

February 28, 2000

EPA-SAB-EPEC-00-005

Honorable Carol M. Browner
Administrator
U.S. Environmental Protection Agency
1200 Pennsylvania Ave., NW
Washington, DC 20460

Subject: Review of An Integrated Approach to Metals in Surface Waters and Sediment

Dear Ms. Browner:

At the request of the EPA Office of Water, the Ecological Processes and Effects Committee (EPEC) of the Science Advisory Board (SAB) met on April 6-7, 1999 to review the Agency's proposal for assessing the bioavailability and toxicity of metals in surface waters and sediments. In addition to its current water quality criteria, the Agency has worked with outside researchers to develop the Biotic Ligand Model to predict the acute toxicity of metals to aquatic organisms and has developed sediment quality guidelines based on the Acid Volatile Sulfide (AVS) approach. The Committee's comments on the Biotic Ligand Model are contained in a companion SAB document (EPA-SAB-EPEC-00-006). The focus of the present report is on the AVS-based sediment guidelines and on other aspects of an integrated approach to the management of metals in the aquatic/sediment environment.

It has long been recognized that contaminated sediments can cause adverse effects even where waters are meeting water-quality based criteria. As a result, the Agency has been working to develop sediment quality guidelines that can be applied in conjunction with water quality criteria to protect human health and aquatic life. The SAB strongly supports the Agency's development of sediment quality guidelines to fill this existing gap in environmental protection.

The approach that the Agency has selected for developing sediment guidelines is based on the theory that chemical equilibrium principles can be used to predict the partitioning of sediment contaminants among the sediment phases (e.g., mineral sediments, sediment organic carbon, and interstitial water). The Agency has sponsored work demonstrating that when the concentration of acid-volatile sulfide, a binding agent for metals in sediments, exceeds that of simultaneously extracted metal, metals toxicity is not observed. The Agency has also presented data on the observed relationship between metals concentrations in sediment interstitial (pore)

water and toxicity. The proposed sediment guidelines for metals mixtures rely on these two components to predict which sediments are “unacceptably contaminated” with respect to metals.

In the attached report, the Committee reviews the overall approach being proposed for sediment guidelines. We commend the Agency for developing an important body of scientific work with broad practical application and for developing a powerful predictive tool that is suitable for use in sediment assessment. The Committee also, however, provides advice regarding the appropriate use of the AVS method in the field and discusses some important limitations of the method, many of which were outlined in a 1995 SAB review of the subject. Recognizing these limitations, the Committee recommends that the language in the Guidelines Statement be refined.

The Committee supports the Agency’s quest to integrate approaches to management of surface waters and sediments. In the attached review, we suggest possible refinements to the array of tools that the Agency is developing for this purpose.

The Committee has appreciated its long working relationship with the Office of Water on the important topic of sediment quality guidelines and hopes that the attached report will contribute to the development of scientifically defensible guidelines. We look forward to a reply from the Assistant Administrator for Water.

Sincerely,

/signed/

Dr. Joan M. Daisey, Chair
Science Advisory Board

/signed/

Dr. Terry F. Young, Chair
Ecological Processes and
Effects Committee
Science Advisory Board

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**U.S. ENVIRONMENTAL PROTECTION AGENCY
SCIENCE ADVISORY BOARD
ECOLOGICAL PROCESSES AND EFFECTS COMMITTEE**

**Review of the Integrated Approach for Predicting Metals Toxicity in Surface Waters and
Sediments (Including the Equilibrium Sediment Guidelines)**

April 6-7, 1999

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1. EXECUTIVE SUMMARY

The Ecological Processes and Effects Committee of the Science Advisory Board met in April 1999 to review the Agency's proposed approach to assessing the bioavailability, and hence toxicity, of metals in sediments. The approach, which is based on equilibrium partitioning theory, assumes the bioavailable fraction of total sediment metals to be the difference between the Simultaneously Extracted Metal (SEM) and the Acid Volatile Sulfide (AVS), a binding factor for metals in sediments. The Agency also presented recent work demonstrating the utility of normalizing the SEM-AVS to fraction organic carbon in the sediment. The Agency proposes that the SEM-AVS approach be incorporated into sediment quality guidelines for a mixture of metals (cadmium, copper, lead, nickel, silver, and zinc).

The Committee commends the Agency for developing an important body of scientific work with broad practical application far beyond the specific subject of sediment assessment guidelines. The SEM-AVS methodology is soundly grounded in chemical theory and has been verified by a wide range of convincing acute toxicity studies. Recent studies of longer-term effects, including chronic toxicity studies, have added substantially to the body of evidence suggesting that organisms will not be adversely affected by metals when $SEM-AVS < 0$. Additional work regarding the influence of organic carbon on metal bioavailability has allowed the Agency to further refine the method. In short, the SEM-AVS methodology provides a valuable addition to our understanding of the bioavailability (or lack thereof) of metals in certain sediments. It is also a powerful predictive tool, suitable for incorporation into sediment assessment guidelines.

For all of its merits, however, the SEM-AVS methodology also has limitations: first, it is still unclear whether adverse effects on biota are necessarily prevented when AVS exceeds SEM; and second, environmental conditions in many locations will be unsuitable for SEM-AVS use because underlying assumptions of the approach will be violated. For example, AVS does not persist in aerobic conditions, whereas the oxidized zone is where most species concentrate their interaction with their environment. For these reasons, the Committee recommends that SEM-AVS be incorporated into sediment assessment guidelines in a way that assures that SEM-AVS will continue to be used in conjunction with other assessment tools to characterize the safety of sediments, rather than being used as a stand-alone test. The SEM-AVS method may be particularly useful to prioritize sites requiring attention and to explain situations when bioassays show a lack of toxicity even though metal concentrations in sediments are high.

The Committee strongly recommends that the Agency now turn its attention to the appropriate application of SEM-AVS in the field and thereafter to other methods of assessing sediment quality that can be used when SEM-AVS cannot. To facilitate this effort, the Committee provides the following specific observations and recommendations:

- a) The SEM-AVS methodology relies on the observed correlation between toxicity and metals concentrations in the interstitial water under certain chemical conditions. It does not consider explicitly the role of dietary exposures to metals. The Committee recommends, therefore, that the Agency begin at the earliest possible date to assess the currently available literature on the importance of dietary exposure to metal uptake (particularly for cadmium, silver, copper, and zinc) and that the Agency also initiate studies that evaluate the significance of dietary uptake compared to SEM-AVS predictions of metal exposure and effect. These studies are required to determine under what circumstances AVS-SEM can most accurately be used as a "no-effect" test, as the Agency envisions.
- b) Bioaccumulation of metals occurs in circumstances where the SEM-AVS methodology would predict no effect. The potential adverse effects of this bioaccumulation on the organisms themselves is uncertain at this time; adverse effects of bioaccumulated metals on consumer organisms also may be significant. The Committee therefore would like to re-emphasize the importance of incorporating bioaccumulation measures, particularly the effects on consumer organisms, in the Agency's overall sediment assessment approach.
- c) The SEM-AVS methodology is based on equilibrium partitioning theory which, in turn, assumes a steady-state system in which chemistry can be used to predict bioavailability. In nature, however, sediments are not steady-state systems and exposure of organisms to metals (as well as adverse effects) is influenced by biological and ecological processes. The SEM-AVS predictions of toxicity should be verified for a greater range of test organisms, representing a more complete range of behaviors and functional groups. This work can be undertaken in conjunction with the studies recommended in (a) above, that would investigate exposure of organisms to metals via sediment ingestion (particularly targeting organisms whose behavior and ecology maximize their exposure in the field).
- d) Accurate characterization of SEM and AVS in the field is as essential as it is complex. Because sediments are so variable in both space and time, using the right sampling protocols is just as important as using the right toxicity test protocols. Recognizing that any sampling strategy must be both practical and affordable, the Committee recommends that the Agency investigate and then provide clear guidelines for assessing SEM and AVS that consider the biologically active zone (e.g., the vertical distribution of organisms in the sediment) as well as temporal and spatial variability (including vertical and horizontal gradients) of sediment chemical parameters..
- e) There are many sediments for which the SEM-AVS methodology does not apply. In addition to aerobic sediments, these include anaerobic sediments whose redox

conditions are likely to change as a result of, for example, seasonal changes, periodical exposures associated with tidal fluctuations, or resuspension during storms, floods, or dredging operations. The Committee recommends that these limitations be incorporated into the sediment guidelines to assure that the SEM-AVS methodology is not mistakenly used where it is inappropriate.

- f) While the draft "Equilibrium Partitioning Guidelines (ESG) for the Protection of Benthic Organisms" incorporates caveats with respect to most of the concerns above, the Committee suggests that these be emphasized to a greater degree in the final "Guidelines Statement" (pp. 1-108, 109), to help assure appropriate use of the SEM-AVS method. For example, the circumstances in which the SEM-AVS method is clearly inapplicable could be explained in the initial paragraph of the Guidelines Statement. In addition, it would be useful to elaborate on the statement that the ESG is not designed to protect organisms from sediment ingestion or ingestion of contaminated benthos and refer to a discussion within the document that assesses the relative importance of these exposure pathways under a variety of conditions.

Finally, the Committee notes that the format of the Guidelines Statement is reminiscent of a water quality criterion (generally used as a necessary and sufficient test of designated use protection). For example, the guidelines states that if the SEM-AVS component is violated but the IW component is satisfied, "then the sediment meets the guideline and benthic organisms are acceptably protected from metals-induced sediment toxicity." The Committee recommends that the guideline language be modified to reflect the fact that the ESG is an assessment tool designed to be used in concert with other tools, rather than a stand-alone pass/fail test.

