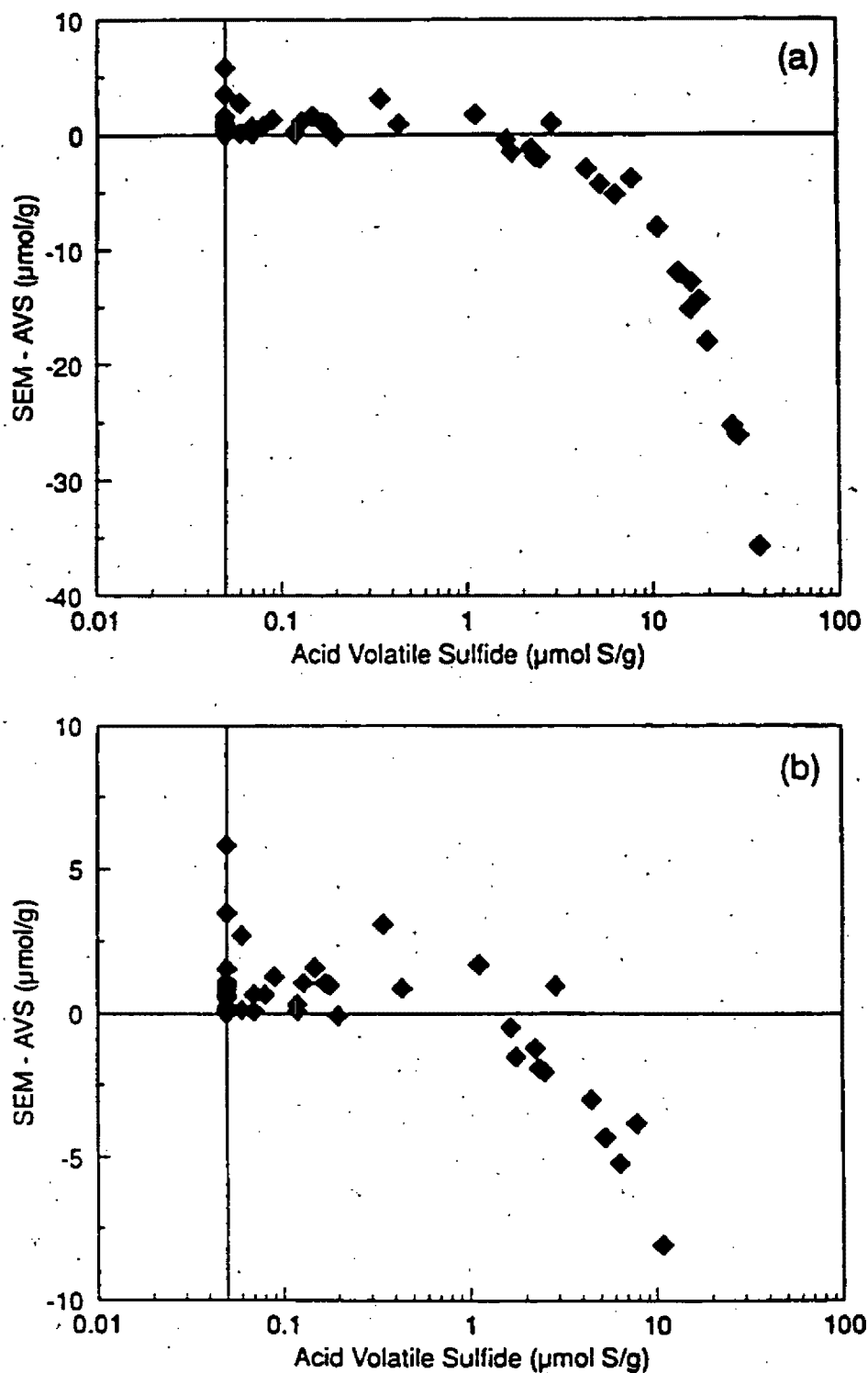


Figure 4-1. SEM minus AVS values versus AVS concentrations in EMAP-Great Lakes sediments from Lake Michigan. Data are from surficial grab samples only (this figure is taken from Leonard et al., 1996, see data in Appendix C). The upper plot shows all values, the lower plot has the ordinate limited to SEM minus AVS values between -10 and +10.

SEM-AVS differences greater than 0. Thirty-six of these had less than 1.0 μmol of ΣSEM metal per gram sediment; and none had over 5.8 $\mu\text{moles/g}$ of excess metal. In theory, sediments with SEM concentrations in excess of that for AVS have the potential to be toxic due to metals. However, the majority of exceedances occur in places where the AVS is very small and the amount of SEM is also very small. For these Lake Michigan sediments, a closer look at both interstitial water metal and toxicity test results is needed. Measurement of the concentrations of metals in interstitial water can be used to determine if the excess metals are bound to other sediment phases, therefore, prohibiting toxicity due to interstitial metal. Interstitial water guidelines toxic units (IWGTU) can be calculated for each metal as the interstitial water concentration divided by the final chronic value for that metal. Interstitial water volumes were sufficient to measure metals concentrations in 20 of the samples. The sum of the IWGTU for cadmium, copper, lead, nickel and zinc in these sediments was less than 0.4 (Leonard et al., 1996a). In 10-d toxicity tests using *Chironomus tentans* and *Hyaella azteca*, no toxicity was observed 81% of the 21 sediments not exceeding the ESG. They conclude that for the toxic sediments that did not exceed the metals ESG, the observed toxicity is not likely due to metals. Further, these sediments are unlikely to be contaminated by metals (Leonard et al., 1996a). These data demonstrate the value of using both SEM-AVS and IWGTUs to evaluate the risks of metals in sediments.

Saltwater sediments:

Saltwater data from a total of 398 sediment samples from five monitoring programs representing the eastern coast of the United States from Chesapeake Bay to Massachusetts are included in Figure 4-2. The EMAP Virginia Province database (U.S. EPA, 1996) consists, in part, of 127 sediment samples collected from August to mid-September 1993 from randomly selected locations in tidal rivers and small and large estuaries from the Chesapeake Bay to Massachusetts (Strobel et al., 1995). The NOAA data is from Long Island Sound, Boston Harbor and the Hudson River Estuary. Sediments were collected from 63 locations in the coastal bays and harbors of the Long Island Sound in August, 1991 (Wolfe et al., 1994). Sediment samples from 30 locations in Boston Harbor were collected in June and July 1993 (Long et al., 1996). Sediment samples from 38 locations in the Hudson River Estuary were collected from March to May 1991 (Long et al., 1995). Sediment samples were collected in the REMAP program from 140 locations from the New York/ New Jersey Harbor Estuary System (Adams et al., 1996). All of the above sediment grab samples were from approximately the top 2 cm of undisturbed sediment.

