



# **AN SAB REPORT: REVIEW OF THE AGENCY'S APPROACH FOR DEVELOPING SEDIMENT CRITERIA FOR FIVE METALS**

**PREPARED BY THE SEDIMENT  
QUALITY CRITERIA  
SUBCOMMITTEE OF THE  
ECOLOGICAL PROCESSES AND  
EFFECTS COMMITTEE**

September 29, 1995

EPA-SAB-EPEC-95-020

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Administrator  
U.S. Environmental Protection Agency  
401 M Street, SW  
Washington, DC 20460

RE: Science Advisory Board (SAB) Review of the Agency's Approach for Developing Sediment Criteria for Five Metals (cadmium, copper, lead, nickel, and zinc)

Dear Ms. Browner:

Contaminated sediments are of major concern to the Agency, because in some instances, such as parts of the Great Lakes or New Bedford Harbor, fish accumulate chemicals from the sediments and, in turn, they may be eaten by humans. A fundamental problem in evaluating the toxic effects of chemicals in sediments is deriving a meaningful estimate of the amount of the chemical in sediment that is available to cause toxic effects (often referred to as the biologically available portion). In the past, the Agency has applied the theory of Equilibrium Partitioning to predict biological availability of organic chemicals. In this review, the SAB is evaluating the Agency's approach for assessing the toxic effects of metals in sediments. As you are aware, the assessment of these toxic effects is a key consideration in the management of contaminated sediments in regulations affecting wetlands, surface water discharges, drinking water supplies, and solid wastes.

The Sediment Quality Criteria Subcommittee of the Ecological Processes and Effects Committee (EPEC) of the Science Advisory Board met in Washington, D.C. on January 4-6, 1995 to review research and data developed to support the use of the Equilibrium Partitioning (EqP) approach to predict availability of five metals in sediments. In this Agency approach, the five metals are separated from sediments by the "simultaneously extracted metal" procedure (SEM). The amount of the five metals (cadmium, copper, lead, nickel, and zinc) that is presumably biologically available to organisms that live and feed in the sediments is the difference between the SEM and the Acid Volatile Sulfide (AVS), a binding factor for metals in sediment. The attached report discusses the findings and recommendations of the Subcommittee.

The Office of Water asked the SAB to evaluate the adequacy of the proposed methodology for establishing sediment quality criteria for the five metals. In particular, OW asked the SAB to:

- a) Consider the adequacy of an existing method (bulk chemical analysis) and each of four new methods proposed by the agency to establish a plausible cause and effect relationship between metals concentrations and organism responses.
- b) Determine whether data from lab, field, and colonization experiments demonstrate a plausible cause and effect link between the simultaneously extracted metal to acid volatile sulfide ratio (SEM/AVS) and/or interstitial water metals concentration (the concentration of metals in water between the sediment particles) and organism response.
- c) Judge whether the four approaches to derive sediment quality criteria for the five metals are sufficiently sound to proceed with criteria development.
- d) Identify any further documentation and research that is needed to develop sediment criteria.

Based on its review and knowledge of the literature, the Subcommittee feels that the SEM/AVS is the best technology developed to date for assessing the significance of the five metals in sediments. The proposed methodology will help to identify sediments that are likely to cause adverse effects and other sediments that are unlikely to cause such effects due to metals. The SEM/AVS approach may significantly reduce the variability currently associated with predictions based on the analysis of bulk sediment samples. Moreover, in its effort to produce sediment quality criteria that are supported by a strong theoretical foundation, the Agency has engaged in thoughtfully targeted research and has provided much useful information with potential wide applicability outside the Agency.

The proposed SEM/AVS methodology is based on sound theory and has been verified by considerable experimental evidence. The Agency has provided strong experimental evidence to support a plausible cause and effect link between SEM/AVS and acute toxicity.

We wish to point out, however, significant limitations to its application currently exist:

- a) Considerable uncertainty remains, however, regarding the levels of SEM/AVS that cause no adverse chronic effects.
- b) Substantial effort is needed to improve the predictive model for bioaccumulation.

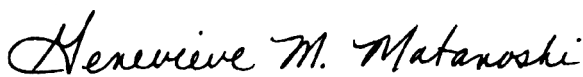
- c) In addition, before the techniques are ready to use as criteria, information is needed to guide the collection of biologically representative samples and samples that represent the spatial variability of AVS in a variety of environmental situations.

Once standardized protocols for determining criteria are developed, the Subcommittee recommends that the Agency produce a consolidated user's manual for use by the EPA and State regulators; industrial, municipal, and federal parties responsible for managing sediments; and by concerned scientists and citizens. The guidance manual should provide estimates of the cost of this analysis and describe the appropriate use of the criteria (various other screening levels) in a variety of environments as well as in a variety of regulatory contexts. In this regard, we recommend that the proposed SEM/AVS approach be used as part of a tiered assessment system (Please refer to Figure 1 on page 6 in this report as an example). We also suggest the guidance discuss the strengths and weaknesses of each of the methods, techniques for collecting representative samples, quality assurance, and quality control procedures (including estimates of interlaboratory variability).


A guidance manual is needed to assure the best use of these and other methods for assessing sediment quality. Such a manual should describe the context in which peer reviewed methods could be used (including any tiered approach). Guidance should also discuss the strengths and weaknesses of the methods, quality assurance and quality control procedures for sediment sampling and analyses. The manual should also receive technical review.

Again, the Subcommittee commends the achievements of the research team supported by the Office of Water. While there are still important research questions to be answered, the studies which have been completed are of exceptionally high quality and the foundation is very good. We look forward to reviewing future results from this research program, its implementation guidance, and to receiving the Agency responses to our recommendations and comments.

Sincerely,



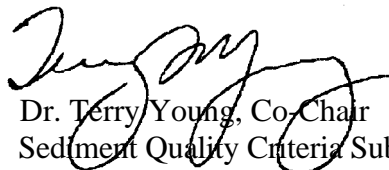
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## **NOTICE**

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## ABSTRACT

This report represents the conclusions and recommendations of the U.S. Environmental Protection Agency's Science Advisory Board regarding the Agency's proposed use of the simultaneously extracted metal to acid volatile sulfide ratio (SEM/AVS) to develop sediment criteria for five metals (cadmium, copper, lead, nickel, and zinc). The review was held January 4-6, 1995 in Arlington, VA by the Sediment Quality Criteria Subcommittee of the Ecological Processes and Effects Committee of the SAB.

The Subcommittee commends the Agency for its high-quality research and for developing a valuable new tool for assessing sediment quality. Use of SEM/AVS to predict the absence of acute toxicity due to the presence of the five metals in sediments is supported by experimental evidence and scientific theory. The Subcommittee cautions, however, that significant limitations to the application of SEM/AVS currently exist. For example, considerable uncertainty remains regarding the levels of SEM/AVS that cause no adverse chronic effects. Similarly, a substantial effort is needed to improve the predictive model for bioaccumulation. In addition, before the techniques are ready to apply as criteria, information is needed to guide the collection of biologically representative samples and samples that represent the spatial variability of AVS in a variety of environmental situations.

The Subcommittee further recommends that SEM/AVS be used as part of a tiered system of sediment quality assessments and that a guidance manual be developed to describe the context in which this and other assessment tools should be used. The manual should discuss the strengths and weaknesses of the methods as well as the quality assurance and quality control procedures for sediment sampling and analyses. The report also provides a list of research priorities, including the investigation of other naturally-occurring binding factors..