The Committee understands that a "Sediment Guidelines User's Guide" is being developed by the Agency to assist potential users of the ESG to apply it in real world applications. This User's Guide should undergo careful peer review to ensure that the various sediment assessment tools are not applied outside their validated conditions.

Given both the strengths and the limitations of the SEM-AVS methodology, it is important to consider how the Agency intends to use the technique in concert with other water quality standards and assessment tools. The Committee urges the Agency to develop a refined conceptual model that incorporates all partitioning phases and routes of exposure in order to guide the Agency's long-term efforts to integrate water column and sediment standards and to assist users to apply current standards and guidelines appropriately. A conceptual model of exposure of organisms to metals in aquatic environments, coupled with a parallel diagram of the Agency's approaches for evaluating that exposure and the resulting effects, would be a very useful tool for the Agency as it attempts to build an integrated water/sediment protection system. An example of this type of presentation generated by the Agency for the Committee highlighted potential gaps in the Agency's currently proposed approach.

The Agency requested the Committee's advice on a series of questions that relate to refinements of the SEM-AVS methodology. A brief summary of the Committee's findings in response to these charge questions follows:

Charge Question 1: By incorporating the fraction organic carbon into the bioavailability equation, has the Agency retained the protective features of the guidelines and improved its predictiveness of toxic effects?

The normalization of SEM-AVS to fraction organic carbon reduced the variability in the exposure estimates and therefore improved the predictive capability of the method, particularly for laboratory experiments. The results for the field experiments are less clear. There may be a mechanistic reason why the fraction organic carbon normalization would do less to improve precision under field conditions; there is some evidence that the effect of organic carbon on bioavailability depends upon the nature of the organic carbon. In any case, the Agency may wish to weigh the benefits of the normalization procedure against the additional variability that must be captured in the sampling design.

Incorporation of the organic carbon normalization should not reduce the degree of protection afforded by the SEM-AVS method, unless the organic carbon is present as biological complexes that tend to increase bioavailability.

Charge Question 2: If the Biotic Ligand Model (BLM) is used to derive or adjust a water quality criterion, is the revised criterion appropriate for use in the interstitial water component of the Metals Mixtures ESG?

Because the chemistry of interstitial water (IW) is not the same as the chemistry in the water column, it would be inappropriate to substitute the BLM-adjusted water column criterion for the water quality criterion in the ESG equation at this time. While the Committee is optimistic that the BLM will be a useful new tool for assessing bioavailability in the water column, we recommend that specific validation experiments be performed before applying the method to interstitial (pore) water. The currently proposed IW component of the ESG relies on comparison of the IW metals concentration to the water quality criteria Final Chronic Value for each metal, corrected only for site-specific hardness; the BLM, if validated for application to interstitial water, would allow consideration of additional site-specific chemistry conditions that affect metals bioavailability.

Charge Question 3: Are the data presented from lab and field experiments with chromium and silver sufficient to support their addition to the Metals Mixtures ESG?

Although the results from acute toxicity tests are promising, further research is required to support the addition of either chromium or silver to the ESG. In addition to undertaking chronic toxicity

tests, the Committee recommends that the Agency address selected questions regarding the chemistry of chromium in the field and other factors affecting the bioavailability of chromium (III) in nature. With regard to silver, the data presented do not provide the same clear demonstration that AVS binding eliminates silver toxicity as has been shown for other metals.

2. BACKGROUND AND CHARGE

2.1 Background

In recent years, the Ecological Processes and Effects Committee has commented on Agency proposals to use Equilibrium-Partitioning (EqP) to predict the availability (and hence, toxicity) of chemicals in sediments, including non-ionic organic chemicals (SAB, 1992) and metals (SAB, 1995). The EqP approach, in which chemicals are assumed to be in equilibrium between sediments and pore water, was proposed as a means of predicting the extent to which sediment chemicals are biologically available, and thus may produce toxic effects. With regard to metals, the bioavailable fraction of sediment metals is assumed to be the difference between the Simultaneously Extracted Metal (SEM) and the Acid Volatile Sulfide (AVS), a binding factor for metals in sediments. In other words, toxicity is not expected for sediments in which $SEM - AVS \leq 0$. In the 1995 review, the Committee concluded that the SEM-AVS methodology was “based on sound theory and [had] been verified by considerable experimental evidence.” The Committee noted, however, the significant limitations to application of the methodology and identified a number of remaining research questions associated with its use.

The Agency currently has ambient aquatic life criteria for 11 individual metals and draft sediment guidance based on the EqP approach for a mixture of five metals (cadmium, copper, lead, nickel, and zinc), the latter of which was reviewed by the SAB in 1995. The proposed Metals Mixtures ESG reviewed by EPEC in April 1999 contains two components: an AVS guideline and an Interstitial Water Guideline. The AVS guideline requires that the molar sum of the SEM for the six metals (silver, copper, lead, cadmium, zinc, and nickel) in sediment not exceed the sediment AVS concentration. The Interstitial Water Guideline requires that the sum of the ratios of each metal to its Final Chronic Value (FCV) not exceed 1. The Guidelines Statement (Section 6 of the proposed ESG) states that “if both of these conditions are violated, or if the AVS Guideline is violated and the sediment is contaminated with silver [for which there is no FCV], then there is reason to believe that the sediment may be unacceptably contaminated by these metals.” If only one of the two conditions is violated, however, this does not mean that the sediment violates the ESG. The Guidelines Statement also states 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 ...conditions is satisfied.” With the exception of the proposed inclusion of silver, the components in the draft document are the same as those presented to the SAB in 1995.

The Guidelines Statement in the proposed ESG does not include organic carbon partitioning because, in the words of the review document, the Agency feels that “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” (p. 1-87). However, in the Charge to the Committee, the Agency asks whether the organic carbon normalization of the AVS guideline will improve its ability

to predict toxic effects, in addition to its intended role as a guideline for predicting “no effects” concentrations.

2.2 Charge

For the current SAB review, the Committee was asked to review the Agency’s proposed refinements to the approaches for deriving aquatic life criteria for metals and sediment guidelines for metals mixtures. The proposed modifications include: use of the Biotic Ligand Model (BLM) to improve prediction of bioavailability of metals both in the water column and in interstitial (pore) water, inclusion of organic carbon normalization in the calculation of sediment metals bioavailability, and inclusion of chromium and silver in the Metals Mixtures ESG. In addition to requesting Committee comments on the proposed refinements, the Charge to the Committee also included a request for comment on whether the linkages between the water column criteria and sediment guidelines would improve the Agency’s ability to integrate predictions of metals toxicity in aquatic environments.

The Committee met in Washington, DC on April 6-7, 1999 to review the following documents: a) *Biotic Ligand Model of the Acute Toxicity of Metals* (U.S. EPA, 1999b), proposed for incorporation into the Agency’s approach for deriving aquatic life criteria for metals in the water column and b) the Agency’s draft guidance, *Equilibrium Partitioning Guidelines (ESG) for the Protection of Benthic Organisms: Metals Mixtures—Cadmium, Copper, Lead, Nickel, Silver, and Zinc* (U.S. EPA, 1999a), referred to as the Metals Mixtures ESG. The Charge to the Committee included the following questions:

Overall Charge Question: Integrated Methodology

- a) Does this integrated metals methodology improve the Agency’s ability to make both protective and predictive assessments of toxicity due to copper, silver and other selected metals in the water column and sediment?

Charge Questions on the Metals Mixtures ESG

- b) By incorporating the fraction organic carbon into the bioavailability equation, has the Agency retained the protective features of the guidelines and improved their predictiveness of toxic effects:
- c) If the Biotic Ligand Model (BLM) is used to derive or adjust a water quality criterion, is the revised criterion appropriate for use in the interstitial water component of the Metals Mixtures ESG?
- d) Are the data presented from laboratory and field experiments with chromium and silver sufficient to support their addition to the Metals Mixtures ESG?

Charge Questions Pertaining to the BLM:

- e) Does the BLM improve the Agency's ability to predict toxicity to water column organisms due to metals (copper and silver) in comparison to the currently applied dissolved metal concentration criterion?
- f) Is the scientific and theoretical foundation of the model sound?
- g) In comparison to the current WER adjustment for aquatic life criteria, will the application of the BLM as a site-specific adjustment reduce uncertainty associated with metals bioavailability and toxicity?
- h) Are the data presented for validation of the BLM sufficient to support the incorporation of the BLM directly into copper and silver documents?

This report contains the Committee's comments on the Metals Mixtures ESG, as well as the inter-relationship between the metals assessment approaches proposed for protection of water column and benthic organisms. The Committee's comments on the Biotic Ligand Model (questions e through h, above) are contained in a companion report (EPA-SAB-EPEC-00-006).

3. STRENGTHS OF THE PROPOSED SEM-AVS METHODOLOGY

3.1 Theoretical Foundation

The EPA and collaborating scientists deserve praise for working to develop a means of incorporating bioavailability principles into guidelines for management of contaminated sediments. Assessment techniques based upon total metal concentrations have limitations that have long been recognized, but the techniques to deal with these limitations have been missing. The research accomplishments presented in this review are notable considering that the endeavor was extremely challenging and the factors that affect bioavailability in sediment are complex. The attempt to find a simplified and unifying approach to incorporate these complexities for managers is admirable.

The proposed ESG for metal mixtures is based upon a decade of study of the influence of acid volatile sulfide (AVS) on metal bioavailability in sediments. The theory behind the proposal is that AVS in sediments controls metal concentrations in interstitial waters, limits bioavailability of metals in bedded sediments through the formation of insoluble sulfides, and thereby controls overall metal availability and toxicity to benthic organisms. Metal exchange among interstitial water, bedded sediments, and sulfide phases is assumed to be controlled by equilibrium partitioning of the metal, which can be described by the physico-chemical properties of each metal. The authors have developed an elegant and convincing set of results supporting the use of AVS theory to explain bioavailability of metals in sediments and their potential to cause toxicity. They have also developed an impressive and extensive publication list, and this work has been very influential with scientists interested in contaminated sediments and with regulatory/water management organizations all over the world.