For saltwater sediments, molar concentration of AVS typically exceeds that for SEM (SEM-AVS < 0) for most of the samples across the entire range of AVS concentrations (Figure 4-2). A total of 68 of the 398 saltwater sediments (17 percent) had an excess of metal, and only 4 of the 68 (6 percent) had over 2 $\mu\text{mol/g}$ excess SEM. As AVS levels increase above this concentration fewer and fewer sediments have SEM-AVS differences that are positive; none occurred when AVS was $> 8.1 \mu\text{mol/g}$. Unlike the sediments from the freshwater EMAP survey in Lake Michigan, interstitial water was not measured in these saltwater sediments. Only five of the 68 sediments (7 percent) having excess of up to $0.9 \mu\text{mol/g}$ SEM were toxic in 10-d sediment toxicity tests with the amphipod *Ampelisca abdita*, whereas 79 of 330 (24 percent) sediments having an excess of AVS were toxic. The data support the interpretation that (1) toxicity was NOT metals-related in the 79 sediments where AVS was in excess over SEM; (2) metals might have caused the toxicity in the five toxic sediments having an excess of metal, but even in the absence of measurements of interstitial water metals concentrations, we speculate that metals toxicity is unlikely because there was only $\leq 0.9 \mu\text{mol/g}$ excess SEM (the molar concentration SEM most often exceeds that of AVS, in sediments having AVS concentrations $\leq 1 \mu\text{mol/g}$); and (3) the absence of toxicity in sediments having an excess of SEM of up to $4.4 \mu\text{mol/g}$ indicates that significant metal-binding potential over that of AVS existed in some sediments. Organic carbon concentrations of from 0.05% to 15.2% (average 1.9 percent) provides for some of this additional metal-binding.

The data above appear to suggest that in the United States direct toxicity caused by metals in sediments is extremely rare. While this might be true, these data by themselves are inconclusive and it would be inappropriate to use the data from the above studies to reach this conclusion. All of the above studies were conducted in the summer when the seasonal biogeochemical cycling of sulfur should produce the highest concentrations of iron monosulfide which should make direct metal-associated toxicity less likely than in the winter/spring months. Accurate assessment of the extent of the direct ecological risks of metals in sediments requires that sediment monitoring occur in the months of minimum AVS concentration; typically November to early May. These yet to be conducted studies must monitor at a minimum SEM, AVS, interstitial water metal and toxicity. The data presented here are not intended to be used to draw conclusions about toxicity due to resuspension or bioaccumulation.

SECTION 5

IMPLEMENTATION

5.1 CONSIDERATIONS IN PREDICTING METAL TOXICITY

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

5.2 SAMPLING AND STORAGE

Accurate prediction of exposure of benthic organisms to metals is critically dependent upon sampling appropriate sediment horizons at appropriate times. This is because of the relatively high rates of AVS oxidation due to natural processes in sediments and the requirement that oxidation must be avoided during sampling of sediments and interstitial water. In fact it is this seemingly labile nature that has led some to question the practical utility of using AVS as a basis for EqP-derived ESG for metals (Luoma and Carter, 1993; Meyer et al., 1994). For example, there have been many observations of spatial (depth) variations in AVS concentrations, most of which indicate that surficial AVS concentrations are less than those in deeper sediments (Besser et al., 1996; Boothman and Helmstetter, 1992; Brumbaugh et al., 1994; Hansen et al., 1996b; Hare et al., 1994; Howard and Evans, 1993; Leonard et al., 1996a; Liber et al., 1996). This likely is due to oxidation of AVS at the sediment surface, a process that is enhanced by bioturbation (Peterson et al., 1996). In addition to varying with depth, AVS can vary seasonally. For example, in systems where overlying water contains appreciable oxygen during cold weather months, AVS tends to decrease, presumably due to a

constant rate of oxidation of the AVS linked to a decrease in its generation by sulfate-reducing bacteria (Herlihy and Mills, 1985; Howard and Evans, 1993; Leonard et al., 1993). Because of potential temporal and spatial variability of AVS, it appears the way to avoid possible under-estimation of metal bioavailability is to sample the biologically "active" zone of sediments at times when AVS might be expected to be present at small concentrations. We recommend that at a minimum AVS and SEM measurements be made using surficial (0-2.0 cm) sediments during the period from November to early May in aerobic aquatic ecosystems. Minimum AVS concentrations may not always occur during cool-weather seasons; for example, systems that become anaerobic during the winter can maintain relatively large sediment AVS concentrations (Liber et al., 1996). Therefore, seasonal measurements of AVS, SEM and interstitial metal concentrations may need to be determined. Importantly, the biologically active zones of some benthic communities may be only the surface few millimeters in depth and in other communities up to a meter. Therefore, for sufficient characterization, multiple sediment horizons may require sampling of interstitial water, SEM and AVS to determine the potential for exposure to metals.

The somewhat subjective aspects of these sampling recommendations have been of concern. However, recent research suggests that the transient nature of AVS may be overstated relative to predicting the fate of all metal-sulfide complexes in aquatic sediments. Observations from the Duluth EPA laboratory made in the early 1990s indicated that AVS concentrations in sediments contaminated by metals such as cadmium and zinc tended to be elevated over concentrations typically expected in freshwater systems (G.T. Ankley, unpublished data). The probable underlying basis for these observations did not become apparent, however, until a recent series of spiking and metal-sulfide stability experiments. The field colonization study of Liber et al. (1996) demonstrated a strong positive correlation between the amount of zinc added to test sediments and the resultant concentration of AVS in the samples. In fact, the initial design of their study attempted to produce test sediments with nominally as much as five-times more SEM (zinc) than AVS; however, the highest measured SEM/AVS ratio achieved was only slightly larger than 1. Moreover, the expected surficial depletion and seasonal variations in AVS were unexpectedly low in the zinc-spiked sediments. These observations suggested that zinc sulfide, which comprised the bulk of AVS in the spiked sediments, was more stable than the iron sulfide that presumably was the source of most of the AVS in the control sediments. The apparent stability of other metal sulfides versus iron sulfide also has been noted in laboratory spiking experiments with freshwater and saltwater sediments.

(Boothman et al., 1996; De Witt et al., 1996; Hansen et al., 1996b; Leonard et al., 1995; Peterson et al., 1996; Sibley et al., 1996).

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

5.2.1 Sediments

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

Sediments not immediately analyzed for AVS and SEM must be placed in sealed airtight glass jars and refrigerated or frozen. Generally, 50 ml or more of sediment should be added to nearly fill the jar. If sediments are stored this way there will be little oxidation of AVS even after several weeks. Sampling of the stored sediment from the middle of the jar will further limit potential effects of oxidation on AVS. Sediments experiencing oxidation of AVS during storage will become less black or grey if oxidized. Because the rate of metal-sulfide oxidation is markedly less than that of iron sulfide, release of metal during storage is unlikely.

5.2.2 Interstitial Water

Several procedures are available to sample interstitial water *in situ* or *ex situ*. Carignan et al. (1985) compared metals concentrations in interstitial water obtained by *ex situ*

centrifugation at 11,000 rpm followed by double filtration (0.45 μm and 0.2 or 0.03 μm) and *in situ* diffusion samplers with a 0.002 μm interstitial size. For the metals of concern in this guidelines document, concentrations of nickel and cadmium were equivalent using both methods and concentrations of copper and zinc were higher and more variable using centrifugation. They recommended the use of *in situ* dialysis for the study of trace constituents in sediments because of its inherent simplicity and the avoidance of artifacts that can occur with the handling of sediments in the laboratory.

