

## USE OF THE SEM AND AVS APPROACH IN PREDICTING METAL TOXICITY IN SEDIMENTS

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It is critically important to consider bioavailability when developing water quality criteria (WQC) and sediment quality guidelines (SQGs). This is one of the most important lessons learned as WQC and SQGs have evolved over the previous 30 years. Bioavailability is particularly important for metals, as they are present in a variety of forms (metal species) in aquatic settings, and these species may differ widely in their degree of availability to aquatic organisms.

The need to consider bioavailability of metals in sediments was motivated by the common observation that similar dry weight metal concentrations (e.g.  $\mu\text{g}$  metal/g dry sediment) exhibit a wide range of effects on sediment organisms when the

sediments are from different locations and have varying properties. This finding is demonstrated in Figure 1, where mortality may vary widely at a fixed sediment concentration. The challenge in deriving meaningful sediment quality guidelines is to learn why these differences in effects occur and to devise a method that accounts for these differences.

A classification method has been developed to quantify the uncertainty in the range over which correct predictions are made of the absence or presence of mortality of sediment-associated organisms (Di Toro et al. 2000). Sediment concentration data are categorized into three classes: absence of effects, uncertain effects and presence of effects. The dashed vertical lines on Figure 1 indicate the threshold concentration bounds that separate these groups. The lower bound represents the concentration below which the prediction of no toxicity is reliable with some prescribed (95%) probability. The upper bound represents the concentration above which toxicity is reliably predicted with this same probability. The interval between these upper and lower bounds represents the range over which the prediction of an effect is uncertain.

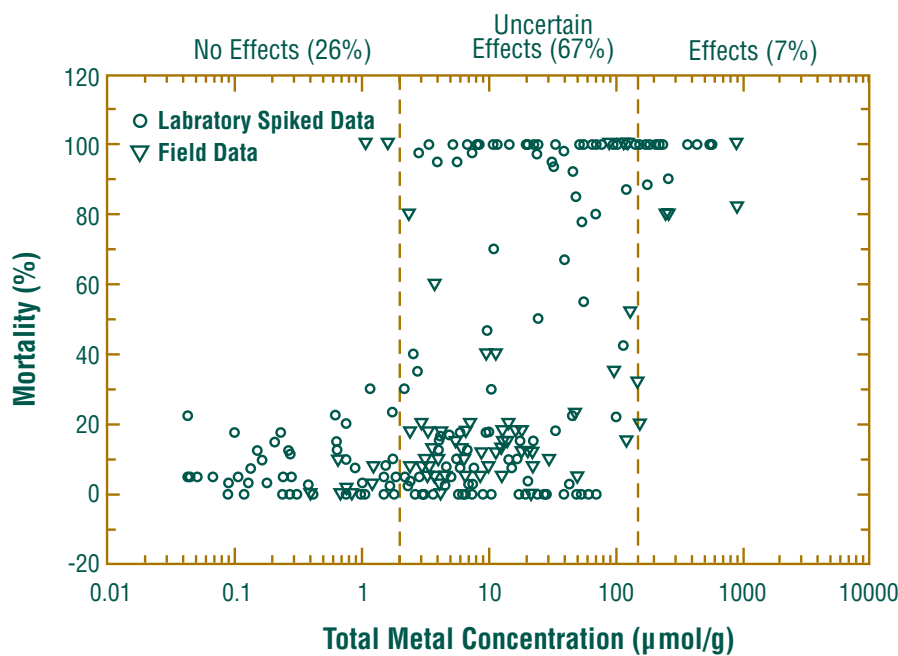
The analysis included exposures to five metals (cadmium, copper, lead, nickel and zinc) either as single metals or mixtures of metals in sediments. For dry weight total metal concentrations, the region of uncertain effects ranges from 2 to 150  $\mu\text{mol/g}$ , which represents approximately 67% of the data. Over this range of sediment metal concentrations, a concentration that is protective in one setting may not be protective in another

### Terminology

**Amphipods:** sediment-dwelling organisms that are mostly located in marine environments, but some are freshwater or terrestrial species

**Benthic sediment:** In an aquatic system, this is a porous medium that makes up the bottom of the water body. It is composed of particles and water, with the water filling the interstices between the particles. This water is commonly referred to as the sediment interstitial water or the sediment pore water.