The most recent work presented in this review provides information that incorporates metal partitioning to organic carbon as an additional binding ligand that influences metal bioavailability. The addition of fraction organic carbon (foc) to the overall conceptual model for assessing bioavailability of metals in sediments is seen as a natural extension of the EqP theory for metals. As demonstrated by data presented to the Committee, toxicity is not always observed when SEM exceeds AVS. This lack of toxicity has been attributed to metal binding to various phases such as iron and manganese oxides as well as organic carbon. The development of an approach to incorporate organic carbon into the metals EqP methodology is an appropriate and timely step toward developing a methodology that can be used to identify those sediments that have the greatest potential to cause environmental effects.

3.2 Experimental Verification

EPEC acknowledges the long-term and chronic sediment studies that were performed in response to previous concerns raised by the Committee that the ESG data consisted primarily of results from acute toxicity studies. Chronic toxicity studies were performed with cadmium (28-days; *Leptocheirus plumulosus*) and zinc (56 days; *Chironomus tentans*). Colonization studies were

performed with cadmium (118 days; laboratory study), cadmium (120-days; field study), equimolar ratios of cadmium, copper, nickel and zinc (120-day; saltwater field study); and zinc (1-year, freshwater field study). The results of these long-term studies demonstrated a lack of toxic effects in all cases where $SEM-AVS < O$, indicating that AVS binding of divalent metals reduced metals bioavailability and prevented chronic effects on survival, growth, reproduction, and colonization. These results provide continuing evidence that EqP theory for metals, as developed, applies to both acute and chronic toxicity. Evidence to the contrary in even one of the experiments would have raised serious concern relative to the ability of the ESG to protect against chronic effects.

While acknowledging extension of ESG data sets to include evaluation of chronic effects of metal contaminated sediments, the Committee has the following concerns associated with chronic effects:

- a) Chronic studies have not been performed on all metals covered by the ESG; lead and silver were not tested¹; and
- b) Chronic toxicity studies were performed with only two species, although colonization studies included many more species.

In summary, long-term/chronic sediment toxicity studies have provided results that are consistent with sulfide binding theory (EqP) and that support the development of ESG. While this is encouraging, the potential for chronic toxicity to occur in situations where $AVS > SEM$ has not been ruled out due to the limited number of studies performed, and due to the mechanisms discussed in Section 4.

¹The Agency subsequently provided information that lead (Pb) had been spiked into the test sediment in the marine field colonization chronic test, but that lead had been inadvertently left out of Table 3-2 in the review document.

4. LIMITATIONS OF THE PROPOSED SEM-AVS METHODOLOGY

4.1 Meeting Key Assumptions

Although the SEM-AVS work has been influential, it is also controversial. The elegance and consistency of the results have convinced some scientists that potential applications are widespread. However, a growing body of scientists are skeptical. The skepticism is not about the theory and experimental evidence that AVS is important for metal behavior in sediments. It is the extent of the application that is in question; and this is very relevant to its use as a regulatory tool. Concerns with the SEM-AVS approach have been raised with respect to its biological limitations and based on studies of the geochemistry of AVS in sediments (e.g., in Meyer et al., 1994), yet the proposed Metals Mixtures ESG document does not present much in the way of these alternative views.

It is complicated, but important, for EPA to understand why the work so elegantly and convincingly presented in this proposal is also controversial. There is a legitimate concern that the Agency and its researchers have not demonstrated that the SEM-AVS approach is applicable as a predictor of sediment toxicity beyond a given set of circumstances. Although it is not discussed in the reports submitted to the SAB, there is also a body of literature that questions application of equilibrium partitioning models, because of their limited capability for dealing with important environmental complexities (Landrum et al., 1992; Farrington, 1989). These limitations are especially important for metals and, at least by implication, affect the applicability of SEM-AVS (Luoma and Fisher, 1997).

Many of the limitations of the proposed SEM-AVS approach relate to the ability of key assumptions to be met under field conditions. For example, the approach assumes equilibrium conditions, that the effects of the metals are no more than additive, and that toxicity can be predicted from metal concentrations in interstitial water. The Metals Mixtures ESG specifically states that ESG approaches “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” (EPA, 1999b). However, there may be few or no aquatic systems where these processes do not occur.

In addition, biogeochemical processes controlling vertical profiles of sulfides in sediments are complex and can promote nonequilibrium conditions, yet the implications of these processes on sampling strategies and data interpretation have not been addressed adequately. Different metals and different sulfide complexes likely have different solubility constants. The importance of diagenetic processes in sediments and the different vertical horizons of the processes in different environments should be considered.

To assess the applicability of the Metals Mixtures ESG, one must assess the extent to which the method’s underlying assumptions can be met in the field and assess the significance of exposure

pathways other than exposure to interstitial water. A number of these concerns were raised by the SAB in 1995, and they continue to be relevant to the Agency's proposed application of a Metals Mixtures ESG as a regulatory tool. Accordingly, the Committee suggests that the Agency consider the following questions (which are discussed in greater detail in the following sections) as it determines how to apply the SEM-AVS method and the ESG:

- a) ***Dietary Exposure/Bioaccumulation***—Is internal metal exposure of the organism independent of the route of uptake, as asserted by EqP, or can dietary exposure increase the internal metal dose received by the organism so that toxicity is expressed even when AVS exceeds SEM? Does bioaccumulation at SEM-AVS < 0 indicate the possibility of chronic toxicity?
- b) ***Biology and Ecology***—Do differences in behavioral and ecological processes among organisms (e.g., strategies for feeding and obtaining oxygen in sediments) influence the applicability of the SEM-AVS approach? What organisms are or are not protected by SEM-AVS?
- c) ***Sediment Dynamics***—Would regulatory applications of SEM-AVS be affected by the dynamic nature of sediments and sediment biogeochemistry? Are there times when the method should or should not be used?
- d) ***Sampling and Variability***—How should variability resulting from biogeochemistry of AVS in sediments, including vertical and horizontal AVS gradients, be accounted for in sampling protocols?

These questions are testable and, in some cases, tests are underway or published. It is important that the Agency understand the basis and implications of these potential limitations before determining how to apply the guidelines in a regulatory context. In the following sections, the Committee will discuss each of these concerns and consider the extent to which the work conducted by the Agency or outside researchers since 1995 has addressed them.

4.2 Dietary Exposure/Bioaccumulation

Equilibrium Partitioning (EqP) theory was originally developed for non-ionic chemicals, following the suggestion by Mackay (1982) that a single chemical potential determines equilibrium between an organism and its environment. Organic chemical bioaccumulation from sediments is determined from knowledge of the hydrophobicity of the chemical and prediction of pore water concentrations (DiToro et al., 1991). Studies by Swartz et al. (1985) and Kemp and Swartz (1988) demonstrated that pore water concentrations controlled cadmium toxicity or cadmium bioaccumulation by benthos. These findings, together with several subsequent studies discussed in the Metals Mixtures ESG, are cited as the evidence that knowledge of pore water metal concentrations is sufficient to

determine metal exposures and toxicity in sediments. In the body of SEM-AVS literature cited in the documents submitted to the SAB, toxicity is consistently correlated with pore water concentrations of metals. Again, this supports the validity of equilibrium partitioning.

The criticisms of the EqP model (when it is applied to metals) stem from an alternative conceptual view of how exposure to metals occurs in nature. The most important aspect of this alternative model is the assumption that the internal dose of metal experienced by an animal is determined by the sum of the contributions from different uptake routes (from diet and from water) and that these are not necessarily in equilibrium. Stated another way, route of exposure does matter, and total internal exposure should be derived from the sum of uptake from each route. As noted by the SAB (1995), if this alternative model is accurate, then studies that use only pore waters as a basis for estimating bioavailability will underestimate under some conditions the total exposures of animals that ingest contaminants in their food (Luoma, 1995; Meador et al., 1995). The multi-pathway conceptual model, described by Clark et al. (1990), McKim and Nichols (1994), Thomann et al. (1995) and Luoma and Fisher (1997), is also supported by direct experimental evidence. Since the late 1970's, experiments have been conducted that show that bioaccumulation pathways by benthic invertebrates can be additive. When water exposures are combined with food exposures, bioaccumulation can exceed uptake from either source alone (see review by Luoma, 1983; Young, 1975; Harvey and Luoma, 1985; Borchardt, 1983; van Hattum et al., 1989; Warnau et al., 1996). In all these experimental studies, prediction of metal exposure from dissolved concentrations alone would have underestimated the total metal burden experienced by the organism.

According to both EqP theory and the additive model: a) toxicity of metals is correlated with the total exposure to metals (i.e., exposure from dietary sources, including sediment ingestion, and from cutaneous and respiratory exposures to pore water or overlying water); b) the empirical finding that toxicity is correlated with interstitial water concentrations of metals would be expected for experimental conditions under which pore water exposure is the dominant (though not necessarily the only) route of exposure; and c) in experiments with metal spiked sediments, pore water concentrations of metals may be higher than contaminated sediments in field conditions and so a stronger correlation with toxicity would be expected. However, it is in field scenarios where pore water:sediment metal ratios are smaller (i.e., lower pore water metal concentrations)—and hence dietary exposures might constitute a greater proportion of the total exposure—that the toxicity predicted by the two models might be expected to diverge.