**KEY WORDS:** AVS, Sediment Quality Criteria, Metals, Uncertainty, Binding factors.

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## 1. EXECUTIVE SUMMARY

The Sediment Quality Criteria Subcommittee of the Ecological Processes and Effects Committee of the Science Advisory Board (SAB) met in Washington, DC on January 4-6, 1995 to review research and data developed to support the use of the Equilibrium Partitioning (EqP) approach to predict metal availability in sediments. In the Agency approach, metals are separated from sediments by the "simultaneously extracted metal" procedure (SEM). The amount of metal that is presumed biologically available is the difference, on a molar basis, between the SEM and the Acid Volatile Sulfide (AVS), a binding factor for metal, in the sediment. This method is currently restricted to evaluating five metals: cadmium, copper, lead, nickel, and zinc.

The Office of Water asked the SAB to evaluate the adequacy of the proposed methodology for establishing sediment quality criteria for the five metals. Specifically, OW asked the SAB to evaluate the capabilities of each of four related methods to predict adverse effects (acute, chronic and bioaccumulation) based on data from lab, field, and colonization experiments; to judge whether any of the four approaches to derive sediment quality criteria for the five metals were sufficiently sound to proceed with criteria development; and to identify any documentation and research needed to develop sediment criteria.

The Subcommittee commends the Agency for the outstanding work that has been accomplished to date. In its effort to produce sediment quality criteria that are supported by a strong theoretical foundation, the Agency has engaged in thoughtfully targeted research and has provided much useful information with wide applicability outside the Agency. The proposed methodologies will be an important component of the ultimate system for identifying sediments that are likely to cause adverse effects and other sediments that are unlikely to cause such effects due to metals.

The criteria are being developed for two uses: (a) assessing the safety of in-place sediments contaminated with particular metals; and (b) predicting how much metal can be added to a sediment without causing adverse environmental effects. Several empirical approaches for assessing toxicity of in-place metals are currently available. Although many of these approaches appear to be useful, they all lack a strong theoretical basis, which impairs their potential predictive ability. One of the strong points of the SEM/AVS approach is that it is based on a solid theoretical foundation, using equilibrium partitioning and metal activity to predict when metals are effectively sequestered and not bioavailable. As a result, the SEM/AVS approach promises ultimately to provide a more reliable and predictive tool than those currently available.

As currently conceived, the SEM/AVS approach would be used as a "no-effect" criterion to identify sediments not expected to cause adverse effects due to the presence of the five metals. In view of this limitation, the Subcommittee concurs with the Agency's intent to use the SEM/AVS method as part of a part of a tiered testing approach, and a general scheme is offered in the report.

The basis for deriving sediment criteria is strongest for “no effects levels” for acute toxicity in marine and fresh waters. Accordingly, the Subcommittee supports the conclusion of Agency scientists that the absence of acute toxicity could be predicted using SEM/AVS data. However, more research is needed -- of the quality presented by this research team -- to establish a chronic toxicity threshold, to determine why bioaccumulation occurs below the putative “no-effect level”, and to establish appropriate thresholds for bioaccumulation. Moreover, before the SEM/AVS approach is ready for use as a criterion, additional research is required to guide the collection of biologically representative samples and samples that represent the spatial variability of AVS in a variety of environmental situations. Recommendations regarding field verification, investigation of oxidation kinetics, development of a standardized protocol, and additional testing of sensitive life stages of benthic organisms, fish, and plankton are also provided in the report. Should the Agency wish to extend the SEM/AVS paradigm to other binding phases, the Subcommittee recommends that clay minerals, metal oxides, carbonates, and related phases be considered in addition to organic carbon.

The Subcommittee also recommends that a guidance manual be developed to assure the best use of these and other methods for assessing sediment quality. Such a manual should describe the context in which peer reviewed methods could be used (including any tiered approach). Guidance should also discuss the strengths and weaknesses of the methods, quality assurance and quality control procedures for sediment sampling and analyses. The manual should also receive technical review.

## 2. INTRODUCTION

Since 1988, the Office of Water has served as the technical manager and focal point for an in-depth research program to develop methods for evaluating the quality of sediments. During this time, the Science Advisory Board (SAB) has reviewed the Apparent Effects Threshold Method (SAB, 1988), the Equilibrium Partitioning method (SAB, 1990a), the Sediment Methods Compendium (SAB, 1990b), and the application of the Equilibrium Partitioning method to the derivation of criteria for non-ionic organic contaminants (SAB, 1992).

More recently, the Agency has attempted to extend the application of Equilibrium Partitioning theory to estimating effects of biologically available metals in sediments. In this review, the SAB evaluated two methodologies that have been investigated by the Agency: the Simultaneous Extraction of Metals/Acid Volatile Sulfide method (SEM/AVS), and the closely-related Interstitial Water method. The SEM/AVS method recognized that many metal sulfides are not biologically available and that the amount of naturally-occurring sulfide therefore governs the amount of metal that is effectively sequestered. In theory, therefore, if the AVS concentration exceeds the SEM concentration, no adverse effects should occur.

### 2.1 Statement of the Charge

The Office of Water asked the SAB to evaluate the adequacy of the proposed methodology for establishing sediment quality criteria for the five metals (cadmium, copper, lead, nickel, and zinc). After discussion with the Sediment Criteria Subcommittee, the following specific questions were developed to help focus the review:

- a) Can metals concentrations on a dry weight basis be used to establish a plausible cause and effect relationship between metals concentrations and organism responses?
- b) Are the data presented from lab, field, and colonization experiments sufficient to demonstrate a plausible cause and effect link between the "simultaneously extracted metal" to acid volatile sulfide ratio (SEM/AVS) and/or interstitial water metals concentration and organism response?
- c) Does the Subcommittee believe that the basis for each of the following four approaches to derive sediment quality criteria for the five metals (presented in Chapter 11, EPA 1994a,b) is sufficiently sound to proceed with criteria development?
  - 1) AVS Criteria: (No Effect Criteria)
  - 2) Interstitial Water Criteria: (No Effect Criteria)
  - 3) AVS and Organic Carbon Criteria: (Effect Criteria)

- 4) AVS and Minimum Partition Coefficient Criteria: (No Effect Criteria)
- d) For any that are not sufficient to proceed with criteria development, what type of research or analysis needs to be conducted to fully support criteria development, or what other direction needs to be pursued?
- e) Are there any major shortcomings associated with the approach?
- 1) Are there chemical or physical characteristics other than organic carbon that should be considered in order to derive sediment criteria that address both no effect and effect organism responses?
  - 2) Are there biological or ecological factors that should be considered in order to derive sediment criteria that address both no effect and effect organism responses?

## **2.2 Subcommittee Review Procedures**

The Sediment Criteria Subcommittee of the Ecological Processes and Effects Committee of the Science Advisory Board met on January 4-6, 1995 to review research and data developed by the Agency to support the use of the equilibrium partitioning approach to predict metal bioavailability in sediments, as applied to cadmium, copper, lead, nickel, and zinc. The Subcommittee was composed of members of the Ecological Processes and Effects Committee, Consultants, and Federal Experts all of whom had specialized knowledge and experience with evaluating metals in sediments. The Federal Experts served as scientists who offered comments based on their professional knowledge and judgement. Prior to the review, each Subcommittee member received copies of the two volume briefing document (EPA, 1994a,b). During the meeting, the Subcommittee received public comments, including comments from industry and from Corps of Engineers scientists who represented the position of the Corps.