More recently Bufflap and Allen (1995) reviewed four procedures for the collection of interstitial water for trace metals analysis. These included *ex situ* squeezing and centrifugation and *in situ* dialysis and suction filtration. This paper should be read by those selecting a interstitial water sampling method. They observed that each method has its own advantages and disadvantages, and that each user must make their own choice given the inherent errors of each method. Importantly, interstitial water must be extracted by centrifugation or squeezing in an inert atmosphere until acidified because oxidation will alter metal speciation. Artifacts may be caused by temperature changes in *ex situ* methods that may be overcome by maintaining temperatures to those *in situ*. Contamination of interstitial water by fine particles is important in all methods as differentiation of particulate and dissolved metal is a function of interstitial size. The use of 0.45 μm filtration, while an often accepted definition of dissolved, may result in laboratory to laboratory discrepancies. The use of suction filtration devices is limited to coarser sediments, and they do not offer depth resolution. The use of diffusion samplers is hampered by the time required for equilibrium (7-14 days) and the need for diver placement and retrieval in deep waters. Acidification of interstitial water obtained by diffusion or from suction filtration must occur immediately to limit oxidation. Bufflap and Allen (1995) conclude that *in situ* techniques have less potential for producing sampling artifacts than *ex situ* procedures. They concluded that of the *in situ* procedures, suction filtration has the best potential for producing artifact free interstitial water samples directly from the environment. Of the *ex situ* procedures they concluded that centrifugation under a nitrogen atmosphere followed immediately by filtration and acidification was the simplest technique likely to result in an unbiased estimate of metal concentrations in interstitial water. At present, EPA recommends filtration of the surface water through 0.4 to 0.45 μ polycarbonate filters to better define that fraction of aqueous metal associated with toxicity (Prothro, 1993). Thurman equates the organic carbon retained on a 0.45 micrometer glass-fiber filter to suspended organic carbon so that this filtration procedure under nitrogen

atmosphere followed immediately by acidification is acceptable for interstitial waters. However in studies comparing collection and processing methods for trace metals, sorption to filter membranes or filtering apparatus has been identified when losses occur (Ozretich and Schults, 1998). Ozretich and Schults, 1998 have recently presented a method combining longer centrifugation times with a unique single-step IW withdrawal procedure which has the potential for minimizing metal losses by eliminating the need for filtration.

In contrast to the above recommendations, EPA recommends the use of dialysis samplers to obtain samples of interstitial water for comparison of measured concentrations of dissolved metals with WQC. This is primarily because diffusion samplers obtain interstitial water with the proper *in situ* geochemistry thus limiting artifacts of *ex situ* sampling. Further, EPA has found that in shallow waters where contamination of sediments is most likely, placement of diffusion samplers is easily accomplished and extended equilibration times are not a problem. Secondly, EPA recommends the use of centrifugation under nitrogen and double 0.45 μ m filtration using polycarbonate filters for obtaining interstitial water from sediments in deeper aquatic systems. Probably most importantly, the extremely large database comparing interstitial metals concentrations with organism responses from spiked and field sediment experiments in the laboratory has demonstrated that, where the interstitial water toxic unit concept predicted that metals concentrations in interstitial water should not be toxic, toxicity was not observed when either dialysis samplers or centrifugation were used (Berry et al., 1996a; Hansen et al., 1996a). Therefore, it is likely that when either methodology is used to obtain interstitial water for comparison with WQC, if metals concentrations are below 1.0 IWGTU sediments should be acceptable for protection of benthic organisms.

5.3 ANALYTICAL MEASUREMENTS

An important aspect to deriving "global" ESG values is that the methods necessary to implement the approach must be reasonably standardized or have been demonstrated to produce results that are comparable to those of standard methodologies. From the standpoint of the proposed metal ESG, a significant amount of research has gone into defining methodologies to obtain interstitial water and sediments (see Section 5-2 above), to extract SEM and AVS from sediments, and to quantify AVS, SEM and the metals in interstitial water.

5.3.1 Acid Volatile Sulfide

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

5.3.2 Simultaneously Extracted Metal

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

5.3.3 Interstitial Water Metal

Interstitial water can be analyzed for the metals cadmium, copper, lead, nickel, silver and zinc by routine atomic spectrochemical techniques appropriate for environmental waters

(e.g. inductively coupled plasma atomic emission or graphite furnace atomic absorption spectrophotometry) (U.S. EPA, 1994b). Because of the need to determine metals at concentrations at or below the threshold of biological effects (i.e., WQC concentrations); additional consideration must be given to preclude contamination during collection, transport and analysis (U.S. EPA, 1995d,e,f,g). (See guidance on clean chemistry techniques in U.S. EPA, 1994c.) Generally, detection limits should be at ≤ 0.1 IWGTU, because the toxic unit contributions of each of the metals must be summed.

5.4 ADDITIONAL BINDING PHASES

Although AVS is an important binding phase for metals, there clearly are other physico-chemical factors that influence metal partitioning in sediments. In aerobic systems, or those with low productivity (i.e., where the absence of organic carbon limits sulfate reduction), AVS plays little or no role in determining interstitial water concentrations of metals. For example, Leonard et al. (1996a) found that a relatively large percentage of surficial sediments from open areas in Lake Michigan did not contain detectable AVS. In fact the great majority (42 of 46) of samples analyzed by Leonard et al. (1996a) contained less AVS than SEM, yet interstitial water metal concentrations of cadmium, copper, nickel, lead and zinc were consistently small or non-detectable. Even in sediments where concentrations of AVS are significant, other partitioning phases may provide additional binding capacity for SEM (e.g., Ankley et al., 1993; Calamono et al., 1990; Slotton and Reuter, 1995). In aerobic sediments both organic carbon and iron and manganese oxides control interstitial water concentrations of metals (Calamono et al., 1990; Jenne, 1968; Luoma and Bryan, 1981; Tessier et al., 1979). In anaerobic sediments, organic carbon appears to be an important additional binding phase controlling metal partitioning, in particular for cadmium, copper and lead (U.S. EPA, 1994a).

Even in substrates with very little metal binding capacity (e.g., chromatographic sand), surface adsorption associated with cation exchange capacity will control interstitial water metal concentrations to some degree (Hassan et al., 1996). Although an ideal ESG model for metals would incorporate all possible metal binding phases, current knowledge concerning partitioning/capacity of phases other than AVS is insufficient for practical application of a multiple phase model for deriving ESG in this sediment guidelines document.

5.5 PREDICTION OF THE RISKS OF METALS IN SEDIMENTS BASED ON EqP

It is important to repeat that conclusions about sediment toxicity based on SEM-AVS concentrations pertain only to cadmium, copper, lead, nickel, silver and zinc. (1) When the molar concentration of AVS exceeds that of SEM (negative SEM-AVS) sediment toxicity due to these metals is unlikely and any observed toxicity is most likely from some other cause. This is important because toxicity observed in sediments having an excess of AVS is often incorrectly assumed to disprove the EqP metals theory. The correct conclusion is that some factor other than metals caused the effect. This can be further substantiated if the toxic unit concept is applied to metal concentrations measured in interstitial water; the absence of significant concentrations of metals coupled with the negative SEM-AVS are powerful evidence that metals are an unlikely cause of the effect. (2) Sediments can only be toxic from the metals cadmium, copper, lead, nickel, silver and zinc when the molar concentrations of SEM exceed those of AVS (SEM-AVS differences are positive). Measurements of interstitial water concentrations of metals are invaluable in demonstrating that the sediments are toxic because of metals, and these measurements will provide insights into the specific metal(s) causing the observed toxicity. (3) It is not uncommon for toxicity to be absent in sediments having concentrations of SEM that exceed those of AVS (SEM-AVS is positive). This is because other metal binding phases in sediments often reduce the concentrations of bioavailable metal. (4) When sediments are toxic, and SEM-AVS is greater than 0.0, the toxicity may or may not be metals-related. Often sediments having SEM-AVS of up to 10 μ moles SEM/g are not toxic because the excess metals are associated with other binding phases. Measurements of interstitial water concentrations of metals are invaluable in demonstrating an absence or presence of bioavailable metal.