In Kemp and Swartz (1988), for example, experimental conditions facilitated high concentrations of cadmium in pore waters compared to sediments (conditions that could cause such an effect include extremely high metal concentrations and short equilibration times). Luoma and Fisher (1997) showed that the K_d (ratio between sediment and water concentrations) in the Kemp and Swartz (1988) experiment was approximately 15. The K_d for cadmium between sediment and water in an estuary is more typically 5000. When a bioaccumulation model was applied, it predicted that pore waters would dominate uptake in the experiment (as was observed), but uptake from food would

dominate the more natural condition. In the latter case, predictions based upon pore waters alone would underestimate exposures by nine fold. The Kemp and Swartz (1988) experiment may represent an unusual circumstance, but it behooves the EPA to be certain that SEM-AVS predictions are not just applicable to the most extreme contamination conditions and sediments only recently contaminated with metals. Most regulatory situations are more complex than this. Verification of SEM-AVS predictions should include experiments with sediments that are contaminated to levels typical of many contaminated environments and protocols that involve times of equilibration and exposure typical of nature.

Luoma and Fisher (1997) concluded that there are mechanistic reasons why organic chemical exposures should be better explained than metal exposures by equilibrium partitioning. The first is that tissue bioaccumulation of metals is not driven by any single principle analogous to hydrophobicity. The chemical potential of metals in food and within tissues is controlled by a myriad of biochemical reactions and a variety of metal forms. They also concluded that a variety of surface and geochemical processes control metals in sediments and this results in controls on metal bioavailability that are complex. For example, Luoma and Bryan (1982) showed that simple normalizations were not sufficient to predict metal bioavailability from field sediments, when a diverse array of sediments were considered.

In addition, some studies (including those presented to the SAB in 1995) have shown that bioaccumulation of metals may occur even when AVS exceeds SEM. Although bioaccumulation by itself is not proof of an adverse effect or toxicity—indeed, bioaccumulation of low levels of metals can occur with no adverse effects—it does provide a measure of the presence and bioavailability of metals in sediments. Further, tissue residue measurements can be indicative of both metal exposure and internal dose (see Figure 1 in Chapman, 1995), except in cases where the metal is regulated by the organism. Since bioaccumulated metals can contribute to an organism's body burden, it is plausible that toxicity could result from uptake via the dietary route. A body of literature exists and, is rapidly growing, that shows the importance of dietary exposure to metal uptake in a variety of species, for a variety of metals, in a variety of circumstances (e.g., see Appendix B). However, the importance of dietary accumulation and the potential for toxicity has not been systematically examined. Experiments designed to separate exposure pathways and evaluate the potential for toxicity to occur via the diet were suggested previously by the SAB (1995), but have not yet been undertaken. The Committee recommends, therefore, that the Agency incorporate research of this nature in future testing programs.

As the Agency moves toward an integrated water/sediment assessment and management scheme, including consistent criteria and guidelines for the different environmental compartments, it will be important to relate the various threshold levels to total exposure (and associated effects) for aquatic and benthic organisms. Bioaccumulation and food chain exposures will be an important link between water column and sediment criteria, and ultimately wildlife criteria. This fact is recognized by the Agency's inclusion in its integrated vision (Figure 1) of possible future tissue-residue based criteria. We encourage the Agency to evaluate the potential to develop tissue residue thresholds that could be used to evaluate the significance of metals bioaccumulation. Moreover, until this question can be resolved, the Committee

recommends that the Agency seriously consider including bioaccumulation in the suite of measures that would be evaluated in a weight-of-evidence approach to sediment assessment.

Sediment Ingestion—A subset of dietary exposure is that which occurs with sediment ingestion. Deposit feeders are benthic invertebrates that ingest whole sediment and receive nutrition by stripping or digesting the scant amounts of organic matter present. The AVS component of the proposed ESG assumes that metal sulfides are not bioavailable. However, benthic deposit feeders can ingest sediment whole into an acidic stomach, where bioavailability of metal sulfides may be altered by changes in pH, oxygen conditions, and digestive enzymes. Deposit feeders can dominate sediment communities. In the Chesapeake Bay, for example, deposit feeders represent 70% of the tidal freshwater communities, and constitute 9-38% of the community in all benthic habitats (Weisberg et al., 1997).

While little is known about the effect of ingestion on mobilizing consumed sediment metals, except for those that are required as micronutrients, low pH, oxidizing gut conditions, long gut residence times (days in bivalves; Decho and Luoma, 1991), and presence of surfactants and strong ligands in gut fluids (Chen and Mayer, 1998) all affect extraction of metals from sediments within the digestive system. These changes in thermodynamic potential in the gut relative to pore water are thought to account for observed bioaccumulation in benthic organisms when sediment AVS exceeds SEM.

To assess the protectiveness of the proposed ESG, one must understand how animals that feed on sediment (rather than just being in contact with interstitial water) accumulate metals and express toxicity to AVS-bound metals. How does the variety of sediment ingesting behavior (e.g., surface versus deep deposit feeding, and selective versus non-selective deposit feeding) alter the predictive nature of the ESG? Some discussion of this issue would be useful because the goal of the Metals Mixtures ESG is to protect benthic organisms, for many of whom sediment ingestion may be a major exposure pathway.

4.3 The Importance of Biological and Ecological Processes

Exposure—The SEM-AVS approach to predicting a “no effect” guideline assumes bioavailability is predicted by equilibrium partitioning. Equilibrium partitioning theory is based on several assumptions as well, e.g., a closed system in steady state where reactions are reversible. In nature, these assumptions frequently are violated.

Recent advances in benthic ecology, biogeochemistry, geology, and benthic boundary physics have revealed the central role of vertical profiles of solutes, organisms, and sediment types in regulating all benthic processes (Meyer et al., 1994). Vertical profiles are heterogeneous in 3-dimensional space, and organism-sediment relationships cause most of this heterogeneity. Organismal bioturbation ventilates, oxygenates, and moves sediments against vertical gradients. Bioturbation can enhance

biological activity, solute transport, and diagenetic rates associated with organismal tubes and burrows (Aller, 1983).

The basic biogeochemical nature of sediments is well known and one of the most important concepts is the vertical distribution of electron acceptors for the biological process of respiration (Fenchel and Jorgensen, 1977). There is a vertical gradient of diagenetic reactions for organic matter degradation in recent sediments based on the thermodynamics of the reactions. Oxidation is the primary reaction in surface sediments, but reduction is the primary reaction in anaerobic sediments, beneath the sediment surface. The denitrification zone probably occurs within the first few cm from the surface, followed by a sulfate reduction zone from 5 to 50 cm beneath the surface, and the methanogenesis zone occurs in the deepest sediments. This simple, yet powerful, view of sediment biogeochemistry has fueled a generation of studies. Yet, the gradients of increasing sulfide in sediments are not accounted for in the SEM-AVS methodology. As a result, the recent history of metal deposition will have a strong influence on how the method might under- or over-estimate excess sulfide at different sediment horizons.

Sediments are not closed systems and have enormous variability due to the many behavioral and ecological processes operating simultaneously in natural systems. Ecological processes that can affect exposure include migration and emigration, exposure time, life history or life cycle strategies, habitat effects (i.e., benthic and pelagic species have very different exposure histories), and feeding modes.

The question, then, is for what range of benthos would ESG be protective? Would the ESG protect animals whose exposures to sediments and pore waters occur via oxidized burrows or micro-environments, where AVS does not persist? Macrofauna that live in sediments employ diverse strategies for obtaining oxygen; these strategies are implemented at scales very different than those used to sample sediments for AVS. AVS studies have not systematically evaluated the relevance of different sampling methodologies to different fauna. Of paramount importance is the question of whether protocols for sampling a fixed layer of surface sediments (e.g., 2 or 3 cm) replicate the AVS experienced by, for example, animals that live on or near the oxidized sediment surface, animals that irrigate sediment burrows with oxidized water from the surface, or animals that migrate out of the sediment periodically. This difficulty is compounded by the fact that the oxidized layer of sediments varies widely in depth among sediments. The concern with the relevance of sediment sampling is supported by studies by Hare et al. (1994) and Warren et al. (1998). These studies directly showed that the response of lake benthos to SEM-AVS predictions of bioavailability varied greatly among several species. The methodology was predictive of metal bioavailability for chironomid species that lived within the deeper sediments. It was not applicable to other benthos. The latter group had life strategies that avoided the anoxic horizons of the sediments, a common biological strategy.

The biogeochemical issues are likely different in coastal marine systems and freshwater systems. Coastal systems are relatively more open compared to more closed freshwater systems. In addition, the chemical milieu of coastal systems is more complex with mixing of fresh and sea water, various sources and sinks of organic matter, widespread availability of sulfate, and complex interactions of various anaerobic respiration pathways. The presence of sulfate is especially important because it will limit the production of sulfide, and thus the availability of excess sulfides. The interaction between metal deposition gradients and spatially and temporally variable geochemical gradients in estuaries needs to be considered in the design of sediment sampling protocols.

In summary, ecological processes limit the applicability of equilibrium partitioning to predict bioavailability, particularly in coastal systems. In each case, the net effect appears to be an underestimation of exposure. In addition, the interactions of these complex ecological processes explain the high variability of geochemical measurements made in sediments and lead to methodological difficulties in applying the SEM-AVS guidelines. As a result, the Agency should amend its conceptual model for water column and sediment criteria to incorporate ecological processes and resulting exposure pathways. In addition it is crucial that the Agency develop a sampling methodology (for SEM, AVS, and other sediment assessment measurements) that accounts for the complex vertical gradients caused by ecological processes.