**Stoichiometric:** the exact amount of a substance required in a chemical reaction, according to a balanced chemical equation



**Figure 1**

Mortality vs. total metal concentration (Di Toro et al. 2000)

setting. The reasons for the varying bioavailability thus need to be understood if sediment quality guidelines are to be established for metals that are appropriately protective of benthic organisms in sediments of differing types.

### *Equilibrium Partitioning*

The equilibrium partitioning (EqP) approach provides a method for incorporating bioavailability considerations into sediment criteria development. The general approach was originally applied to neutral organic chemicals (Di Toro et al. 1991). It was observed that the concentration–response curve for a biological effect was correlated to the interstitial water concentration ( $\mu\text{g/L}$ ), rather than the chemical's total sediment concentration (Adams et al. 1983). This observation provided the key insight into how to quantify the bioavailability of chemicals in sediments.

In addition, the pore water effects concentration, whether for organism mortality, growth or bioaccumulation, was essentially equal to the effects concentration in water-only exposures. Since pore water concentrations that are protective of aquatic life were known (i.e. the WQC has been shown to protect benthic organisms) (Di Toro et al. 1991), all that remained was to convert these pore water

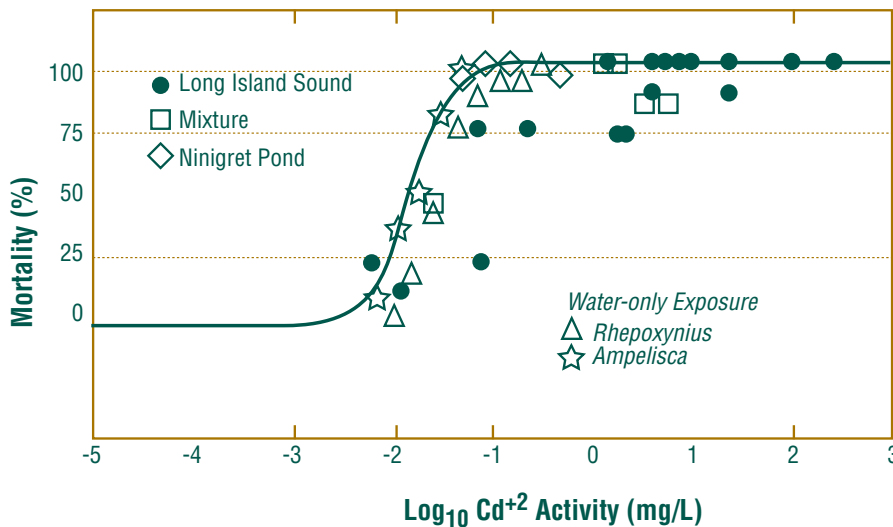
concentrations to bulk sediment concentrations. The term “equilibrium partitioning” reflects the idea that chemical concentrations associated with pore water, sediment and benthic organisms are in a state of equilibrium with each other, such that the concentration of any one is directly related to the others. As such, specification of a pore water concentration that is protective of benthic organisms is readily converted, via well-established sediment-water partitioning relationships, to a bulk sediment chemical concentration that is equivalent in degree of protection (Di Toro et al. 1991). This approach avoids the need to measure the pore water directly, which is a complicated undertaking.

Assuming EqP theory applies, the effects concentrations found for

water-only exposures should be essentially equivalent to effects concentrations in the interstitial water in sediment exposures. The observed mortality to amphipods in three sediments as a function of the interstitial water cadmium activity is shown in Figure 2 (Di Toro et al. 1990). Activity is similar to concentration except it considers the solution's ionic strength and the metal's charge. The water-only response data for two amphipods, *Ampelisca abdita* and *Rhepoxynius hudsoni*, are included for comparison. These data, along with many other examples (US EPA 2000), demonstrate the equivalence of organism response to metal concentrations in interstitial water and in water-only exposures.

### *Acid Volatile Sulphide*

Acid volatile sulphide (AVS) has been used to predict the toxicity in sediments of divalent metals, including copper (Cu), cadmium (Cd), nickel (Ni), lead (Pb) and zinc (Zn) (Di Toro et al. 1992; Ankley et al. 1996; Berry et al. 1996). The rationale is that the AVS present in a sediment reacts with the simultaneously extracted metal—SEM, the reactive metal fraction that is measured in the cold acid extract used to measure AVS. This reaction forms an insoluble metal sulphide that is relatively non-available for uptake by benthic organisms. The amount of AVS



**Figure 2**

Mortality vs. interstitial water cadmium activity for sediments and water-only exposure data (Di Toro et al. 1990)

present in sediments will therefore serve a critical role in setting the limits of metal availability and toxicity in sediments. The data that demonstrate the role of AVS are reviewed subsequently.