The Subcommittee received briefings on the results of field and laboratory research conducted in freshwater and marine environments. Experiments included data on bioaccumulation, colonization and studies of the correlation between AVS and sediment organic carbon, the oxidation of metal sulfides and pore water sampling. Finally, the Agency staff discussed proposed sediment quality criteria for several metals.

During the meeting, the Subcommittee developed an outline of this report and discussed its preliminary findings with the Agency in public session. A draft document was compiled by the Co-Chairs and reviewed by the Subcommittee prior to its release to the Agency and the public. This final report reflects reactions of the Subcommittee to oral and written comments from the public and from a review of the draft document by the Ecological Processes and Effects Committee and the Executive Committee of the Science Advisory Board.

### 3. COMMENTS ON THE APPROACH

We compliment the EPA's study team on the extent and quality of the work they have conducted to develop the Equilibrium Partitioning (EqP) and SEM/AVS approaches. In an effort to produce sediment quality standards that are supported by a strong theoretical foundation, the Agency has engaged in original and thoughtfully targeted research, has produced numerous peer-reviewed publications, and has provided much useful information with potential wide applicability outside the Agency. **We commend the team for laying the groundwork to ensure that regulatory decisions are based on sound science.**

As a result of this research, the Agency has identified a potentially useful new methodology which complements the relatively few tools currently available for sediment assessment. The Subcommittee supports the Agency's continued efforts to develop this methodology. However, we also want to point out its limitations and indicate where additional research is needed to improve the technical basis of the approach.

#### 3.1 Proposed Uses of the SEM/AVS method

The criteria are being developed for two uses: (a) assessing the safety of in-place sediments contaminated with particular metals; and (b) predicting how much metal can be added to a sediment without causing adverse environmental effects. Three types of adverse effects are considered: acute effects, chronic effects, and bioaccumulation. Several empirical approaches for assessing toxicity of in-place metals are currently available. Although many of these approaches appear to be useful, they all lack a strong theoretical basis, and therefore have limited predictive ability. One of the strong points of the SEM/AVS approach is that it is based on a solid theoretical foundation, using equilibrium partitioning and metal activity to predict when metals are effectively sequestered and not bioavailable. As a result, the SEM/AVS approach promises ultimately to provide a more reliable predictive tool than those currently available, and one which may allow more informed environmental management decisions.

In its present state of development, the SEM/AVS approach, would provide a "no effect" criterion for acute and chronic toxicity (but not necessarily for bioaccumulation). In other words, the method would be used to identify sediments that are not expected to cause acute toxicity due to the presence of the five metals if physical and chemical conditions in the sediment do not change. The method cannot at present predict when metals would be toxic or bioavailable in sediment moreover, because other binding phases may also limit the bioavailability of metals in sediment. Research on additional binding phases might allow this methodology to be used to predict when sediments are likely to cause adverse effects.

#### 3.2 Sample Tiered Screening System

As the Agency notes in its briefing document (EPA, 1994a, page 1-5): "A likely application of EqP sediment criteria would be in a tiered approach." We strongly concur, both

because the currently proposed methodology provides a no-effect criterion (and only for five metals) and because other screening methods should be used in combination with EqP-derived chemical criteria to provide an overall approach that is both streamlined and defensible.

In Figure 1 we suggest a possible tiered testing approach for toxicity. This is a conceptual approach, and is intended only to provide the context for the comments that follow. However, this approach is consistent with that provided in the manual entitled "Evaluation of Dredged Materials for Proposed Ocean Disposal-Testing Manual" (commonly referred to as the "Green Book") (EPA and USACE, 1991) and the Inland Testing Manual for disposal of dredged material in waters of the U.S. (EPA and USACE, 1994).

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Figure 1 - A Possible Tiered Testing Approach for Toxicity

Tier I takes advantage of readily-available screening tools to identify "safe" sediments. Possible screening tools include: existing effects-based empirical approaches (e.g., Long et. al.,

1995); and to some extent, using data on the co-occurrence of organisms and contaminants (whose predictability improves if data are normalized to account for naturally-occurring metals, such as aluminum in bulk sediment samples); and/or comparisons with reference areas and comparisons with cores from pre-anthropogenic times.

Tier II includes chemical screens, such as those derived from EqP methodologies.

The biological effects testing for in-place sediments at Tier III may take different forms depending on the site and circumstances, but must involve appropriately sensitive organisms. Biological effects testing should not be restricted to laboratory toxicity testing with benthic organisms, because other biological effects measures (e.g., benthic community structure) or bioaccumulation may also be appropriate in some instances, and because sediment metals may have adverse effects on other aquatic organisms (e.g., fish). Note that the box labelled "Prioritize/Other Analyses" is purposefully not specified, nor are the arrows leading from that box qualified. This box represents research that should be done, to determine when biological effects testing or bioaccumulation testing are necessary, and the form of such testing.

## 4. SEM/AVS THEORETICAL FOUNDATION

### 4.1 SEM/AVS Theory

One of the most attractive attributes of the SEM/AVS method is its strong theoretical underpinning. The theory not only explains experimentally-determined toxicity in a satisfying way, but also may eventually provide the capability to predict adverse effects.

The equilibrium partitioning conceptual model is a basic element of the proposed SEM/AVS (and SEM-AVS and interstitial water) protocol. The model assumes that metal (i.e., Cd, Cu, Ni, Pb, and Zn) activity controls metal bioavailability, that metal activity in all reactive or biologically available phases is equilibrated, and that overall metal activity can be predicted from pore water metal concentrations. In its application to SEM/AVS protocols, the theory also assumes that metal activity is controlled by the most unreactive phase, which is assumed to be the metal sulfide (although the theory, in principle, allows for consideration of other phases).

It is often assumed that pore water is the only route of exposure considered by equilibrium partitioning method. In fact, the method assumes that the pore water and the sediment are in equilibrium, therefore it does not matter whether the chemical is taken up rapidly via the gut and slowly via the water or vice versa. In short, the theory implies that the toxicity of metals to organisms is the same regardless of whether metal exposure is from pore water or particles (i.e., due to ingestion).

### 4.2 Limitations

An alternative possibility discussed by several critics of equilibrium partitioning is that metal activity may differ in different exposure phases. If so, the logic continues, then complete exposure to metals can only be predicted from a sum of the contributions from the different routes. Ram and Gillett (1993) point out that the importance of the diet in total uptake of chlorinated organics varies significantly based on different additive models. The authors reviewed three possible models describing the uptake of chlorinated organics from sediments by benthic-dwelling organisms: a) sediment pore water via the body surface and in particular oxygen exchange surfaces; b) sediment ingestion; and c) the sum of pore water and sediment ingestion. They concluded that uptake from overlying water and ingested sediment is the most likely model and that "It is inadvisable to apply the equilibrium partitioning approach to sediment quality criteria...if the aim is to predict possible concentrations in benthic organisms." These and other experiments have demonstrated that for some chemicals ( i.e., those with high Log P) or for some organisms ( e.g., clams and oligochaetes) the diet may actually contribute more to body burden than uptake across respiratory membranes. None of the referenced experiments have shown that toxicity is increased as a result of considering the diet separate from the water exposure route. Mackay and co-workers have recently modelled total body burden, irrespective of the route of uptake, as a key parameter in predicting toxicity. In short, studies that use only pore water as a basis for estimating free metal activity may underestimate total exposures.