Effects—It is also time to turn greater attention to the role of biology, including differential sensitivities for different life stages of a species and inter-species differences, in predicting toxic effects from sediment metals. The Metals Mixtures ESG document notes that mortality in laboratory and spiked field samples as a function of SEM-AVS was organism independent (p. 1-42). However, in Figure 3-1 it appears that midges always had low mortality and the polychaete always had high mortality. Only the amphipods appear to exhibit the full range of mortality across the full range of concentrations. Part of the problem is fewer tests at low ranges for polychaetes and high ranges for midges. The document should discuss more fully the importance of differences in species sensitivity and the implications of these differences for application of the ESG.

There is a complex explanation for differential species responses based on ecological processes. Table 3-1 of the Metals Mixtures ESG document contains data that show toxicity in oxic environments when AVS is non-detectable and SEM is high, and in contrast that anaerobic environments are not toxic when AVS is high and SEM is low. Therefore, it follows that infaunal or burrowing species would have adaptations such that they are tolerant to high AVS, but sensitive to metals. Epibenthic or surface crawlers would be the opposite. This is supported by the observations that *Capitella*, a burrowing deposit feeder, has high mortality (Figs. 3-1 to 3-6) compared to *Neanthes*, a surface-dwelling polychaete (pages 1-74, 75). Because of different feeding strategies, burrowers tend to be deposit feeders and surface dwellers tend to be omnivores, burrowers can have higher metal loads due to direct sediment ingestion, whereas surface dwellers may be exposed to metals primarily from ingestion of water and contaminated prey. In addition, metals may bind to organic particles, which deposit feeders select by an unknown mechanism. So, it is possible that the net result

is burrowers have the highest exposure to metals through gut linings, which are acidic and could release metals for absorption, and are more sensitive to exposure.

The data presented on predicting organism toxicity by SEM-AVS normalized for organic matter in the laboratory, field, and colonization experiments is convincing. The selection of test organisms and the confinement in field experiments, however, is always a worry in toxicity testing. Getting around the confinement problem in chronic tests by using colonization substrates raises the question about representativeness of the colonizing organisms. In the case of the selected metals, a functional approach to the selection of test organisms would seem useful. That is, the organisms that have been used or would be potentially considered for use in laboratory or field testing to support the ESG could be categorized functionally on the basis of the expected site of action of the metal as predicted from their morphology (e.g., exposed gills, poorly protected cutaneous surfaces) or feeding behavior (e.g., ingestors of fine particulate organic matter [FPOM]). Among the invertebrates, ingestion categories of most direct importance would be filter or suspension feeders (FPOM filtering collectors) and sediment ingestors or deposit feeders (FPOM gathering collectors). Other functional groups, such as coarse particulate organic matter (CPOM) detritivores (shredders), benthic algal grazers (scrapers), and predators would experience exposure indirectly through food chain accumulation. With regard to digestive surface exposure, obligate sediment ingestors would be the choice to represent maximum effects.

A case in point concerning the appropriateness of test organisms to support the ESG would be the comparison between the freshwater amphipod *Hyaella*, which is a facultative periphytic algal scraper, and the snail *Helisoma*, which is an obligate algal scraper. Neither would be expected to ingest much sediment, except that associated with algal colonies. Most larval midges in the tribe Chironomini (e.g., *Chironomus tentans*) would be expected to ingest primarily sediments because they are benthic deposit feeders. The obligate filter feeders, such as bivalve mollusks and some marine polychaetes, would be predicted to exhibit maximum response to all metal-organic complexes in the interstitial water. A further important separation of test organisms would be their ability to withstand anaerobic conditions, which would significantly effect metal bioavailability. For example, the ability of many Chironomini midge larvae to withstand anaerobic conditions should be considered in their selection of test organisms to support ESG. The above considerations should be given at least equal status with ease of collection and/or culture when selecting test organisms.

It would be useful to include in the ESG document a table summarizing the functional attributes of the test organisms that were used in the laboratory and field studies supporting the ESG.

5. APPROPRIATE USE OF THE PROPOSED SEM-AVS METHODOLOGY

5.1 Accounting for Spatial and Temporal Variability

If the SEM-AVS method is to be used to help classify sediments as toxic or not toxic, then such use of this measure will depend upon the accurate characterization of the SEM-AVS for the sediments of interest. This characterization probably will be statistical. For any system, SEM-AVS values will vary in time and space as the integration of spatial-temporal variation in inputs of metals to surface waters and the variability or periodicity (e.g., seasonal) in the physical (i.e., advection, dispersion, sedimentation, sediment resuspension, sediment particle size), chemical (i.e., chelation, complexation, precipitation, sediment type), and biological (i.e., bioaccumulation, sequestration, trophic interactions) processes that determine the transport, distribution, and fate of metals in sediments. AVS concentrations in sediments vary vertically due to oxidation of surficial sediments, bioturbation of sediments, seasonal changes in the concentration of oxygen in overlying waters, and varying activity of sulfur-reducing microbes. Microbial activity also varies with depth in sediments depending on supply of organic material, availability of sulfate, and sediment substrate type.

Given these sources of variability, appropriate sampling designs will be necessary to apply the SEM-AVS methodology in specific locations. For example, the biologically active zone of the surficial sediments should be included in sampling; the depth to which sediment samples are routinely taken must be determined based on data and good science, rather than an arbitrary depth such as 2 cm. It is likely that no single depth value will be appropriate for all sediments across the nation because the redox-discontinuity zone varies in space and time, and with sediment texture, circulation patterns, and supply of organic material. Samples should be taken periodically, in relation to the physical mixing characteristics (e.g., stratification, turn-over) and seasonal changes of production dynamics. Spatial and temporal variability in the oxidation-reduction (redox) potential of the sediments should also be quantified in developing sediment sampling designs on a site-specific basis; typically, the deeper the sample, the more reduced (anoxic) sediment is included. The characteristic variability in space and time of environmental processes that determine SEM-AVS measures, combined with the area and depth, of the sediment system of interest, will likely constrain the statistical power of practical and affordable sampling designs. An important implication of such variability is that sediments might only be classified as toxic or non-toxic in probabilistic terms with an associated risk of incorrect classification.

One possible way to address such concerns would be to attempt to characterize the nature of the variance of the physical, chemical, and biological processes for different types of aquatic systems. Such information might be used to develop a general model for quantifying the variability of SEM-AVS measures and using this information to a) estimate the performance characteristics for statistical designation of sediments as toxic or not toxic, and b) identify which of the controlling processes contributed the major components of variation in SEM-AVS measures. The results of the latter

“sensitivity” analysis might be used to effectively and economically allocate resources toward sufficiently powerful sampling designs that would result in sediment classifications that met pre-specified (risk-based) criteria for accuracy and reliability. Such quantification of characteristic variability in sediment environments might require substantial investments in basic measurements and monitoring if existing data prove inadequate.

In addition to the inherent variability of AVS concentrations in the field, AVS and the geochemical milieu of sediments are notoriously difficult to sample, preserve, and measure correctly. Sulfide is volatile and easily oxidized, and sediment disruption and oxidation results from the act of sampling and analysis.

In its 1995 review, the SAB raised concerns about the applicability of the SEM-AVS method in the field, where it will be applied in a regulatory context. The current Metals Mixtures ESG document does not provide additional confidence in the method with regard to these concerns. For example, it does not appropriately reflect the limitations of the method when it specifies that the ESG "are intended to apply to sediments permanently inundated with water, intertidal sediment, and to sediments periodically inundated for durations sufficient to permit development of benthic assemblages" (p.1 -15); sediments that are periodically exposed would experience oxidation of sulfides, with potential release of bound metals. Similarly, guidance regarding the collection of samples does not reflect the fact that AVS and SEM can vary considerably within the top 2 cm. The oxidized zone is where most species concentrate their interaction with their environment and where AVS concentrations are lowest; the implications of fixed depth sampling, relative to concentrated sampling in the oxidized zones should be evaluated. Development of the protocol also should address variability of AVS concentrations as measured by recommended sampling protocols, as compared to variability in oxidized sediments carefully collected from the sediment-water interface.

The Committee recognizes that sampling protocols must be practical. Simplifying assumptions, however, should be applied only with full recognition of the potential to over- or under-estimate adverse biological effects. With this in mind, we suggest that the following questions be considered in the design of sampling protocols: Where does one sample? How does vertical sampling, or pooling sediments over different sediment horizons, affect the applicability of the SEM-AVS model? Does it matter if there are excess sulfides deep in sediments, but not in surface sediments? How is bioavailability influenced by bioturbation or sediment turnover? How does the SEM-AVS model perform in the context of temporally varying salinity gradients in the same locations over temporal scales relevant to tidal cycles, and long-term hydrological cycles (e.g., floods and droughts, and stochastic storm events)? The answers to these questions would incorporate the complexity introduced by ecological processes and increase the ability of the SEM-AVS method to predict metals bioavailability.

In short, it is most important that a highly specific sampling protocol be developed to guide regulatory applications of SEM-AVS methodologies. If sampling protocols result in inconsistencies or inappropriate estimates of AVS, then inaccurate predictions of “non-toxic” or “toxic” sediments may occur. It does not appear that systematic studies necessary to develop such a protocol have been conducted in environments where the protocol would potentially be implemented for regulatory purposes.

5.2 When the Methodology Does Not Apply

Using the SEM-AVS methodology, perhaps normalized to sediment organic carbon content, to classify sediments as toxic or non-toxic may prove ill advised under certain circumstances. As discussed above, the method might not be effective in assessing sediment toxicity where the primary route of exposure for organisms of concern is ingestion of contaminated prey, although the SEM-AVS measures might assist in characterizing prey contamination from direct exposure to metals in sediments or pore water. In addition, if the spatial distributions of different sediment types (e.g., sand, silts, clays), redox potentials, and fractions organic content are highly variable within the system of concern, the SEM-AVS methodology may prove impractical because of the necessary sampling design required to accurately describe such variability. This limitation might be further compounded by spatial and temporal variability in the distribution and abundance of sediment dwelling organisms (i.e., bioturbation), including sulfate reducing bacteria. Finally, if the sediments of concern are typically well oxidized, the proposed methodology also will be of little use in assessing bioavailability and toxicity of sediment metals.