### Application to Metal Mixtures— Use of AVS and SEM

As alluded to above, sulphide is an important binding component in modelling metal sorption in sediments (Boulegue et al. 1982; Morse et al. 1987). Metal sulphides are very insoluble. In the presence of excess sulphide, most of the reactive metal will form insoluble metal sulphides. It is therefore critical to quantify the available sulphide when evaluating the relationship between free aqueous phase metal and solid phase metal in sediments. AVS is a very good measure of the portion of the solid phase sulphide that reacts with free metal (Di Toro et al. 1990).

The five divalent metals, Cd, Ni, Cu, Pb and Zn, will bind to sulphide. This means, in essence, that they will all exist in the form of their respective metal sulphide if the AVS is present at a concentration in excess of the reactive forms of the sediment metals. In this case, only low free metal concentrations would be present in the pore water and available to cause toxicity to the organism. On the other hand, if the total concentration of the SEMs is greater than the concentration of AVS, the excess fraction of the metals may potentially exist as free metal and could cause toxicity. It is stated that it could “potentially exist” as

free metal because other constituents in the sediment pore water (e.g. organic carbon) can bind the free metal, thereby reducing its availability to aquatic organisms and ultimately its toxicity.

The appropriate measure of the sediment metal concentration to use in comparing the concentration of sediment metals to AVS is the SEM concentration. As indicated above, this is the sum of all of the divalent metals that is extracted simultaneously with the sulphide in the analytical procedure used to measure AVS, and is denoted as  $\Sigma SEM$ . For divalent metals, one mole of SEM will react with one mole of AVS. Recently, silver (Ag) has been included as an SEM (Berry et al. 1999; US EPA 2000). However, for silver the stoichiometric relationship differs slightly, such that one mole of SEM silver reacts with two moles of AVS.

### Adaption of EqP Approach to Predict Metal Toxicity

The EqP model provides the basis for the development of causal sediment concentrations that predict the toxicity or lack of toxicity in sediments (Di Toro et al. 1990). The predicted sediment LC50 concentration ( $C_s$ ,  $\mu\text{mol/kg}$  dry wgt.) that corresponds to a measured LC50 ( $\mu\text{mol/L}$ ) in a water-only exposure of the same test organism is

$$C_s = K_p LC50 \tag{1}$$

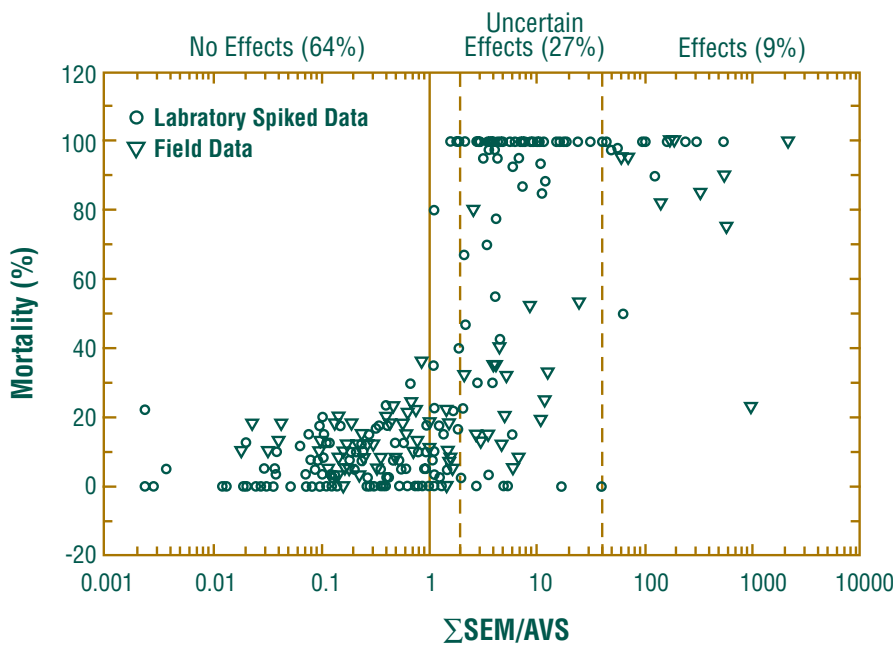
where  $K_p$  is the partition coefficient between pore water and sediment solids (L/kg). For divalent metals that form insoluble metal sulphides, Equation 1 becomes

$$\Sigma SEM = AVS + K_p LC50 \tag{2}$$

The basis for the  $\Sigma SEM/AVS$  method is to observe that if the partitioning term  $K_p LC50$  is neglected, the critical concentration is