SECTION 6

GUIDELINES STATEMENT

The procedures described in this document indicate that, except possibly where a locally important species is very sensitive, benthic organisms should be acceptably protected in freshwater and saltwater sediments if any one or both of the following two conditions is satisfied: (a) If the sum of the molar concentrations of SEM cadmium, copper, lead, nickel, silver and zinc is less than or equal to the molar concentration of AVS or (b) the sum of the dissolved interstitial water concentration of cadmium, copper, lead, nickel, silver and zinc divided by their respective WQC is less than or equal to 1.0.

(a) AVS Guidelines:

$$\sum_i [SEM_i] \leq [AVS] \quad (4-5)$$

where

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

(b) Interstitial Water Guidelines

$$\sum_i \frac{[M_{i,d}]}{[FCV_{i,d}]} \leq 1 \quad (4-8)$$

where

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

If any one of these two conditions are violated, this does not mean that the sediment violates the ESG and is unacceptable. For example, if SEM exceeds AVS, or if the AVS in a sediment is non-detectable, then condition (a) will be violated. However, if there is sufficient sorption to particles,

or organic carbon or other binding phases so that condition (b) is satisfied, then the sediment meets the guideline and benthic organisms are acceptably protected from metals-induced sediment toxicity.

If both of these conditions are violated, or if the AVS Guideline is violated and the sediment is contaminated with silver then there is reason to believe that the sediment may be unacceptably contaminated by these metals. Further testing and evaluations would, therefore, be useful in order to assess actual toxicity and its causal relationship to the five metals. These may include acute and chronic tests with species that are sensitive to the metals suspected to be causing the toxicity. Also, *in situ* community assessments, sediment TIEs and seasonal characterizations of the SEM, AVS and interstitial water concentrations would be appropriate (Ankley et al., 1994).

The ESG approaches are intended to protect benthic organisms from direct toxicity associated with exposure to metal-contaminated sediments. They are not designed to protect aquatic systems from metal release associated, for example, with sediment suspension, or the transport of metals into the food web either from sediment ingestion or the ingestion of contaminated benthos. This latter issue, in particular, should be the focus of future research given existing uncertainty in the prediction of bioaccumulation of metals by benthos (Ankley, 1996).

It is repeated here that these guidelines apply only to the six metals discussed in this document, copper cadmium; lead, nickel, zinc and silver. Procedures for sampling and analytical methods for interstitial water and sediments are discussed in Section 5, Implementation.

SECTION 7

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APPENDIX A

APPENDIX A

Glossary of Abbreviations and Equations

ACR	Acute-Chronic Ratio
Ag	Silver
AVS	Acid Volatile Sulfide
ASTM	American Society for Testing and Materials
Cd	Cadmium
C_d	Freely dissolved interstitial water concentration of contaminant
C_p	Total interstitial water concentration of contaminant
C_s	Concentration of contaminant in sediment
C_{soc}	Concentration of contaminant in sediment on an organic carbon basis
CCC	Criteria Continuous Concentration
CFR	Code of Federal Regulations
CLOGP	Computer program for generating partition coefficients
CMC	Criteria Maximum Concentration
CV	Coefficient of Variation
CWA	Clean Water Act
DOC	Dissolved Organic Carbon
EDTA	Ethylene diamine tetraacetic acid
EMAP	Environmental Monitoring and Assessment Program
ESG	Equilibrium Partitioning Sediment Guidelines
ESG_{oc}	Organic carbon-normalized Equilibrium Partitioning Sediment Guidelines
f_{oc}	Fraction of organic carbon in sediment
EqP	Equilibrium partitioning
FAV	Final Acute Value
FCV	Final Chronic Value
$\{Fe^{2+}\}$	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)
FeS	Iron monosulfide
FPV	Final Plant Value
FRV	Final Residue Value
GC/EC	Gas Chromatography/Electron Capture
GC/MS	Gas Chromatography/Mass Spectrometry

GFAA	Graphite Furnace Atomic Absorption
IWGTU	Interstitial Water Guidelines Toxic Unit
IWTU	Interstitial Water Toxic Unit
K_{FeS}	solubility product for $FeS(s)$ $[(mol/L)^2]$
K_{MS}	solubility product for $MS(s)$ $[(mol/L)^2]$
K_{OC}	Organic carbon: water partition coefficient
K_{OW}	Octanol: water partition coefficient
K_p	Sediment: water partition coefficient
K_{SP}	Solubility product constant
LC50	Concentration estimated to be lethal to 50 percent of the test organisms within a specified time period.
L	Liter
$\{M^{2+}\}$	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)
m^3 or cu m	Cubic meter
μg	Microgram
μm	Micrometer
$\mu mole$	Micromole
mg	Milligram
mg/l	Milligram per liter
ml	Milliliter
mm	Millimeter
NA	Not Applicable, Not Available
ND	Not Determined, Not Detected
ng	Nanogram
Ni	Nickel
NOAA	National Oceanographic and Atmospheric Administration
NOEC	No Observed Effect Concentration
NST	National Status and Trends monitoring program
NTA	Nitrilotriacetic acid
Pb	Lead
pH	Negative logarithm of the effective hydrogen ion concentration
OEC	Observed Effect Concentration
POC	Particulate Organic Carbon

APPENDIX B

ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion
REMAP	Regional Environmental Monitoring and Assessment Program
$\{S^{2-}\}$	activity of S^{2-} (mol/L)
$[S^{2-}]$	concentration of S^{2-} (mol/L)
[SEM]	simultaneously extracted metal concentration ($\mu\text{mol/g}$)
$[\text{SEM}]_{\text{Cd}}$	simultaneously extracted Cd concentration ($\mu\text{mol/g}$)
$[\text{SEM}]_{\text{Cu}}$	simultaneously extracted Cu concentration ($\mu\text{mol/g}$)
$[\text{SEM}]_{\text{Ni}}$	simultaneously extracted Ni concentration ($\mu\text{mol/g}$)
$[\text{SEM}]_{\text{Pb}}$	simultaneously extracted Pb concentration ($\mu\text{mol/g}$)
$[\text{SEM}]_{\text{Zn}}$	simultaneously extracted Zn concentration ($\mu\text{mol/g}$)
SAB	U.S. EPA Science Advisory Board
SD	Standard Deviation
SLC	Screening Level Concentration
SEM	Simultaneously Extracted Metals
SOP	Standard Operating Procedure
STORET	EPA's computerized water quality data base
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TU	Toxic Unit
TVS	Total Volatile Solids
U.S. EPA	United States Environmental Protection Agency
WQC	Water Quality Criteria
Zn	Zinc
$\alpha_{\text{Fe}^{2+}}$	$\{\text{Fe}^{2+}\}/[\Sigma\text{Fe}(\text{aq})]$
$\alpha_{\text{M}^{2+}}$	$\{\text{M}^{2+}\}/[\Sigma\text{m}(\text{aq})]$
$\alpha_{\text{S}^{2-}}$	$\{S^{2-}\}/[\Sigma\text{S}(\text{aq})]$
$\beta_{\text{Fe}^{2+}}$	$(\alpha_{\text{Fe}^{2+}} - \gamma_{\text{Fe}^{2+}})^{-1}$
$\beta_{\text{M}^{2+}}$	$(\alpha_{\text{M}^{2+}} - \gamma_{\text{M}^{2+}})^{-1}$
$\gamma_{\text{Fe}^{2+}}$	activity coefficient of Fe^{2+}
$\gamma_{\text{M}^{2+}}$	activity coefficient of M^{2+}
$\gamma_{\text{S}^{2-}}$	activity coefficient of S^{2-}
$[\Sigma\text{Fe}(\text{aq})]$	concentration of total dissolved Fe(II) (mol/L)
$[\Sigma\text{M}(\text{aq})]$	concentration of total dissolved M(II) (mol/L)
$[\Sigma\text{S}(\text{aq})]$	concentration of total dissolved S(II) (mol/L)