The ESG states that the proposed guideline approaches “are not designed to protect aquatic systems from metal release associated, for example, with sediment suspension.” The Committee agrees that the Metals Mixtures ESG should not be used as a “no effect” threshold in aquatic environments where sediment resuspension or transport is expected because sediment resuspension greatly increases the potential for re-oxidation of AVS-bound metals. This limitation in the ESG is important because sediment suspension, whether associated with extreme storm events, tidal or riverine transport, dredging operations, or other activities, is quite common in aquatic systems. We recommend that the Agency consider how sediments should be assessed in high energy zones and provide further guidance in the future. A similar caveat should be added to the guideline statement for sediments whose redox conditions are likely to change due to periodic exposures associated with tidal fluctuations or seasonal changes. The Committee recommends that these limitations of the SEM-AVS approach be incorporated into both the Metals Mixtures ESG and the sediment user’s guide to assure that the SEM-AVS methodology is not mistakenly used where it is inappropriate.

6. AGENCY-PROPOSED MODIFICATIONS TO THE SEM-AVS METHODOLOGY

6.1 Organic Carbon Normalization

Charge Question 1: By incorporating the fraction organic carbon into the bioavailability equation, has the Agency retained the protective features of the guidelines and improved its predictiveness of toxic effects?

The Metals Mixtures ESG is based on the assumption that bioavailability and any subsequent toxicity are predicted by relationships among metal concentrations in sediments, pore water, and tissue. Although equilibrium partitioning provides a mechanistic basis for predicting the partitioning of metals between particulate and dissolved compartments (i.e., pools), the associated relationships between partitioning and metal toxicity are based on empirical observations that are characterized by large variances. The fraction organic carbon (foc) normalized approach is an extension of the EqP methodology developed for non-ionic organic chemicals. It recognizes that divalent metals in anaerobic sediments will bind to sulfides first until the labile sulfides are exhausted and then will bind to other phases such as organic carbon. The incorporation of this binding phase into the bioavailability equation therefore improves the overall ability of the SEM-AVS method to identify sediments that are toxic.

The primary limitations identified by the Committee include potential implications of the foc normalized SEM-AVS methodology for accurately assessing biological exposure to metals and translating exposures to estimates of toxic response, both acute and chronic. Regarding exposure estimation, the foc normalization provides a largely theoretical explanation for metal toxicity data that were not consistent with previous equilibrium-based analyses of sediment exposure and toxicity. It has been proposed that organic carbon reduces the bioavailability of metals. As suggested by results shown in Figure 3-1 of the Metals Mixtures ESG document, the normalization of SEM-AVS to fraction organic content reduced the variability in the exposure estimates. However, there remain some important issues that might realistically constrain the general applicability of the foc normalization. We point out that some studies have shown inconsistent results, indicating that foc normalization does not appear to reduce bioavailability of metals consistently. Additionally, test results appear to be dependent in part on the nature of the organic carbon (Lee and Luoma, 1998). Such inconsistencies may lead to inappropriate applications of the foc normalization with subsequent incorrect conclusions that particular sediments are probably not toxic.

Further, while the foc normalization generally might increase the precision of exposure estimates for metals, there was not necessarily a corresponding improvement in the precision of the estimated toxic response to exposure, particularly in the analysis of field sediment samples. Mortalities for many of the organisms of interest ranged between nearly 0 and 100% across foc normalized estimates of exposure to metals. Such variability in toxic response reduces the power of this methodology for

developing the exposure-response functions that are essential for risk assessment. Similarly, estimates of acute toxicity (lower bound exposures adjusted to organic carbon) did not correctly identify many sediments as nontoxic as determined from sediment bioassay results. Nevertheless, the Committee recognized that the foc normalization did seem to improve the relationship between exposure and response in the analysis of limited field data for aquatic midges. Additionally, the methodology also improved the ability to quantify the upper bound exposure that defined a 95% chance that amphipod mortality would exceed 50% under laboratory test conditions. However, the Committee was concerned that the overall methodology is primarily empirical and that the foc normalization might improve the effectiveness of the SEM-AVS method only for those conditions where the collected data pertain to the actual form of the metals that are biologically available and toxic.

Another concern lies in the spatial and temporal variability of sediment organic carbon content. Physical, chemical, and biological processes that determine the input, transport, and ultimate distribution of carbon exhibit characteristic scales of variability (e.g., seasonal) that must be considered in the design of sampling programs aimed at accurately and precisely measuring organic carbon in sediments. Similarly, the foc normalization does not improve the ability of the SEM-AVS method to characterize the toxicity of aerobic (or oxidized) sediments. This limitation also applies to oxic microclimates often created by sediment dwelling organisms and to variations of AVS caused by bioturbation in surficial sediments (e.g., top 2 centimeters). Finally, the foc normalized SEM-AVS method does not address dietary routes of exposure to metals in the sediment environment; many sediment dwelling organisms direct their feeding activities on available carbon when they ingest sediments.

In summary, the incorporation of the foc into the SEM-AVS methodology improves the overall ability of the approach to predict when sediments are likely to be toxic to benthic invertebrates. With foc normalization, the method has a precision of about one order of magnitude, which is an improvement of a factor of 10. The Committee believes the SEM-AVS normalized to foc content is an appropriate method for screening and establishing priorities among contaminated sediments. This method, however, should be applied with caution and used in combination with other approaches including sediment bioassays and or field bioassessments. The Committee does not support the use of the foc normalized SEM-AVS as a stand-alone, definitive method for identifying “toxic” and/or “non-toxic” sediments without supporting biological data.

6.2 Application of the Biotic Ligand Model (BLM) to Sediment Guidelines

Charge Question 2: If the BLM is used to derive or adjust a water quality criterion, is the revised criterion appropriate for use in the interstitial water component of the Metals Mixtures ESG?

As noted in a companion SAB report (EPA-SAB-EPEC-00-006) on the Biotic Ligand Model, the Committee is optimistic that the BLM represents a technical improvement in the state-of-the-science for assessing bioavailability of metals in water over a wider array of environmental conditions than previously used. The BLM methodology also offers advantages over the currently used Water-Effect Ratio (WER) approach in the derivation of site-specific acute water quality criteria. It appears that a logical next step would be to evaluate/validate the BLM for application to sediments via the interstitial water component of the Metals Mixtures ESG. If this approach is successful, it would allow for additional variables, such as dissolved organic carbon (DOC), to be accounted for in the assessment of bioavailability of metals in sediment pore waters.

In theory, the BLM would be applicable to sediment interstitial water because hardness, pH, and DOC are important toxicity modifying factors for interstitial waters, as they are in overlying waters. However, several important issues require additional attention before the Committee would recommend the general application of the BLM to sediments or sediment pore waters. First, the BLM currently has been validated to varying degrees for only two metals, with few benthic species and/or pore water test procedures (EPA-SAB-EPEC-00-006). The Metals Mixtures ESG, on the other hand, includes a number of other metals for which the BLM has not been sufficiently validated. Second, the BLM was originally developed for conditions characteristic of the water column. By comparison, the chemistry of interstitial water, including the relationships between particulate and dissolved organic carbon and the binding of metals, is less well understood and characterized. Pore waters may contain different kinds and higher concentrations of constituents than the water column immediately above. A critical component of verifying the model, therefore, will be demonstrating its ability to appropriately predict binding to pore water DOC under a variety of different conditions. It would be useful to initiate further testing of the BLM with mixtures of metals in pore water matrices, compared against SEM predictions, in order to determine its effectiveness for predicting net toxicity of pore water under varying chemical conditions. An interesting experiment would be to physically concentrate overlying water above sediments to achieve the same approximate DOC concentration as in the pore water below, then test each in bioassay in the absence of sediment to see if pore water is “just more concentrated overlying water.” In short, experiments are needed over much wider concentration ranges and with interactions of various DOC constituents found in pore water before adopting the use of the BLM for sediments.

A BLM-adjusted WQC would not be appropriate for use in the interstitial water component of the Metals Mixtures ESG because the site-specific water chemistry used to derive the adjusted criterion would not be the same as the water chemistry of the pore water (even from the same site). The BLM-adjusted WQC is specific to a given site, as is a WER-adjusted value. Application of the BLM to

interstitial water would require measurements of the site interstitial water chemistry (pH, DOC, hardness, etc).

Alternatively, if the BLM were used to derive a metal-specific (e.g., copper) equation or algorithm which would replace the existing acute hardness equation in a national water quality criterion, the new equation/algorithm would, in theory, be applicable to sediment interstitial water; however, site-specific pore water chemistry data would still be needed to apply the algorithm to interstitial water. The currently proposed IW component of the Metals Mixtures ESG relies on comparison of the IW metals concentration to the water quality criteria Final Chronic Value for each metal, corrected only for site-specific hardness; the BLM, if validated for application to interstitial water, would allow consideration of additional site-specific chemistry conditions that affect metals bioavailability.

In summary, the Committee is encouraged by the BLM 's performance for predicting toxicity of metals in the water column, and believes there is potential to apply it to assessing the toxicity of metals in pore waters. At the same time, the Committee believes further research is needed to demonstrate the model's performance for interstitial water applications.

6.3 Inclusion of Chromium and Silver in the Sediment Guidelines

Charge Question 3: Are the data presented from lab and field experiments with chromium and silver sufficient to support their addition to the Metals Mixtures ESG?