The issue of whether the equilibrium partitioning model or the additive model controls bioavailability remains scientifically controversial. The literature indicates that the diet is an important route of exposure but there is a good deal of controversy as to how this route of exposure should be integrated into the overall equilibrium model. In addition, the passage of sediment through the gut may in fact change equilibrium partitioning and metal binding to sulfides by changing the pH, redox potential, and forming metal-organo ligands (Woodward et al., 1993).

## 5. EXPERIMENTAL EVIDENCE: LABORATORY AND FIELD VALIDATION

### 5.1 Acute Studies

Ten-day lethality tests were conducted with both field-collected and laboratory-spiked sediments using a variety of freshwater and marine organisms. Table 6-3 of the briefing document (EPA, 1994a) summarizes the accuracy of prediction of the toxicity of sediments as a function of SEM/AVS and Interstitial Water Toxic Units (IWTUs). Predictions of sediment not likely to be toxic because of metals based on SEM/AVS < 1 or IWTUs < 0.5, were extremely accurate (96 to 98%). However, predictions of sediments likely to be toxic based on SEM/AVS > 1 or IWTUs > 0.5 were less accurate (57 to 79%).

The Subcommittee supports the conclusion of Agency scientists that the absence of acute toxicity could be predicted using SEM/AVS and IWTU data. However, the accuracy of these predictions may have been overestimated by using a critical value of 24% mortality as the basis for differentiating between "toxic" and "nontoxic" categories. This critical value was published by Mearns et al. (1986) following an interlaboratory comparison of the performance of a particular test with one species of amphipod. It was not based upon power analyses of the data from each of the species to which the value now has been applied by the Agency. The apparent concordance between predicted and actual toxicity may change if critical values are used that are specific to each of the tests. The Subcommittee recommends that the Agency reevaluate these predictions using a more conservative estimate of toxicity. For example, results from the EPA (1994a,b) round-robin testing with Hyalella azteca and Chironomus tentans indicate about 15% mortality may be a more appropriate value for these two species. Twenty percent mortality would be appropriate for Ampelisca abdita.<sup>1</sup>

Notwithstanding this recommended adjustment to the Agency's data presentation, we agree with the briefing document's conclusion (EPA, 1994a, p. 6-23) that "SEM/AVS ratios of  $\leq 1.0$  can accurately predict field sediments not likely to be acutely toxic" to benthic invertebrates as a result of Cd, Cu, Ni, Pb, and/or Zn contamination. **However, the Subcommittee would like to point out that the no-effects level for SEM/AVS < 1 has not yet been determined.**

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<sup>1</sup> Personal Communication with Dr. Glenn Thursby, EPA, Narragansett.

## 5.2 Chronic Tests<sup>2</sup>

The utility of SEM/AVS and IWTUs was also evaluated in a chronic laboratory test that exposed the estuarine amphipod Leptocheirus plumosus to cadmium-spiked sediments.<sup>3</sup> In this test, toxic effects on survival, growth, and reproduction were not observed at Cd SEM/AVS < 2 or Cd IWTUs < 1. These data also support the conclusion that sediment is not likely to be toxic due to contamination by the five metals at SEM/AVS < 1 or IWTUs < 0.5; however, insufficient data were available to determine if sediments would be consistently toxic at higher SEM/AVS or IWTUs. Indeed, no chronic responses were recorded because mortality occurred.

The Subcommittee believe that there is a need for additional chronic toxicity studies with exposure periods of at least 28 days. Longer exposure periods are needed to insure that the test organism tissues have come to steady state with sediment-metal concentrations. In the briefing document, several studies demonstrated the occurrence of bioaccumulation in circumstances where acute toxicity was not observed (see below). Hence, longer exposure to the same sediment might result in sublethal or lethal effects.

## 5.3 Bioaccumulation Tests

Chapter 8 of the briefing document (EPA, 1994a) describes results of bioaccumulation studies for both field-collected and laboratory-spiked sediments with a variety of freshwater and marine organisms. According to EqP theory, metals should not be bioavailable if pore-water concentrations of metals are low or if SEM/AVS ratios are < 1. However, several of the bioaccumulation studies raised the possibility that metals may be bioavailable even when SEM/AVS<1, because bioaccumulation was often observed in this range. For example, results summarized in Table 8-2 indicate accumulation of Ni and Cd at SEM/AVS ratios < 1 for all exposures. Similarly, Carlson et al. (1991), Pesch et al. (1995), Ingersoll et al. (1994), and Hare et al. (1994) report significant accumulation of metals at SEM/AVS ratios < 1. Note in particular, Pesch et al. (1995) demonstrated significant accumulation of metals at SEM/AVS ratios < 1 with polychaetes which were depurated;<sup>4</sup> Besser et al. [in review and in press] have demonstrated accumulation of metals at SEM/AVS ratios < 1 with midges that were depurated; and Hare et al. (1994) found depurated organisms accumulated metals at ratios < 1 (e.g., Procladius and Sergentia). Detectable bioaccumulation was also shown in the Canadian Lake Study reported at the briefing between SEM/AVS ratios of 0.1 and 1.0.

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<sup>2</sup> Results of long-term exposures on colonization are discussed in Section 5. 4 of this report.

<sup>3</sup> This information was presented by Dr. Rick Swartz at the meeting but was not included in the Agency briefing document.

<sup>4</sup> See Figures 8-2 and 8-3 in the briefing document.

Similarly, numerous samples at SEM/AVS > 1 or IWTUs > 0.5 were not toxic in laboratory exposures,<sup>5</sup> yet bioaccumulation was consistently elevated at SEM/AVS > 1.<sup>6</sup> The lack of toxicity at the higher concentrations was explained by the binding of metals by sources other than sulfide (i.e., organic carbon). These data suggest, however, that the lack of observed toxic effects may still be accompanied by exposure to metals through either pore water or whole sediment. A key factor that is missing is the ability to relate body residue levels with observed effects. The question arises when elevated tissue levels are observed at SEM/AVS either greater or less than 1.0, whether or not the body burden is approaching the point where effects might be seen.

These results are significant for two reasons. First, bioaccumulation is a sensitive indicator of exposures to bioavailable metal from all sources (pore water, ingestion, surface binding). The observation of dose-response relationships below the purported SEM/AVS=1 "switch" indicates that determining how and why bioaccumulation occurs at these concentrations is critical to defining the mechanistic underpinnings of the SEM/AVS theory. This mechanism should be defined for both invertebrates and sensitive vertebrates for all routes of exposure.

Second, although bioaccumulation does not necessarily indicate an adverse effect on the test organism, it does expose consumers of the organism to elevated doses of metals that may become bioavailable. For example, potentially bioavailable metals ingested by fish may include metals in the gut and tissues of invertebrates (Woodward et al., 1993; Farag et al., 1994). Research should investigate the significance of such exposures to the consumer and its predators.

Sublethal whole organism toxicity tests, longer term studies of population dynamics (for example with amphipods), or expansion of the colonization studies are examples of sensitive tests that might be employed to further understand the significance of the bioaccumulation response indicated to date. Such studies can be elaborate, expensive and/or time consuming. Therefore, they would be best considered after the completion of a series of detailed bioaccumulation studies to benefit from generalizations that may result from a less elaborate bioaccumulation approach. While the results of the acute and chronic toxicity studies tend to substantiate the SEM/AVS method, the occurrence of bioaccumulation at SEM/AVS<1 raises the possibility that effects may occur but have not been observed because of the limited sensitivity or duration of the toxicity tests.