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

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 B-3 and B-4 for M(II) and Fe(II) can be solved for $[MS(s)]$ and $[FeS(s)]$ and substituted in the mass balance Equation B-5 for S(II):

$$-\alpha_{S^{2-}}^{-1} [S^{2-}] + \alpha_{Fe^{2+}}^{-1} [Fe^{2+}] + \alpha_{M^{2+}}^{-1} [M^{2+}] = [M]_A \quad (B-9)$$

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

$$-\alpha_{S^{2-}}^{-1} [S^{2-}] + \frac{1}{\gamma_{S^{2-}} [S^{2-}]} \left(\frac{\alpha_{Fe^{2+}}^{-1} K_{FeS}}{\gamma_{Fe^{2+}}} + \frac{\alpha_{M^{2+}}^{-1} K_{MS}}{\gamma_{M^{2+}}} \right) = [M]_A \quad (B-10)$$

The positive root can be accurately approximated by:

$$\frac{1}{\gamma_{S^{2-}} [S^{2-}]} = \left(\frac{\alpha_{Fe^{2+}}^{-1} K_{FeS}}{\gamma_{Fe^{2+}}} + \frac{\alpha_{M^{2+}}^{-1} K_{MS}}{\gamma_{M^{2+}} \gamma_{S^{2-}}} \right)^{-1} [M]_A \quad (B-11)$$

which results from ignoring the leading term in Equation B-10. This is legitimate because the

APPENDIX B

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

$$\gamma_{M^{2+}}[M^{2+}]\gamma_{S^{2-}}[S^{2-}] = K_{MS} \quad (B-1)$$

$$\gamma_{Fe^{2+}}[Fe^{2+}]\gamma_{S^{2-}}[S^{2-}] = K_{FeS} \quad (B-2)$$

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

$$\alpha_{M^{2+}}^{-1}[M^{2+}] + [MS(s)] = [M]_A \quad (B-3)$$

$$\alpha_{Fe^{2+}}^{-1}[Fe^{2+}] + [FeS(s)] = [FeS(s)]_i \quad (B-4)$$

$$\alpha_{S^{2-}}^{-1}[S^{2-}] + [MS(s)] + [FeS(s)] = [FeS(s)]_i \quad (B-5)$$

where

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

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

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

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 B-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, $\beta_{Fe^{2+}} + \beta_{M^{2+}} K_{MS}/K_{FeS} > 1$. 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:

$$\{Me^{2+}\}/[M]_A < K_{MS}/K_{FeS} \quad (B-17)$$

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 (B-2) is invalid and the above equation no longer applies. Instead, the only solid-phase sulfide is metal sulfide and

$$[MS] = [FeS]_i \quad (B-18)$$

so that, from the metal mass balance equation

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

this completes the derivation of Equations 2-8 and 2-9.

term in parentheses in Equation B-10 is small relative to $[M]_A$ due to the presence of the sulfide solubility products. As a result, $[S^{2-}]$ is also small since it is in the denominator. Hence, the leading term in Equation B-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 B-1:

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

so that

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

where

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

and

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

Equation A-13 can be expressed as

APPENDIX C

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

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

a AVS LOD=0.05 um S/g

b Insufficient pore-water volume for metals analysis

c Cadmium LOD=0.01 ug/L (0.0002 IWCTU)

d Copper LOD=0.2 ug/L (0.0003 IWCTU)

e Lead LOD=0.1 ug/L (0.0001 IWCTU)

f Nickel LOD=0.5 ug/L (0.0005 IWCTU)

Source: Columns for Sample, TOC, SEM, AVS, SEM-AVS and IWCTU taken directly from Leonard et al., 1996a. Column for survival from personal communication with Leonard, 1998.

APPENDIX C

APPENDIX D
Concentrations of SEM, AVS, Toxicity and TOC for EMAP, NOAA NS & T and REMAP Databases

STUDY ^a	SEM umol/g	AVS umol/	SEM-AVS ugmol/g	SURVIVAL ^b %	SIGNIFICANCE ^c %	TOC
EMAP-VA	.289	1.400	-1.111	100.	0	.60
EMAP-VA	1.500	.742	.758	98.	0	2.68
EMAP-VA	.066	.029	.037	99.	0	.17
EMAP-VA	.134	.028	.106	103.	0	.14
EMAP-VA	.266	3.740	-3.474	99.	0	.49
EMAP-VA	.266	1.080	-.814	102.	0	.56
EMAP-VA	1.292	1.230	.062	107.	0	1.80
EMAP-VA	.347	.087	.260	102.	0	.30
EMAP-VA	.750	.948	-.198	99.	0	.95
EMAP-VA	.212	.283	-.071	108.	0	.37
EMAP-VA	.497	.490	.007	103.	0	1.00
EMAP-VA	.624	13.400	-12.776	113.	0	1.58
EMAP-VA	.032	.024	.008	101.	0	.11
EMAP-VA	.988	81.100	-80.112	101.	0	3.36
EMAP-VA	.604	3.340	-2.736	107.	0	1.38
EMAP-VA	.031	.331	-.300	98.	0	.09
EMAP-VA	1.597	72.400	-70.803	102.	0	4.19
EMAP-VA	1.065	8.480	-7.415	93.	0	3.17
EMAP-VA	.189	6.460	-6.271	103.	0	.32
EMAP-VA	.018	.034	-.016	99.	0	.15
EMAP-VA	.079	.976	-.897	97.	0	.14
EMAP-VA	.421	3.210	-2.789	111.	0	.49
EMAP-VA	.798	68.000	-67.202	104.	0	2.84
EMAP-VA	.903	3.150	-2.247	99.	0	2.85
EMAP-VA	1.202	67.700	-66.498	105.	0	2.28
EMAP-VA	.159	3.310	-3.151	104.	0	.51
EMAP-VA	.246	4.870	-4.624	106.	0	.71
EMAP-VA	.687	2.420	-1.733	93.	0	1.70
EMAP-VA	.699	.430	.269	91.	0	2.05
EMAP-VA	1.663	116.000	-114.337	100.	0	4.12
EMAP-VA	.083	1.300	-1.217	99.	0	.14
EMAP-VA	.740	.976	-.236	101.	0	2.30
EMAP-VA	.878	1.220	-.342	98.	0	2.84
EMAP-VA	.044	.025	.019	106.	0	.15
EMAP-VA	.910	3.430	-2.520	104.	0	3.00
EMAP-VA	.567	.621	-.054	104.	0	.76
EMAP-VA	.734	25.000	-24.266	107.	0	2.21
EMAP-VA	2.171	5.610	-3.439	102.	0	2.57
EMAP-VA	3.423	138.000	-134.577	100.	0	4.14
EMAP-VA	.197	.892	-.695	107.	0	.37
EMAP-VA	.162	3.590	-3.428	82.	0	.81
EMAP-VA	2.803	11.900	-9.097	101.	0	2.36
EMAP-VA	.472	12.500	-12.028	101.	0	2.77
EMAP-VA	2.079	26.600	-24.521	94.	0	3.18
EMAP-VA	.445	.056	.389	106.	0	.20
EMAP-VA	2.228	15.100	-12.872	103.	0	2.92
EMAP-VA	.847	17.300	-16.453	99.	0	2.38
EMAP-VA	1.402	52.700	-51.298	109.	0	2.70
EMAP-VA	1.425	22.300	-20.875	88.	0	3.14
EMAP-VA	.263	.079	.184	84.	0	.27
EMAP-VA	2.936	29.600	-26.664	100.	0	4.15
EMAP-VA	.394	.031	.363	87.	0	.18
EMAP-VA	3.074	10.400	-7.326	104.	0	2.47
EMAP-VA	2.555	.402	2.153	96.	0	2.18
EMAP-VA	.452	.480	-.028	100.	0	1.07
EMAP-VA	.173	.201	-.028	98.	0	.22
EMAP-VA	.578	.257	.321	101.	0	.65
EMAP-VA	.209	3.460	-3.251	96.	0	.36