The information presented to the Committee indicates that when sufficient AVS is present in sediment, the binding/precipitation of chromium and silver will prevent acute toxicity from occurring much the same as has been demonstrated for divalent metals. The Committee is encouraged by these data and supports the Agency's desire to further evaluate the EqP approach to determine its application to silver and chromium. However, at the present time the Committee has reservations about including either of these metals in the ESG without further research. Committee concerns are the following:

- a) Most of the data available to assess the methodology are based on acute toxicity and the data sets are not extensive. For example, the chromium test results presented in Table 3-1 (p. 1-58) did not provide sufficient insight into acute toxicity at lower IWTUs (less than 100).
- b) Additional chronic toxicity studies are needed to verify model application to assessing chronic toxicity for chromium;
- c) Conditions under which Chromium (III) can be oxidized to Chromium (VI) have not been fully explored and this oxidation could provide a means whereby a more toxic form of chromium is available to cause effects. Cr(VI) appears to be the

most bioavailable form of dissolved chromium, but uptake is slow enough that long term studies are needed to evaluate potential effects.

- d) Conditions under which MnO_2 are expected in sediments should be identified since this chemical can oxidize Cr(III) to Cr(VI).
- e) Cr (III) is absorbed by bivalves and polychaetes from some food types that might occur in sediments (Wang et al., 1997).
- f) Biokinetic studies indicate that low assimilation rate of Cr (III) from highly contaminated sediments represents a significant route of exposure (Wang et al., 1997).
- g) SEM-AVS and EqP theory predict that silver should almost never be bioavailable and cause toxicity when found in sediments with $[\text{AVS}] \geq [\text{Ag}]/2$. However, both laboratory and field studies indicate this is not the case. As a result, application of the SEM-AVS approach to silver may not be protective of benthic organisms.
- h) There are insufficient chronic data for silver.
- i) The data presented in Figure 8, p. 2-36, are not entirely consistent with the theory that AVS binding/reactions with silver should eliminate all toxicity when sufficient AVS is present. In the graphs presented, the AVS normalization of the data does not provide the same clear demonstration that AVS binding eliminates silver toxicity as has been shown for other metals.
- j) Figure B on p. 2-63 shows acute mortality of $>24\%$ at $\text{IWTU} < 0.5$. This appears inconsistent with the Guidelines and with the interpretive table on p. 2-60.

These concerns suggest that additional research is needed before incorporating chromium and silver into the ESG.

7. AN INTEGRATED APPROACH TO METALS

In presentation materials and briefing documents supplied to the Committee, the Agency defined its vision for an integrated metals methodology that would lead to a consistent set of metals criteria for the “total aquatic environment” (i.e., both sediments and overlying waters). This integrated methodology included the proposed ESG and proposed applications of the Biotic Ligand Model for water column and sediment pore water assessments of bioavailability, as well as possible future development of tissue residue-based criteria. In addition to specific comments on the BLM and the Metals Mixtures ESG, the Charge to the Committee asked:

Does this integrated metals methodology improve our ability to make both protective and predictive assessments of toxicity due to copper, silver and other selected metals in the water column and sediment?

The Committee supports the Agency’s quest for an integrated approach to assessment and regulation of metals in the environment. A useful approach for understanding the relationships among environmental compartments, drivers, exposure pathways, and the various water and sediment criteria measures is to construct a conceptual model. During the presentation to the Committee, such a model was used to highlight the Agency’s vision for the inter-relationships among the various criteria and to highlight areas where additional work will be needed (Figure 1). In addition to guiding the Agency’s own efforts to integrate management of water and sediments, a conceptual model of this type would be a critical component of the Sediment Guidelines User’s Guide and the technical guidance documents such as the Metals Mixtures ESG, so that users are informed of the interrelationships among various standards and guidelines.

The Committee noted, however, that the conceptual model presented does not include some potentially important considerations. The labeling of suspended metals as “not bioavailable” raises particular concern because suspended solids in the water column bind metals and are a major source of food for filter feeders. In addition, the conceptual model appears to assume that SEM-AVS can be used as a stand-alone test of the bioavailability of metals in sediments. We recommend that the Agency consider carefully the limitations discussed in Sections 4 and 5 of this review when revising its conceptual model.

Other components that the Agency should consider incorporating in a conceptual model include a) the biological role of organic matter complexes as partitioning phases in both the water column and sediment components of the model, and b) the distinction between the sites of biological action of the metal toxicity, namely respiratory, cutaneous, and digestive surfaces. The dissolved organic complexes are undoubtedly important in interstitial sediment water. In particular, sediment-ingesting invertebrates will engulf both organic and mineral particles in the correct size range and, therefore, adsorption of metals to mineral sediment and complexing with dissolved organic matter

to form fine particulate organic matter (FPOM)--and the equilibria between these components and the pore water-- are important to factor into the general model. The distinction between the sites of biological action that are relevant for water column vs. sediment exposures will bear directly on the choice of organisms to be used to evaluate effects of metal contamination. If complexing with dissolved organic matter is introduced, then food chain effects can be considered in both water column and sediment environmental compartments. Similarly the free solution (non-complexed) form of the metals can directly affect respiratory and cutaneous surfaces in both compartments. It is likely that the food chain effects shown in Figure 1 would almost always be mediated through uptake from (microbial) or ingestion of (invertebrates) organic particulate complexes.

A possible means of incorporating these additional considerations into a conceptual model is illustrated in Figures 2 and 2a. The scientific picture of water/sediment/biota interactions presented in these figures could be supplemented with notations relating to Agency standards and guidelines, as was done in Figure 1.

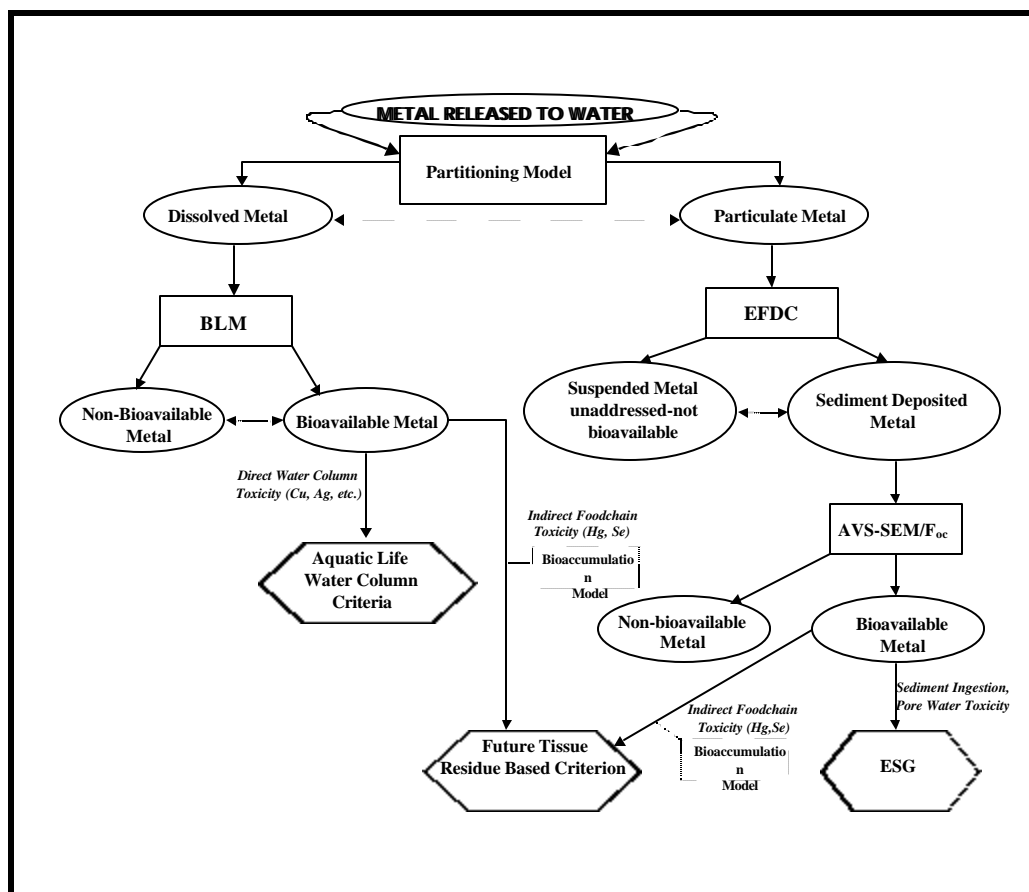


Figure 1. Agency Briefing Slide

As part of its attempt to integrate water and sediment criteria and guidelines, the Agency has suggested that the Biotic Ligand Model (BLM) methodology could be incorporated into both. While the use of the BLM with the ESG shows promise and clearly warrants additional research, our theory and understanding of complex geochemical and biological interactions in sediment/water systems is not yet sufficiently advanced to enable adoption of a single unified set of criteria to ensure protection of both pelagic and benthic organisms. There is no evidence to suggest that this cannot be achieved over time by gaining further experience with the BLM in pore water tests, but at present the BLM cannot replace the need for sediment and interstitial water evaluation by empirical bioassay procedures (EPA-SAB-EPEC-00-006). The ESG and BLM do not yet provide a sufficient basis upon which to assess and manage water quality concerns associated with contaminated sediment/water systems. The BLM is a predictive, but not a definitive, tool for setting acute toxicological criteria for either matrix. Furthermore, it does not address important additional considerations for sound water quality management, including chronic effects mediated by non-dissolved metal species, and acute mechanisms of action and routes of exposure not directly related to impairment of physiological function or uptake at the external surface of the organism.