The Subcommittee concurs with the Agency's conclusion that additional bioaccumulation studies should be conducted to determine more clearly the true thresholds of bioavailability and toxicity of metals in the AVS extracts and pore water. We recommend that such studies be designed with the following in mind:

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<sup>5</sup> See Figures 6-13 and 6-14 in the briefing document.

<sup>6</sup> See Figures 8-1, 8-2, 8-3, 8-4, 8-6, 8-7 and Table 8-2 in the briefing document.

- a) Defining appropriate sediment horizons for sampling pore-water metals and SEM/AVS to better define appropriate exposures of organisms to metals in aerobic zones of sediment. Laboratory tests of the bioaccumulation and toxicity of the five metals necessarily caused some oxidation of sulfides. However, the degree and effects of oxidation upon test results were not quantified, leading to some degree of uncertainty.
- b) Determining contributions of adsorbed or digested materials to the total body burden of metals in test organisms. The role that kinetics play in the uptake of metals across the gut walls of benthic invertebrates needs to be investigated. Equilibrium theory indicates that when sediment metal concentrations are at equilibrium with the interstitial water, the route of uptake is not of major importance. However, if the thermodynamic potential is altered in the gut of the organism such that uptake from sediment is favored over that from interstitial water, there is a potential for the equilibrium approach to underestimate the potential for bioaccumulation.
- c) Further evaluation of the potential effects of dietary metals on aquatic organisms.

#### **5.4 Field Verification**

The field verification experiments performed thus far consist of colonization experiments at two freshwater sites and a colonization experiment with marine sediments using natural unfiltered sea water in a laboratory environment. These experiments represent a good first effort to determine whether the SEM/AVS method accounts for the bioavailability of elevated concentrations of the five metals on a chronic basis in natural sediments. The evidence is consistent with laboratory toxicity studies which indicate that sulfide-metal binding is an important process and may be a dominant factor controlling the bioavailability of select metals in freshwater and marine sediments.

The Subcommittee believes that additional field verification would provide greater confidence in various aspects of the overall approach. The areas of concern include the following:

- a) The sensitivity and accuracy of the overall method needs further evaluation.
- b) There has been insufficient field testing of sensitive early life stages of benthic invertebrates and of fish with benthic life stages. Greater emphasis on chronic testing is needed.
- c) The applicability of the method to different sediment types in both saltwater and freshwater environments requires additional clarification.

- d) The proposed SEM/AVS method may not adequately explain the lack of chronic toxicity in highly contaminated sediments. The ability to explain and/or understand the lack of toxicity to organisms for sediments with very high concentrations of metals is key to establishing the credibility of the approach.

Further field verification of the SEM/AVS approach should make it possible to address many of the concerns raised above. Two approaches are recommended although we recognize that other options exist. The first approach we recommend is a suite of additional experiments. For example, the studies of bioaccumulation and toxicity in spiked sediments transplanted into inland ponds provided useful information under controlled conditions with the advantage of environmental realism attained in a field setting. It would be worthwhile for the Agency to conduct similar studies in saltwater to verify bioaccumulation and toxicity. Additional experiments might include site specific colonization experiments (chronic evaluation) at sites where the SEM/AVS ratio is greater than or equal to 1.0 and at sites where the SEM/AVS ratio may be less than 1.0, but the site is known to contain "high" levels of metals.

Second, additional field data sets can be used to evaluate the sensitivity and accuracy of the SEM/AVS method. Because the proposed SEM/AVS approach and several empirical approaches used to derive numerical guidelines differ considerably in methodology, it is important to compare their relative predictability, reliability, and accuracy in field verification studies. In addition, a large number of state, provincial and federal agencies have prepared or are preparing sediment quality guidelines for total concentrations of metal in bulk sediments. The differences in proposed no-effect levels obtained from the SEM/AVS and empirical approaches could be quantified for similar field data sets with a view towards explaining the differences, comparing the accuracy of the predictions, and establishing the conditions under which each can be reliably used.

Existing EMAP data sets also can be further evaluated. The Agency's recent efforts to evaluate SEM/AVS ratios and species abundance data using the EMAP data set discussed at the meeting provided insights that were not presented in the briefing document. The Agency's intent was to demonstrate adverse impacts at the population level, which is admirable. Comparisons of measures of benthic community structure with SEM/AVS concentrations would be powerful confirmation of the impacts of excess SEM. However, the data trends that one would expect on the basis of SEM/AVS normalization of the data were not consistently observed. We recommend further evaluation of the data, especially for those sites where the SEM/AVS ratio is greater than or equal to 1.0 and where toxicity tests indicate the sediments are toxic.<sup>7</sup> A sediment toxicity identification evaluation may be needed to confirm that the toxicity is due to metals. At sites where the SEM/AVS ratio may be less than 1.0, but no toxicity is observed, the site should be

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<sup>7</sup> The subcommittee cautions, however, that use of pre-existing data sets -- even those of excellent quality such as EMAP -- requires considerable attention to detail. As the Agency recognizes, its preliminary attempt to correlate population impacts with SEM/AVS using EMAP data collected from numerous different estuaries for this purpose was flawed. The EMAP-E data set is composed of one to several samples collected at randomly chosen stations within many different estuaries in the northeast and Gulf regions. The data were not collected along a single pollution gradient in which all other variables were constant. Although the data suggest a correspondence between the SEM/AVS ratios and species richness, this apparent relationship may well be a function of covariance with numerous natural factors such as salinity, depth, flow velocity, slope, grain size, and predatory pressure that are known to have major impacts upon species richness.

evaluated in light of species abundance measures, sensitive toxicity tests and bioaccumulation measurements. Additionally, EMAP data from other locations, especially in the Southeastern United States, and freshwater systems, should be evaluated in light of the benefit of SEM/AVS normalization of the data.

## 6. METHODOLOGICAL REFINEMENTS

The above discussion addresses the strengths and weaknesses of the research to date, and suggests additional work that may be undertaken to further validate the SEM/AVS method. In this section, we suggest additional work that the Agency should consider in order to refine the method and make it usable, and to address other issues related to criteria and standards designed to protect against metal toxicity.

### 6.1 Metal Sulfide Oxidation Kinetics

The long-term potential for sediment bound Cu, Cd, Ni, Pb, and Zn to exert toxicity to benthic and epibenthic species depends on more than metal association with sulfide (AVS) phases. Even if, for a given sediment at a given time, AVS represents the major binding phase, attention must be paid to the fate of these metals upon oxidation of their sulfides. Seasonal variations in oxidation conditions at the sediment-water interface is the rule, so that metal sequestered during one season may be released during another. Likewise environmental remediation of contaminated water bodies typically includes improvements in DO which implies that associated contaminated sediments would be expected to become more oxic, potentially releasing sulfide-bound metals. In addition, benthic infaunal deposit feeders typically create micro-oxidized environments as they migrate through sediments. This again may liberate metals from the sulfide phase.