APPENDIX D

STUDY ^a	SEM umol/g	AVS umol/	SEM-AVS ugmol/g	SURVIVAL ^b %	SIGNIFICANCE ^c %	TOC
NOAA- BO	1.753	17.697	-15.944	94.	0	1.41
NOAA- BO	2.447	10.958	-8.511	94.	0	4.45
NOAA- BO	1.839	68.306	-66.467	95.	0	2.54
NOAA- BO	1.296	56.838	-55.542	96.	0	3.05
NOAA- BO	1.697	9.089	-7.392	97.	0	2.68
NOAA- BO	1.390	43.801	-42.411	97.	0	3.27
NOAA- BO	2.310	51.857	-49.547	97.	0	3.35
NOAA- BO	.399	3.899	-3.500	99.	0	.80
NOAA- BO	2.481	19.604	-17.123	99.	0	3.31
NOAA- BO	1.736	148.969	-147.233	99.	0	2.94
NOAA- BO	.958	18.622	-17.664	99.	0	1.77
NOAA- BO	9.192	120.622	-111.430	100.	0	4.61
NOAA- BO	1.525	81.842	-80.317	102.	0	2.96
NOAA- BO	.678	5.679	-5.001	103.	0	1.45
NOAA- HR	5.037	69.320	-64.283	0.	1.	5.02
NOAA- HR	4.202	21.980	-17.778	41.	1.	3.47
NOAA- HR	1.174	27.540	-26.366	11.	1.	1.88
NOAA- HR	1.855	14.170	-12.315	18.	1.	4.44
NOAA- HR	3.092	51.770	-48.678	101.	0	3.86
NOAA- HR	2.997	79.710	-76.713	112.	0	3.09
NOAA- HR	2.581	61.050	-58.469	119.	0	2.86
NOAA- HR	2.869	28.080	-25.211	81.	0	2.50
NOAA- HR	5.442	25.900	-20.458	95.	0	2.20
NOAA- HR	2.618	1.080	1.538	109.	0	2.67
NOAA- HR	5.061	12.240	-7.179	97.	0	2.98
NOAA- HR	2.376	4.390	-2.014	108.	0	2.49
NOAA- HR	6.998	63.450	-56.452	0.	1.	1.98
NOAA- HR	4.480	20.780	-16.300	20.	1.	2.98
NOAA- HR	4.662	23.720	-19.058	14.	1.	3.19
NOAA- HR	5.896	51.580	-45.684	2.	1.	4.78
NOAA- HR	3.103	59.780	-56.677	77.	1.	3.99
NOAA- HR	1.662	7.230	-5.568	19.	1.	2.61
NOAA- HR	3.512	25.840	-22.328	0.	1.	4.44
NOAA- HR	.273	.050	.223	91.	0	.07
NOAA- HR	.335	.036	.299	93.	0	.07
NOAA- HR	1.664	18.760	-17.096	69.	1.	.69
NOAA- HR	2.674	3.630	-.956	3.	1.	1.00
NOAA- HR	5.532	29.210	-23.678	96.	0	3.18
NOAA- HR	4.029	18.440	-14.411	51.	1.	2.20
NOAA- HR	4.614	20.530	-15.916	91.	0	1.94
NOAA- HR	3.379	30.120	-26.741	88.	0	2.80
NOAA- HR	4.240	19.320	-15.080	101.	0	3.15
NOAA- IIR	4.303	22.570	-18.267	102.	0	3.02
NOAA- HR	5.209	14.570	-9.361	101.	0	3.21
NOAA- HR	4.801	35.370	-30.569	70.	1.	2.98
NOAA- HR	4.697	54.710	-50.013	38.	1.	3.47
NOAA- IIR	2.600	56.730	-54.130	37.	1.	1.47
NOAA- HR	1.013	10.160	-9.147	29.	1.	.77
NOAA- HR	1.527	15.130	-13.603	68.	1.	.95
NOAA- HR	.505	.630	-.125	105.	0	.25
NOAA- HR	3.341	43.920	-40.579	86.	0	2.55
NOAA- HR	3.449	37.860	-34.411	76.	1.	3.63
NOAA- BA	.270	.950	-.680	96.	0	.26
REMAP-BA	.341	.156	.185	84.	0	.06
REMAP-BA	.888	12.971	-12.083	92.	0	4.05
REMAP-BA	.722	4.948	-4.226	85.	0	.40
REMAP-BA	.362	.936	-.574	98.	0	.26
REMAP-BA	2.138	3.295	-1.157	95.	0	.43
REMAP-BA	3.008	3.941	-.933	95.	0	.18
REMAP-BA	.151	.555	-.404	96.	0	.15