EPEC applauds the Agency's efforts to produce an integrated water/sediment management system. We suggest that a revised conceptual model is essential to this endeavor. The conceptual model can be used to assess whether environmental compartments or routes of exposure are being addressed and also to assess whether the Agency's guidance is inadvertently providing incentives to accumulate metals in one compartment versus another. It may not be necessary to use the same assessment method (such as the BLM) in both water and sediments to achieve these purposes. While the BLM is not yet ready for application in both water and sediment methodologies, this does not mean that the Agency has failed to improve its integration of water and sediment management. Appropriate use of the SEM-AVS methodology, along with development of assessment methods for the elements of the conceptual model that are still unaddressed, will greatly improve the Agency's ability to protect the "total aquatic environment" from toxic effects due to metals.

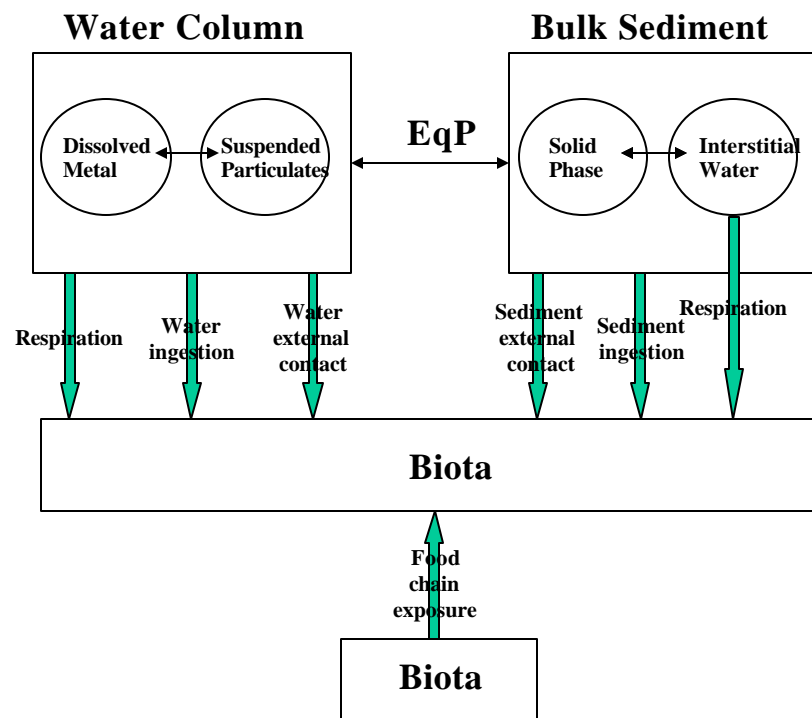


Figure 2. Multipathway Exposure Model

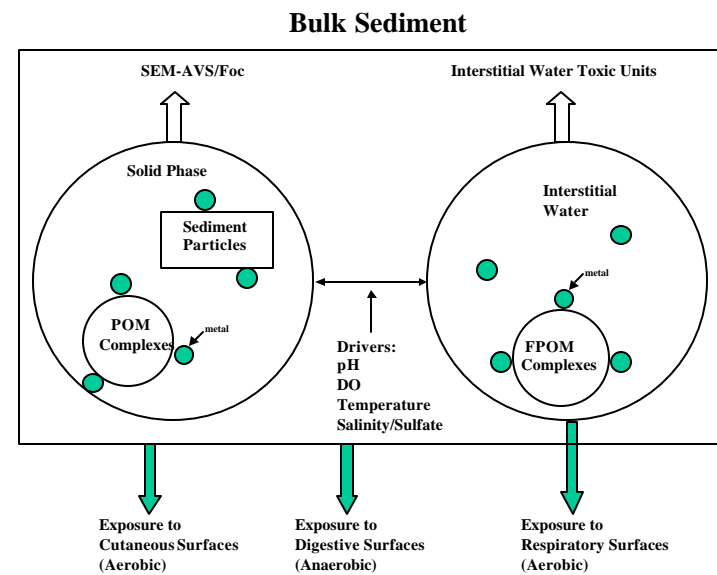


Figure 2a. Detail of Bulk Sediment Compartment

8. SUMMARY

The Agency and its funded scientists have developed an elegant body of scientific work showing that the availability of metals in sediments, as modeled by the excess of SEM over AVS, correlates well with observed toxicity in a range of laboratory studies. The development of a Metals Mixtures ESG that incorporates the SEM-AVS theory is an important endeavor and one that the Committee supports. Work conducted since the previous SAB review of the methodology—including field manipulation experiments and a limited number of chronic studies of metals toxicity—is a step in the right direction, and the work relating organic carbon normalization of the SEM-AVS to observed toxicity is well done and enhances the ESG approach. Moreover, promoting the routine measurement of AVS in addition to total organic carbon (TOC) is sound advice. However, there are underlying limitations to the applicability of the SEM-AVS approach that are not addressed by organic carbon normalization. The Agency has not yet convincingly shown that the SEM-AVS model adequately describes the realities of metals exposure in the environment and there are reasons to believe that premature application of the ESG could yield inconsistent results, especially in the absence of a peer-reviewed sampling protocol. The most common result may be to incorrectly identify sediments as “not toxic” when that is not the case.

In this report, the Committee comments on the proposed modifications to the ESG approach and suggests that the Agency focus future research efforts on better understanding the biological and ecological—to complement chemical—aspects of metals toxicity in the aquatic environment. The report reflects the Committee’s conclusion that, although introduction of “chemical corrections” such as organic carbon normalization into the ESG calculations might reduce the variability in toxicity as a function of SEM-AVS, such corrections do not address the underlying question of the method’s applicability in a variety of field conditions. In order to further validate the applicability of the ESG model in the field, greater attention needs to be given to biological questions, e.g., the possibility of chronic effects of sediment metals in sediments with low metal-binding capacity or less than extreme metal concentrations; the relative importance of dietary exposures to metals and metal sulfides; drivers of bioavailability in the gut of benthic organisms; differential toxicities among benthic species; and the role of behavior and microhabitat in moderating exposure to sediment metals. These research questions primarily relate to the use of the SEM-AVS method to identify “no effects” levels of sediment contamination. For this reason, the Committee recommends that additional experimental work be undertaken to verify the applicability of the proposed methods in the field and/or to develop complementary tools with which to predict toxicity of metals in environments where the assumptions of the ESG approach cannot be met. Specific concerns exist for bioaccumulation and chronic toxicity in aerobic sediments with low AVS and low organic carbon.

The Committee reiterates a number of concerns with the EqP approach that were outlined in the 1995 SAB review of the proposed EqP-based criteria for five metals, and emphasizes that a number of these concerns remain valid today. While the ESG document may clearly acknowledge the

limitations of the method's applicability, these limitations make it vital that the Agency provide clear guidance to potential users regarding real world applications. The Committee understands that such guidance (including applicability of the ESG method to the dredged material program) will be included in a "Sediment Guidelines User's Guide" under preparation by the Agency. This User's Guide should also undergo careful peer review to ensure that the various sediment assessment tools are not applied outside their validated conditions.

In response to the Charge questions, the Committee concludes that: a) the incorporation of the fraction organic carbon (foc) into the SEM-AVS methodology improves the overall ability of the approach to predict when sediments are likely to be toxic to benthic invertebrates, but does not render the method suitable for use as a stand-alone method for identifying "toxic" and/or "non-toxic" sediments without supporting biological data; b) the Biotic Ligand Model should be validated for pore water applications before being used in the Interstitial Water component of the Metals Mixtures ESG; and c) further research is required before adding either chromium or silver to the Metals Mixtures ESG.

For these reasons, the Committee recommends that SEM-AVS be incorporated into sediment assessment guidelines in a way that assures that SEM-AVS will continue to be used **in conjunction with** other assessment tools to characterize the safety of sediments, rather than being used as a stand-alone test. The SEM-AVS method may be particularly useful to prioritize sites requiring attention and to explain situations when bioassays show a lack of toxicity even though metal concentrations in sediments are high. The Committee strongly recommends that the Agency now turn its attention to the appropriate application of SEM-AVS in the field and thereafter to other methods of assessing sediment quality that can be used when SEM-AVS cannot.

The Committee applauds the Agency's efforts to integrate its approaches to the management of water column and sediment metals, while noting that the conceptual model presented to the Committee describing the relationships among environmental compartments, exposure pathways, and criteria measures was incomplete. The Committee urges the Agency to develop a refined conceptual model that incorporates all partitioning phases and routes of exposure in order to guide the Agency's long-term efforts to integrate water column and sediment standards and to assist users to apply current standards and guidelines appropriately.

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APPENDIX A: ACRONYMS AND ABBREVIATIONS

AVS	Acid Volatile Sulfide
BLM	Biotic Ligand Model
CPOM	Coarse Particulate Organic Matter
DOC	Dissolved Organic Carbon
EqP	Equilibrium Partitioning
ESG	Equilibrium Sediment Guidelines
FCV	Final Chronic Value
foc	fraction organic carbon
FPOM	Fine Particulate Organic Matter
IW	Interstitial Water
IWTU	Interstitial Water Toxic Unit
SEM	Simultaneously Extracted Metal
TOC	Total Organic Carbon
WER	Water-Effect Ratio
WQC	Water Quality Criteria

APPENDIX B. RESEARCH ON THE SIGNIFICANCE OF DIETARY BIOACCUMULATION OF METALS

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AN SAB REPORT: REVIEW OF AN INTEGRATED APPROACH TO METALS ASSESSMENT IN SURFACE WATERS AND SEDIMENTS

**PREPARED BY THE ECOLOGICAL
PROCESSES AND EFFECTS
COMMITTEE OF THE SCIENCE
ADVISORY BOARD**