Sediment oxidation has not been significantly addressed by the program, nor has the operational distinction between oxic and anoxic sediments been clearly defined. Some of the presentations clearly demonstrated that metals are apparently released from sulfide phases during long term experiments but the rates of release have not been investigated. Rates of oxidation of the metal sulfide phase would be expected to vary. Some metals may be systematically released (or become more available) relative to others during periodic (e.g., seasonal) oxidation events. Such information is necessary to evaluate the long-range biological significance of metal contaminated sediments.<sup>8</sup>

### 6.2 Large- and Small-Scale Spatial Variability

Eventual field application of the SEM/AVS technique will require a systematic resolution of questions about SEM and AVS profiles in natural sediments. A crucial question is how to collect samples. Studies to date show that, in general, AVS follows the depth profile expected from the principles of diagenetics. However, it is also expected that such profiles could vary with sediment type, water chemistry, physical and biological processes. They also vary seasonally and could vary on small spatial scales. A defensible strategy for maximizing geographic consistency in implementation of the SEM/AVS tool requires an understanding of such variability. Field studies are necessary to systematically demonstrate differences in SEM and AVS profiles, for example

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<sup>8</sup> EPA should identify sediment sampling procedures that minimize the release of AVS from samples during collection, packaging and shipment.



among sediments of different pore size, in different flow regimes, and in environments with different sulfate concentrations. The effects of re-suspension on profiles, as well as other processes that might change seasonally, could be studied by comparing different field sites. Comparisons of profiles between different types of rivers, in lakes, in estuaries and in coastal (intertidal and subtidal) environments will eventually be necessary.

The scale of variability is a critical question in developing a standardized approach for investigating biologically effective AVS. Currently recommended methods homogenize sediments from a consistent depth (2 cm). Data show that the gradient of AVS is steep within the 0-2 cm layer in the few sediments carefully studied. Thus criteria for determining the depth of sampling must be carefully detailed, especially if a site-specific method is recommended. A very difficult question that requires additional study is evaluation of the bioavailability of metals from oxidized microzones created by organisms burrowing in sediment. Specific studies might consider the difference between availability from the microzone and availability from a homogenized sediment around the microzone.

In addition to vertical profiles, horizontal variation in SEM and AVS should also be discussed. For example, Brumbaugh et al. (1994) reported that SEM/AVS ratios for individual cores within a 10 by 10 meter station varied by almost 100 fold.<sup>9</sup> However, although variability between cores was quite high, the authors also reported the average SEM or AVS in composite samples was similar to the average SEM or AVS in individual cores. Similar investigations should address the possibility of under- or over-estimating exposure in the field as a result of compositing sediment samples.

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<sup>9</sup> See also Besser et al. in press.

### 6.3 Applicability

The above-mentioned concerns regarding oxidation conditions and other factors that result in spatial and temporal variability are a subset of the broader issue of applicability: where and when will the SEM/AVS method be useful?

Some additional effort will be required to evaluate the range of sediment types to which the method is applicable. Field validation of the method in different sediment types (including more sandy sediments, recently disturbed sediments, and sediments recently deposited from a dredge) in a broader range of locations would help to define the appropriate conditions for applying (or not) the SEM/AVS method. We note that most of the field verification data used thus far were collected in the northeastern USA or in the Midwest; a range of sediment types should be used in the various follow-up studies to better represent the southeast, the Gulf coast, the Pacific coast, Hawaii, and Alaska. In this way, the Agency can also begin to assess the geographic extent of sediments that are contaminated with excess SEM and verify that these sediments represent toxicological problems.

Another issue relating to applicability of the method is its optimum use as one among a suite of tools for assessing mixtures of contaminants within sediments of various types. One of the difficulties in evaluating the data presented, particularly the field studies, is that multiple contaminants and sorptive phases may have been present. It is clear that metals do sorb to organic material (and other phases) in addition to AVS, although AVS binding is theoretically strong and therefore should be the dominant mechanism. The presence of other toxic compounds, i.e. organic contaminants such as pesticides and aromatic hydrocarbons, in some of the samples would create toxicity not predicted or accounted for by the SEM/AVS equilibrium partitioning measurements. Since it is often not known or not clear what contaminants are present, the conditions under which this methodology can be appropriately used or not used need to be carefully defined. **The Agency must remind those who would use this method that SEM/AVS is intended to determine when metals present on sediments are not toxic.**

### 6.4 Standardized Methodology

Standardized analytical methods and QA/QC techniques are needed for sampling and measuring SEM and AVS. In addition, if the Agency intends to propose that interstitial water metals concentrations be measured simultaneously, in order to increase the reliability of the SEM/AVS methodology, standard protocols must be developed for extraction and analysis of pore waters. Such methods should improve the exclusion of microparticulates and account for the effects of precipitation and dissolution of metals that may occur with changes in pH or redox. Although the briefing document recommends centrifugation under nitrogen or carefully-controlled use of a peeper, the Agency recognizes that current pore water extraction methods are controversial, that some or all may selectively exclude toxicants (including metals), and that rigorous testing will be required to develop a reliable method. Adding to this challenge, the preferred method must also be practical for widespread use (see, for example, the briefing

document's description (EPA, 1994a, p. 9-47) of the potential difficulties of using a glove box to extract pore water).

**Once standardized protocols are developed, and issues with regard to spatial variability, temporal variability, and applicability of the method to various sediment types have been examined, the Subcommittee recommends that the Agency develop a consolidated user's manual.**

## **6.5 Additional Methodological Refinements**

The Subcommittee concurs with the Agency's suggestion to investigate using SEM-AVS calculations (differences) as opposed to SEM/AVS calculations (ratios), because of the information that is lost in the latter conversion. Re-assessing the results of past experiments using differences appears useful.

We also note that organism behavior affects toxicity. This was clearly shown in the briefing document and presentations, and has been shown by other authors (e.g., Landrum et al 1994) as a factor which can result in EqP overestimating toxicity. The consequences of organism behavior need to be included in uncertainty analyses.

## 7. SEM/AVS: SUMMARY

The SEM/AVS method determines the amount of cadmium, copper, nickel, lead and zinc in the sediment that is potentially not bioavailable. It is therefore a threshold test; contamination lower than the threshold amount should not cause adverse effects and contamination higher than the threshold amount may cause adverse effects (unless the metal is not bioavailable for some other physical or chemical reason). In short, the logical use of SEM/AVS is as a "no-effect" criterion, as the Agency has proposed. The Subcommittee is not yet entirely satisfied, however, that the experimental evidence warrants the assumption that there are no effects below a ratio of 1.0.

The most convincing experimental evidence presented in support of the SEM/AVS method is the relationship between acute toxicity and SEM/AVS (or pore water metal activity). It appears that the method can be used to predict the lack of acute toxicity in sediments at SEM/AVS ratios  $<1$ , if spatially and biologically representative samples have been collected. Above ratios of 1, however, toxicity cannot be reliably predicted, because other phases in addition to AVS may control the bioavailability of metals. Additionally, it was noted that the accuracy of acute toxicity predictions in the SEM/AVS  $<1$  "quadrant" may have been overestimated by using the 24% mortality benchmark to classify samples as toxic.

The experiments that assessed the relationship between chronic toxicity or bioaccumulation and SEM/AVS produced results that are not as clear as the acute toxicity experiments. The colonization study, although elegant in conception and implementation, lacked exposures between ratios of 0.1 and 1.5. Preliminary bioaccumulation studies raise the possibility that the SEM/AVS ratio  $<1$  is not a "switch", and indicate that bioavailable metal may occur in circumstances not expected from the development of the SEM/AVS theory to date. Detectable bioaccumulation has been shown in a number of experiments, both above and below SEM/AVS=1. Additional work is needed to determine whether the SEM/AVS approach can be used to define conditions where sediment sorbed metals can be bioaccumulated by benthic organisms. These investigations also could be designed to provide additional insight into the contributions of adsorbed or digested material to total exposure, thereby strengthening understanding of the theoretical basis for the EqP and SEM/AVS approaches.