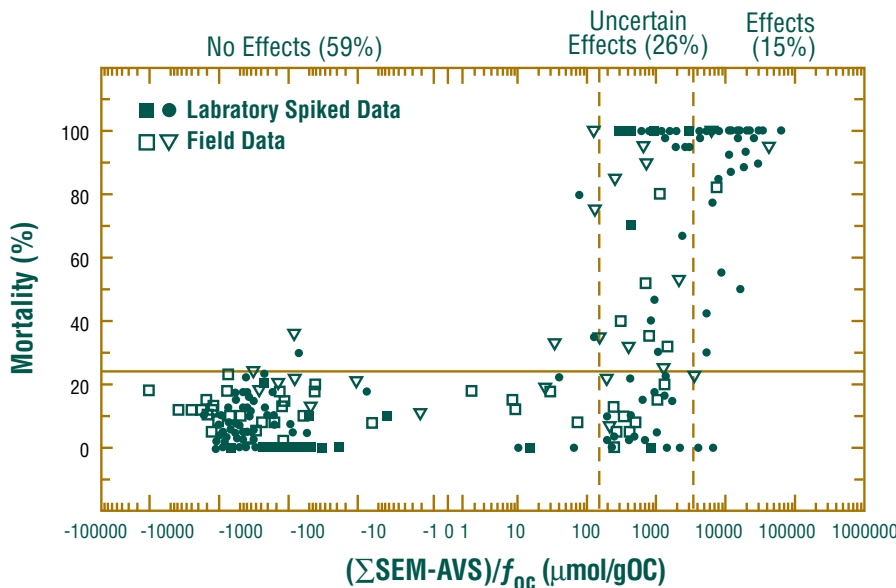
$$\Sigma SEM = AVS \tag{3}$$

If equi-molar concentrations of  $\Sigma SEM$  and AVS are present in a sediment, there is no excess  $\Sigma SEM$  available to cause toxicity. As such, for  $\Sigma SEM/AVS$  ratios less than or equal to 1, no metal toxicity would



**Figure 3**

Mortality vs.  $\Sigma\text{SEM}/\text{AVS}$  (Di Toro et al. 2000)



**Figure 4**

Mortality vs. excess SEM normalized to organic carbon concentration (Di Toro et al. 2000)

be predicted. For  $\Sigma\text{SEM}/\text{AVS}$  ratios greater than 1, the potential for metal toxicity exists from the excess  $\Sigma\text{SEM}$ .

To demonstrate that this approach is valid, the same mortality data that were shown in Figure 1 were compared with the sediment  $\Sigma\text{SEM}$  concentration normalized to AVS where the  $\Sigma\text{SEM}$  was computed by

summing the individual SEM from the five metals (Figure 3). The solid line indicates an  $\Sigma\text{SEM}/\text{AVS}$  ratio of 1.0. The areas of no effects, uncertain effects and effects are differentiated by the dashed lines. As shown, the ratio method can predict the lack of toxicity, but not the onset of toxicity. The range of the  $\Sigma\text{SEM}/\text{AVS}$  ratio over which the prediction of effects is uncertain, 2 to 40, includes approximately 27% of the data. Based on these results, the  $\Sigma\text{SEM}/\text{AVS}$  ratio method is considered a better predictor of effects than total sediment concentration (Figure 1).

### Organic Carbon Normalization of Excess $\Sigma\text{SEM}$

The  $\Sigma\text{SEM}/\text{AVS}$  ratio's inability to predict toxicity is due, in part, to the neglect of the partitioning term  $K_p\text{LC50}$ . The key to improving the prediction of toxicity is to approximate the partitioning term. Organic carbon is an important partitioning phase for metals in soil and in water because of the tendency for positively charged metal ions to bind to negatively charged sites that are associated with natural organic matter (NOM). This complexation with NOM reduces the availability of the SEM to the organism. The partitioning can be expressed as a function of the organic carbon partition coefficient (i.e.  $K_{oc}$ ) and fraction organic carbon (i.e.  $f_{oc}$ ):

$$K_p = f_{oc} K_{oc} \tag{4}$$

The  $f_{oc}$  quantifies the amount of NOM available for binding with the free metal, such that the greater the  $f_{oc}$ , the more metal binding to NOM and the less free metal available for the organism to take up. Using this expression in Equation 2 and rearranging yields