STUDY ^a	SEM umol/g	AVS umol/	SEM-AVS ugmol/g	SURVIVAL ^b %	SIGNIFICANCE ^c %	TOC
NOAA- LI	2.813	35.050	-32.237	86.	0	3.83
NOAA- LI	1.235	2.080	-.844	84.	0	1.58
NOAA- LI	2.198	14.690	-12.492	84.	0	2.80
NOAA- LI	3.624	21.800	-18.176	83.	0	2.48
NOAA- LI	3.594	27.410	-23.816	82.	0	2.59
NOAA- LI	1.342	37.970	-36.628	82.	0	1.85
NOAA- LI	2.462	46.450	-43.988	82.	0	3.18
NOAA- LI	.964	1.000	-.036	81.	0	1.60
NOAA- LI	.332	4.010	-3.678	81.	0	1.29
NOAA- LI	2.311	79.890	-77.579	81.	0	3.69
NOAA- LI	.623	6.610	-5.987	80.	0	.67
NOAA- LI	.896	16.370	-15.475	80.	0	1.11
NOAA- LI	.544	2.170	-1.626	79.	1.	.27
NOAA- LI	.641	2.060	-1.419	79.	1.	1.56
NOAA- LI	.355	1.390	-1.035	79.	1.	.64
NOAA- LI	.222	4.180	-3.958	77.	1.	.45
NOAA- LI	2.262	39.960	-37.698	77.	1.	2.67
NOAA- LI	1.307	.380	.927	76.	1.	1.56
NOAA- LI	1.963	51.820	-49.857	76.	1.	3.46
NOAA- LI	2.785	61.020	-58.235	76.	1.	3.81
NOAA- LI	4.333	16.080	-11.747	75.	1.	3.48
NOAA- LI	1.927	3.710	-1.783	75.	1.	1.60
NOAA- LI	.004	24.580	-24.576	74.	1.	2.87
NOAA- LI	3.831	9.250	-5.419	73.	1.	3.08
NOAA- LI	.808	.960	-.152	71.	1.	1.19
NOAA- LI	1.783	40.630	-38.847	70.	1.	2.50
NOAA- LI	2.622	61.840	-59.218	70.	1.	3.49
NOAA- LI	.597	1.090	-.493	69.	1.	.76
NOAA- LI	1.181	3.730	-2.549	68.	1.	.91
NOAA- LI	1.862	50.390	-48.528	67.	1.	2.81
NOAA- LI	2.726	62.760	-60.034	67.	1.	2.81
NOAA- LI	2.102	33.630	-31.528	64.	1.	3.42
NOAA- LI	2.471	7.220	-4.749	63.	1.	2.80
NOAA- LI	1.870	17.120	-15.250	61.	1.	3.29
NOAA- LI	1.607	17.810	-16.203	59.	1.	2.07
NOAA- LI	4.942	100.800	-95.858	54.	1.	3.15
NOAA- LI	2.705	83.010	-80.305	53.	1.	3.62
NOAA- LI	2.087	26.730	-24.643	47.	1.	3.45
NOAA- LI	1.514	30.880	-29.366	42.	1.	2.69
NOAA- LI	2.629	32.050	-29.421	39.	1.	2.68
NOAA- LI	3.194	35.390	-32.196	37.	1.	3.17
NOAA- LI	.872	25.810	-24.938	34.	1.	1.83
NOAA- LI	1.080	11.300	-10.220	16.	1.	1.91
NOAA- LI	.123	5.310	-5.187	10.	1.	.22
NOAA- BO	2.914	2.893	.021	8.	1.	3.05
NOAA- BO	2.218	2.369	-.151	15.	1.	2.89
NOAA- BO	2.609	43.959	-41.350	26.	1.	3.74
NOAA- BO	3.650	101.984	-98.334	29.	1.	1.83
NOAA- BO	1.634	5.237	-3.603	36.	1.	1.72
NOAA- BO	1.267	3.256	-1.989	52.	1.	1.53
NOAA- BO	2.892	80.584	-77.692	83.	0	6.98
NOAA- BO	2.511	2.241	.270	86.	0	2.12
NOAA- BO	.661	13.490	-12.829	87.	0	1.00
NOAA- BO	2.458	23.077	-20.619	87.	0	3.15
NNOAA- BO	1.872	48.062	-46.190	89.	0	3.25
NOAA- BO	.959	53.288	-52.329	90.	0	2.39
NOAA- BO	2.480	7.599	-5.119	90.	0	4.45
NOAA- BO	.784	22.486	-21.702	91.	0	1.88
NOAA- BO	.943	8.831	-7.888	91.	0	1.78
NOAA- BO	1.683	42.399	-40.716	92.	0	3.41

STUDY*	SEM umol/g	AVS umol/	SEM-AVS ugmol/g	SURVIVAL ^b %	SIGNIFICANCE ^c %	TOC
REMAP-LS	1.894	25.394	-23.500	93.	0	.98
REMAP-LS	3.149	64.643	-61.494	93.	0	.90
REMAP-LS	.632	1.310	-.678	87.	0	1.51
REMAP-LS	1.057	4.647	-3.590	90.	0	2.44
REMAP-LS	.638	.218	.420	92.	0	3.52
REMAP-LS	1.087	.312	.775	90.	0	7.36
REMAP-LS	3.711	17.184	-13.473	88.	0	3.99
REMAP-LS	2.990	59.256	-56.266	80.	0	5.24
REMAP-LS	8.894	60.816	-51.922	85.	0	3.63
REMAP-LS	1.277	23.266	-21.989	92.	0	3.18
REMAP-LS	3.925	42.727	-38.802	90.	0	3.85
REMAP-LS	5.632	114.770	-109.138	86.	0	4.29
REMAP-LS	6.809	135.354	-128.545	91.	0	4.36
REMAP-LS	7.645	150.012	-142.367	92.	0	6.04
REMAP-LS	4.012	43.663	-39.651	86.	0	3.73
REMAP-LS	3.905	26.229	-22.324	89.	0	3.93
REMAP-NB	.942	6.531	-5.589	84.	0	.67
REMAP-NB	3.515	7.134	-3.619	87.	0	.75
REMAP-NB	2.216	11.243	-9.027	86.	0	1.22
REMAP-NB	3.323	7.573	-4.250	85.	0	1.25
REMAP-NB	3.391	4.820	-1.429	83.	0	1.05
REMAP-NB	3.443	3.982	-.539	95.	0	.88
REMAP-NB	2.466	20.273	-17.807	82.	0	1.40
REMAP-NB	2.294	11.046	-8.752	84.	0	.95
REMAP-NB	5.768	5.028	.740	75.	1.	1.77
REMAP-NB	1.013	11.079	-10.066	90.	0	.76
REMAP-NB	2.479	25.687	-23.208	83.	0	.99
REMAP-NB	.554	2.634	-2.080	84.	0	.60
REMAP-NB	5.222	22.617	-17.395	83.	0	1.48
REMAP-NB	5.116	7.352	-2.236	9.	1.	1.45
REMAP-NB	14.791	109.780	-94.989	8.	1.	9.15
REMAP-NB	4.917	.530	4.387	89.	0	3.10
REMAP-NB	.398	.218	.180	94.	0	2.42
REMAP-NB	4.855	9.606	-4.751	83.	0	2.62
REMAP-NB	3.290	10.105	-6.815	60.	1.	5.70
REMAP-NB	5.822	51.460	-45.638	41.	1.	2.22
REMAP-NB	9.167	93.563	-84.396	25.	1.	6.48
REMAP-NB	6.214	42.415	-36.201	68.	1.	3.24
REMAP-NB	.794	2.651	-1.857	93.	0	2.36
REMAP-NB	4.985	43.663	-38.678	53.	1.	3.90
REMAP-NB	5.280	1.934	3.346	83.	0	6.10
REMAP-NB	2.268	6.300	-4.032	16.	1.	1.99
REMAP-NB	6.678	17.559	-10.881	77.	1.	15.20
REMAP-NB	2.833	45.222	-42.389	54.	1.	2.02
REMAP-RB	.333	22.315	-21.982	93.	0	1.23
REMAP-RB	.756	1.216	-.460	92.	0	.33
REMAP-RB	.582	.821	-.239	94.	0	.30
REMAP-RB	1.012	.567	.445	94.	0	.30
REMAP-RB	1.596	.447	1.149	95.	0	.17
REMAP-RB	.326	.156	.170	93.	0	.08
REMAP-RB	2.709	3.120	-.411	70.	1.	.42
REMAP-RB	5.485	14.666	-9.181	92.	0	2.29
REMAP-RB	3.596	19.503	-15.907	62.	1.	.88
REMAP-RB	5.329	4.321	1.008	91.	0	.97
REMAP-RB	.337	2.901	-2.564	97.	0	.53
REMAP-RB	.986	.156	.830	96.	0	.12
REMAP-RB	.856	.156	.700	96.	0	.51
REMAP-RB	5.364	39.700	-34.336	91.	0	1.17
REMAP-RB	1.706	23.515	-21.809	93.	0	3.21
REMAP-RB	.371	4.210	-3.839	91.	0	3.54