**The Subcommittee strongly recommends that additional research be performed to evaluate the potential for chronic effects and bioaccumulation to occur where SEM/AVS  $<1$  (or SEM-AVS  $<0$ ). The evaluation is needed to support the Agency's contention that the approach can be used to predict no-effect levels.** In view of this recommendation, the Agency may wish to investigate whether a no-effect criterion at some level less than 1 (or difference less than zero) would be a more defensible approach. The lower 90% or 95% confidence interval from an uncertainty analysis might be used for this purpose.

In addition to the above concerns, significant questions regarding oxidation kinetics, temporal and spatial variability, and other factors governing appropriate application of the

methodology remain to be answered . Despite the above, however, the Subcommittee concludes that the SEM/AVS methodology is a promising tool in sediment quality assessment and that targeted research should proceed to further develop the method. For example, the SEM/AVS method provides a basis for concluding that when SEM is less than AVS, observed toxicity may be due to materials other than metals. It also seems clear that in situations where the AVS concentrations are high, the metal concentrations low, and other contaminants are not present, that SEM/AVS provides a strong indication of no probable acute toxic effect.

## **8. SEDIMENT INTERSTITIAL WATER CRITERIA: THEORY, LABORATORY AND FIELD VERIFICATION**

The use of sediment interstitial water metal concentrations as a predictor of acute and chronic metal toxicity provides a useful approach to predict when sediment metal concentrations may be toxic to aquatic life. This approach allows for a direct comparison with toxicity values obtained from traditional water exposure toxicity tests and allows for the use of water quality criteria. Use of interstitial water toxicity estimates in combination with SEM/AVS estimates of free metal concentration appears to provide a potentially useful tool that will be more robust than either approach alone for predicting when sediments will not be toxic to aquatic organisms.

There are four major drawbacks to the interstitial water approach for performing sediment quality assessments or deriving criteria. The first drawback is that the interstitial metal-water concentration must be measured. Current approaches for measuring sediment interstitial water concentrations have not been standardized and a variety of approaches are being used. This is an area that needs additional research, as mentioned earlier (Bufflap and Allen, 1995). The second drawback is that sophisticated non-routine techniques are required in order to accurately measure low concentrations (a few ug/l) of metals in interstitial water. It is also difficult to account for the effects of DOC, hardness, and salinity on the pore water matrix, as pointed out in the briefing document. The third drawback is that multiple chemicals are present at any one time in sediment interstitial water and an additive model is used to sum the toxicity units. This approximation is correct most, but not all of the time. There are only limited chronic toxicity data to support the additive model. The fourth drawback is that there are some non-equilibrium circumstances where interstitial water does not predict all routes of uptake.

Additional field verification of the interstitial approach is needed. Such measurements could be built into a larger sediment research program aimed at evaluating the EMAP sediment data or field colonization studies. An important part of this field verification is collecting matching data for SEM/AVS, interstitial water-metals concentrations, and chronic toxicity measurements with planktonic early life stages of benthic invertebrates and fish. An additional important aspect of field verification is the need for bioaccumulation measurements when the interstitial water toxic units are greater than or equal to 1.0 and SEM/AVS is less than or equal to 1.0.

## 9. OTHER BINDING PHASES

To date, the Agency's program has emphasized AVS as the major binding phase which controls the bioavailability of metals (Cu, Ni, Cd, Pb, Zn) in sediments. To extend the paradigm, the Agency is tentatively considering investigation of binding by organic carbon as its next research priority. While binding by organic carbon is undoubtedly significant -- indeed, Fu et al. (1992) make the case that "humic substances are the major absorbent for cadmium, and perhaps other metals, in oxic sediments" -- other phases in sediments also play a significant role in binding metals, especially under aerobic conditions.<sup>10</sup> The presence of other metal binding phases is mentioned in the Briefing Document<sup>11</sup> and referenced in relevant studies by the principal investigators (e.g., Ankley et al., 1993). In particular, metal oxides (e.g., Fe, Mn, Al) are important in binding metals (Jenne, 1968); cadmium and other metals are bound by Fe and Mn oxyhydroxides in oxic sediments; interactions with hydrous metal oxides and carbonates are also important in some geographic regions.

The suite of sediment assessment tools envisioned by the Agency will ultimately include methods that address lack of bioavailability due to these other binding phases. **The Subcommittee recommends that the role of the array of additional binding phases such as clay minerals, oxides and carbonates be investigated before settling on organic carbon as the next research priority.**<sup>12</sup> Initial, theoretical sensitivity analyses comparing the potential control by other phases could be carried out assuming the necessary chemical thermodynamic data are available.

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<sup>10</sup> In this regard, we note that the correlation between SEM and organic carbon might be equally significant if clay minerals (using Al as a proxy) were considered the additional binding phase.

<sup>11</sup> See line 8, page 5-9; line 1, page 5-16; lines 20-22, page 6-10 for examples.

<sup>12</sup> Such studies could be conducted in the context of establishing minimum partitioning coefficient by using end member sediment (i.e. sediments dominated by, or composed solely of, one solid phase) rather than by using sand (quartz is not an important binding phase).

## 10. USE OF DRY WEIGHT METALS MEASUREMENTS IN CRITERIA

**The Subcommittee believes that in-place bed sediments should be assessed with multiple tools, including the SEM/AVS criterion for the five metals where appropriate.**

There is evidence that the envisioned SEM/AVS approach correctly identifies non-toxic samples in many cases. However, since this approach is applicable thus far to only five metals, EPA should recognize that other tools are useful in assessing and estimating the potential hazard of already-contaminated sediments.

Background concentrations of total metals normalized to dry weight can be used with SEM/AVS as a complementary screening tool. Currently, normalized background values are available for the same five metals addressed by the SEM/AVS criterion, plus a number of other metals. Background concentrations have been determined from relatively clean areas, from pre-anthropogenic sedimentary strata as metal/aluminum ratios, and as effects-based guidelines calculated from empirical observations of toxicity. Often they are conservative and frequently they correctly predict non-toxicity in sediments. (For example, a similar percentage of samples is correctly classified as toxic or not toxic in Figure 6-7 and Figure 6-8 of the briefing document if 10-100  $\mu\text{mol/g}$  dry weight or if an SEM/AVS ratio of 1, respectively, are used to predict toxicity.) Since background concentrations often are lower than SEM concentrations in AVS, they can be used as an initial screen in assessments of bed sediments. SEM/AVS analyses would not be warranted if trace metals failed to equal or exceed background levels.