$$\frac{(\Sigma\text{SEM} - \text{AVS})}{f_{oc}} = K_{oc} \text{LC50} \tag{5}$$

If  $(\sum\text{SEM}-\text{AVS})/f_{\text{oc}}$  is greater than  $K_{\text{oc}}\text{LC50}$ , then the LC50 for that sediment would be exceeded and the sediment would be predicted to be toxic. The excess  $\sum\text{SEM}$  data in Figure 3 were normalized to organic carbon concentration (Figure 4). The range of uncertainty is 150 to 3400  $\mu\text{mol}/\text{g}_{\text{oc}}$ , and contains approximately 26% of the data. This corresponds roughly to the predictive capability of the  $\sum\text{SEM}/\text{AVS}$  ratio method. However, the organic carbon normalized excess  $\sum\text{SEM}$  method is the preferred approach since it is based on a partitioning theory and the ratio method is not. For silver, organic carbon normalization appears not to be appropriate (Di Toro et al. 2000).

### *Application to Chronic Exposures*

The data employed in the above analyses are mostly from 10-day exposure studies. The results of much longer-term chronic toxicity tests with metal-spiked sediments were compared with the organic carbon normalized excess  $\sum\text{SEM}$  approach. A total of 27 data sets were available (US EPA 2000). The chronic data support the lower bound for excess  $\sum\text{SEM}$  derived from acute toxicity tests since all except one of the sediments exhibited no effects below 150  $\mu\text{mol}/\text{g}_{\text{oc}}$ . Therefore it appears that the boundary for chronic effects is in excess of 150  $\mu\text{mol}/\text{g}_{\text{oc}}$ . Because chronic exposures also include dietary intake, attention recently has been directed at how the potential for effects arising from this route of exposure might further reduce the uncertainty in toxicity predictions (see Fact Sheet No. 6).

### *Utility of the SEM and AVS Approach*

The  $\sum\text{SEM}$  and AVS approach can be easily applied to assess whether SEMs are causing observed effects or if effects would be expected from the levels of SEM present in the sediment. The required analytical parameters are the concentrations of the six SEMs, the AVS concentration and the  $f_{\text{oc}}$  in the sediment.

This methodology has been applied at several sites in the United States to determine if the sediment-associated SEMs would be expected to cause effects. At a former tannery site in Michigan, AVS and SEM tests were performed in conjunction with toxicity tests to demonstrate that the metals were sufficiently bound such that toxicity was not observed. This study led to a revised remedial action plan for the site in which a long-term monitoring program was implemented in lieu of sediment removal. Similar sediment investigations were also conducted for a reservoir in Massachusetts and it was again found that the  $\sum\text{SEM}-\text{AVS}$  methodology could explain why toxicity was not observed.

A concern with the approach is that surficial metal sulphides in sediments could be oxidized, thereby releasing bound metal to the pore water. The most critical time when this may occur is in late winter or early spring, so collection of samples at this time is suggested as part of the monitoring program so that this potential effect is maximized.

### *Summary*

In summary, bulk sediment metal concentration is a poor predictor of the potential for effects to benthic organisms. The  $\sum\text{SEM}$  and AVS approach indicates that when the ratio of  $\sum\text{SEM}/\text{AVS} < 1$ , toxicity due to the SEM metals is not expected. Similarly, using the more recently developed carbon normalized criterion, toxicity is not expected when organic carbon normalized excess  $\sum\text{SEM}$  is less than 150  $\mu\text{mol}/\text{g}_{\text{oc}}$ . Potential refinements to the overall approach are being considered, including consideration of the dietary route of exposure (see Fact Sheet No. 6) and the biotic ligand modelling (see Fact Sheet No. 7).

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## Fact Sheet on Environmental Risk Assessment

This is the tenth in an occasional series of *Fact Sheets* to be produced by ICMM on metal-specific issues in environmental risk assessment. Authorship selection and editorial review are coordinated by Dr. Anne Fairbrother of Parametrix, Inc. Each *Fact Sheet* is reviewed for technical merit by Dr. Erik Smolders of Katholieke Universiteit (Catholic University) Leuven, Belgium, and by a panel of experts in metal-related regulatory issues. While the *Fact Sheets* reflect the views of the authors, they are intended to provide an objective review of each topic. ICMM hopes these publications provide insights into complex issues in regulatory science, and welcomes questions and comments.

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