STUDY*	SEM umol/g	AVS umol/	SEM-AVS ugmol/g	SURVIVAL ^b %	SIGNIFICANCE ^c %	TOC
REMAP-BA	.115	.156	-.041	99.	0	.08
REMAP-BA	.543	.156	.387	94.	0	.07
REMAP-BA	.103	.156	-.053	85.	0	.05
REMAP-BA	.167	.932	-.765	97.	0	.16
REMAP-BA	.073	.156	-.083	99.	0	.05
REMAP-BA	.294	.156	.138	91.	0	.34
REMAP-BA	.120	.156	-.036	84.	0	.83
REMAP-BA	.109	.156	-.047	92.	0	.92
REMAP-BA	.185	.156	.029	90.	0	4.48
REMAP-BA	.120	.156	-.036	88.	0	.83
REMAP-BA	.347	.156	.191	89.	0	1.26
REMAP-BA	.120	.156	-.036	81.	0	.62
REMAP-BA	2.275	16.592	-14.317	69.	1.	1.81
REMAP-BA	.344	.012	.332	91.	0	3.85
REMAP-BA	.258	.343	-.085	94.	0	.77
REMAP-BA	.119	.156	-.037	84.	0	2.23
REMAP-BA	.258	.156	.102	91.	0	.88
REMAP-BA	.494	.156	.338	86.	0	2.10
REMAP-BA	.109	.156	-.047	89.	0	4.07
REMAP-BA	.266	.156	.110	86.	0	1.06
REMAP-JB	.327	.393	-.066	93.	0	.29
REMAP-JB	.230	6.400	-6.170	83.	0	.19
REMAP-JB	2.026	47.793	-45.767	51.	1.	.77
REMAP-JB	14.550	389.857	-375.307	0.	1.	1.52
REMAP-JB	3.332	243.322	-239.990	37.	1.	.83
REMAP-JB	3.763	201.687	-197.924	79.	1.	.97
REMAP-JB	.357	10.923	-10.566	95.	0	.26
REMAP-JB	.524	3.974	-3.450	98.	0	.35
REMAP-JB	.244	4.502	-4.258	84.	0	.27
REMAP-JB	1.247	48.130	-46.883	91.	0	.54
REMAP-JB	2.478	47.376	-44.898	36.	1.	1.12
REMAP-JB	1.744	.156	1.588	69.	1.	1.14
REMAP-JB	.131	1.184	-1.053	94.	0	.21
REMAP-JB	.846	.927	-.081	73.	1.	1.58
REMAP-JB	4.399	116.954	-112.555	93.	0	6.55
REMAP-JB	3.884	237.650	-233.766	89.	0	8.45
REMAP-JB	.673	21.769	-21.096	77.	1.	4.11
REMAP-JB	3.150	43.975	-40.825	91.	0	5.47
REMAP-JB	.270	4.491	-4.221	91.	0	.74
REMAP-JB	.162	.873	-.711	98.	0	1.40
REMAP-JB	2.880	153.755	-150.875	92.	0	7.70
REMAP-JB	.323	1.684	-1.361	93.	0	.20
REMAP-JB	.413	3.056	-2.643	94.	0	1.20
REMAP-JB	.377	3.056	-2.679	92.	0	1.30
REMAP-JB	.099	.686	-.587	93.	0	.75
REMAP-JB	1.100	58.945	-57.845	96.	0	3.86
REMAP-JB	.209	1.466	-1.257	93.	0	.58
REMAP-JB	.213	.780	-.567	95.	0	.69
REMAP-LS	.954	1.542	-.588	83.	0	.26
REMAP-LS	2.759	6.498	-3.739	96.	0	.45
REMAP-LS	.711	10.240	-9.529	97.	0	.56
REMAP-LS	1.915	12.596	-10.681	97.	0	.21
REMAP-LS	2.186	17.605	-15.419	95.	0	.27
REMAP-LS	2.480	23.523	-21.043	99.	0	.32
REMAP-LS	.606	2.501	-1.895	98.	0	.25
REMAP-LS	3.289	91.773	-88.484	95.	0	.77
REMAP-LS	3.241	56.100	-52.859	97.	0	1.14
REMAP-LS	.616	1.070	-.454	95.	0	.15
REMAP-LS	1.506	26.201	-24.695	96.	0	.95
REMAP-LS	2.485	28.248	-25.763	96.	0	.25

STUDY ^a	SEM umol/g	AVS umol/	SEM-AVS ugmol/g	SURVIVAL ^b %	SIGNIFICANCE ^c %	TOC
REMAP-RB	.193	.156	.037	92.	0	2.52
REMAP-RB	.869	19.617	-18.748	85.	0	2.39
REMAP-RB	1.288	.593	.695	92.	0	2.44
REMAP-RB	1.650	.624	1.026	91.	0	2.68
REMAP-RB	2.422	.156	2.266	98.	0	2.60
REMAP-RB	.512	.156	.356	93.	0	.42
REMAP-RB	4.198	4.086	.112	90.	0	2.63
REMAP-RB	5.081	36.490	-31.409	89.	0	2.08
REMAP-RB	6.095	5.957	.138	4.	1.	3.03
REMAP-RB	8.471	8.078	.393	91.	0	5.30
REMAP-RB	3.370	17.247	-13.877	94.	0	3.91
REMAP-RB	1.198	.156	1.042	94.	0	1.03
REMAP-UH	2.127	12.446	-10.319	83.	0	3.43
REMAP-UH	1.360	1.790	-.430	99.	0	1.26
REMAP-UH	1.197	3.373	-2.176	92.	0	5.85
REMAP-UH	1.975	17.136	-15.161	45.	1.	2.33
REMAP-UH	2.829	25.189	-22.360	84.	0	.91
REMAP-UH	2.830	56.401	-53.571	96.	0	1.21
REMAP-UH	1.385	44.588	-43.203	88.	0	1.03
REMAP-UH	1.519	11.549	-10.030	82.	0	1.06
REMAP-UH	3.186	86.235	-83.049	93.	0	1.39
REMAP-UH	2.086	11.713	-9.627	82.	0	.79
REMAP-UH	1.799	12.631	-10.832	37.	1.	1.06
REMAP-UH	.930	10.093	-9.163	89.	0	.43
REMAP-UH	.459	.156	.303	98.	0	.13
REMAP-UH	.889	2.623	-1.734	95.	0	.21
REMAP-UH	.833	2.464	-1.631	86.	0	4.96
REMAP-UH	1.317	15.563	-14.246	88.	0	2.56
REMAP-UH	2.480	32.123	-29.643	87.	0	3.06
REMAP-UH	.626	9.949	-9.323	97.	0	2.58
REMAP-UH	1.500	5.427	-3.927	89.	0	2.71
REMAP-UH	.723	1.341	-.618	89.	0	3.89
REMAP-UH	4.158	13.504	-9.346	96.	0	4.78
REMAP-UH	2.241	27.788	-25.547	70.	1.	2.66
REMAP-UH	2.907	29.285	-26.378	95.	0	5.15
REMAP-UH	.852	1.591	-.739	93.	0	2.03
REMAP-UH	2.294	53.955	-51.661	15.	1.	4.37
REMAP-UH	2.995	33.995	-31.000	88.	0	3.55
REMAP-UH	2.981	44.910	-41.929	94.	0	2.97
REMAP-UH	.677	10.323	-9.646	91.	0	3.32

- a) Sources: EMAP-VA is U.S. EPA, 1996
 NOAA-LI is Wolfe et al., 1994
 NOAA-BO is Long et al., 1996
 NOAA-HR is Long et al., 1995
 REMAP is Adams et al., 1996
- b) Conclusion of significance varies for three databases.
 EMAP significance based on percent survival of control
 NOAA significance based on percent survival less than 80%
 REMAP significance based on percent survival less than 80%
- c) Significance: 0 - No significant toxicity
 1 - Significant toxicity