## 11. RESEARCH NEEDS AND PRIORITIES

In the previous sections of this review, the Subcommittee has provided numerous suggestions regarding additional research that would provide a stronger foundation for sediment quality criteria based on the SEM/AVS method. These recommendations are summarized in priority order in Table 1 below. **We strongly recommend that the Agency begin to pursue research required to complete the rest of a tiered sediment assessment system.**

For example, the currently-proposed use of the SEM/AVS method is to predict sediments that are not likely to be toxic. Methods are also required that can be used to predict toxic sediments. The SEM/AVS method correctly predicted toxicity in acute tests in only 7 of 26 (27%) samples in which SEM>AVS in saltwater studies. Many samples expected to be toxic when SEM>AVS were not toxic, possibly due to the binding of metals by other phases. Moreover, SEM/AVS theory predicts that toxicity will occur only when excess SEM occurs and metals are found in the pore water. It would be useful if EPA confirmed that when SEM>AVS metals dissolved in the pore water actually were toxic. Toxicity tests with sensitive taxa such as daphnids and sea urchin gametes should be performed on fresh and saline pore waters, respectively, to confirm their toxicity.

Similarly, tools that can be used in low AVS and oxic sediments are required. Finally, many toxic metals (such as mercury, silver, chromium, and selenium) are not addressed by the SEM/AVS method, yet they merit substantial environmental concern.

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TABLE 1. SUMMARY OF RESEARCH NEEDS  
(Listed in Decreasing Order of Priority and Urgency)

### A. General Needs for Sediment Criteria

1. Procedures for obtaining a representative sample of contaminated sediment.
2. Conceptual framework for integrating the SEM methods into a Tiered Approach.

### B. Specific Needs for the SEM/AVS Methodology

1. Improving the pore water preparation to account for method-induced changes in biologically available metals.
2. Establishing (confirming) a toxicity threshold in terms of SEM/AVS (or SEM-AVS).

3. Establishing a bioaccumulation threshold in terms of SEM/AVS (or SEM-AVS) and the route of exposure.
4. Evaluating spatial and temporal variability in AVS and SEM.
5. Evaluating if factors other than AVS and organic carbon control metals bioavailability.
6. Field verification of the criteria, especially with sensitive life stages of benthic organisms, benthic fish, and algae.
7. Field data to evaluate the sensitivity and accuracy of SEM/AVS method.
8. Cumulative effects measures of contaminants on toxicity and bioaccumulation.

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## APPENDIX A. SPECIFIC COMMENTS

The term "dialysis" should be replaced by "passive diffusion" when referring to pore water sampling because dialysis is generally reserved for membranes with much smaller pore sizes. "Peepers" should be described as diffusion samplers not dialysis samplers.

In the briefing document, Chapters 1, 10 and 11 should state at SEM/AVS ratios  $< 1$  toxicity is seldom observed; however, bioaccumulation may still occur. The qualifier at the end of Chapter 8 (page 8-21) regarding the limitations of AVS to predicted metal bioaccumulation from sediment should also be included in Chapters 1, 10, and 11 (e.g., top of page 11-1 and bottom of page 11-2). The document needs to more clearly differentiate between bioavailability as measured by toxicity vs bioavailability as measured by bioaccumulation.

Figure 4-1. What do the three lines represent?

Page 5-3. Why discuss *Rhepoxynius hudsoni*? Are not only data for *Ampelisca* presented in this chapter? Is this in reference to the statement on page 5A1, 2nd paragraph? If *R. hudsoni* data are presented in this chapter, then relabel the figure legends.

Page 5-4, 2nd paragraph. The statement is made that AVS, SEM, and dry weight concentrations varied but were typically within 20%. Was there any consistent trend? Ankley et al. [5] report a fairly sizable drop in AVS over 10 days ( $> 20\%$ ; Table 6.2). Note: Kemble et al. (1994) reported consistent SEM and AVS in 28-day tests with amphipods.

Figure 5-1 (and others), Define "ND".

Figure 5-8. Any ideas why there was high mortality at low Cd IWTUS?

Page 5-27, 2nd paragraph. Ankley et al. [22] is not listed in the references. Did this study evaluate Cd or Cu?

Page 6-1 5, 3rd paragraph. IWTUs are discussed for amphipods. What about for oligochaetes?

Page 6A-2, 1st paragraph, last sentence. Why were 30 volume additions/day used? Could this not reduce AVS or overlying water concentrations?

Table 7-6. The statement is made that chronic lethality or sublethal effects are possible at SEM/AVS ratios  $< 1$ . This point should also be made in Chapters 1, 10, and 11.

Could some of the temporal variability discussed in Chapters 7 and 9 (e.g., page 7-2, last paragraph) have resulted from horizontal variation in AVS?

Page 9-1 2. The description of sulfide oxidation rates should include additional detail. How were the sediments placed into the test chambers? Are these rates for very thin layers of sediment without overlying water? The rate of oxidation would probably depend on depth and overlying water amount.

Page 9-46 and page 9-47. Suggesting minimum partition coefficients based on sorption of metals to sand is questionable. Would not the presence of organisms alter this partitioning, themselves being organic? Partitioning is not as absolute as AVS binding.

Page 9-51, top. The ion-electrode procedure is only glossed over. A recommendation can be made for widely ranging AVS concentrations with this detection method.

Page 10-3, top. "Pore water and SEM/AVS should be considered a snapshot measure" -- However, the SEM/AVS would be a greater time interval, perhaps weeks unless a turnover or major precipitation event occurs.

Page 10-6, last sentence. Bioaccumulation tests should be recommended in addition to toxicity tests.

Page 11-6, last sentence; page 3-1, 3rd paragraph, last sentence; page 5- 1, 1st paragraph; page 5-27, last paragraph. Dissolved organic carbon is suggested as an important binding phase for metals. Yet, equation 11-7 only accounts for TOC, hardness, and pH.

Page 11-8. Should SEM Co, Hg, and Ag be included in the sum molar SEM concentration? Are there data to support this approach? Further discussion of Hg, Ag, Co are needed, especially because Hg and Ag are the least soluble sulfides. Are these metals considered less reliable or is it assumed that they will be much lower in concentration and therefore insignificant?

Page 11-10. Are the FCVs for metals protective of benthos?

Page 11-19, 1st paragraph. WQC are established to protect 95 % of the species, WQC are not intended to protect for "no effects". However, the statement on page 1-2, 2nd paragraph is consistent with the used of criteria (to prevent "unacceptably affects" on benthic organisms).

A discussion of "reactive" versus "refractory" organic carbon as it relates to AVS formation begs for further discussion. How does one measure these two forms? Is metal sorption different? Are there examples of each type of organic carbon?

Page 3-11, 2nd paragraph. Comparisons are made in this chapter between pore-water and water-only exposures regarding toxicity. Have these comparisons been made for bioaccumulation?

Citation #1 5 at the end of Chapter 1 5 should be cited as: Ingersoll, C.G., W.G. Brumbaugh, F.J. Dwyer, and N.E. Kemble. Bioaccumulation of metals by Hyalella azteca exposed to contaminated sediments from the upper Clark Fork River, Montana. Environ. Toxicol. Chem. 13:2113-2020.

Page 6-30, 3rd paragraph. The statement is made that sampling problems occurred with the spiking of Cd in freshwater sediments. Please explain.

Page 6-31, 2nd paragraph. How accurately could IWTU alone predict toxicity? What if IWTU were normalized to hardness, pH, and DOC?

Deletion of samples from the evaluation of metal toxicity because of the potential for effects of organic contaminant should be more quantitative than the approach described in Chapter 6. For example, on Page 6-9 of the briefing document, the statement is made that organic contaminants contributed to the toxicity of Bear Creek sediments. However, insufficient data are presented to support this conclusion. Were these or other samples analyzed for organics?

TOC measurements are critical and require QA/QC to ensure their reliability. Also, note that not all TOC is the same. How is this factored into the calculations?



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