

Short Communication

PREDICTING THE TOXICITY OF SEDIMENT-ASSOCIATED TRACE METALS WITH SIMULTANEOUSLY EXTRACTED TRACE METAL: ACID-VOLATILE SULFIDE CONCENTRATIONS AND DRY WEIGHT-NORMALIZED CONCENTRATIONS: A CRITICAL COMPARISON

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Abstract—The relative abilities of sediment concentrations of simultaneously extracted trace metal: acid-volatile sulfide (SEM: AVS) and dry weight-normalized trace metals to correctly predict both toxicity and nontoxicity were compared by analysis of 77 field-collected samples. Relative to the SEM:AVS concentrations, sediment guidelines based upon dry weight-normalized concentrations were equally or slightly more accurate in predicting both nontoxic and toxic results in laboratory tests.

Keywords—Sediment criteria Sediment quality guidelines Trace metals Sediment toxicity

INTRODUCTION

The concentrations of trace metals such as arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc are commonly elevated in aquatic sediments near urban and industrial areas. Interpretive tools have been developed to aid in the identification of probable sources [1] and assessments of potential ecological hazards of these substances [2-6]. Derived from different approaches, such tools pose difficult choices to environmental scientists and managers regarding the design of monitoring programs and the interpretation of chemical data.

Two distinctly different approaches have been used to develop effects-based, numerical, sediment quality guidelines (SQGs) or criteria. Both approaches have strengths and weaknesses, and the numerical values from both can be widely applied in many circumstances [7].

In empirical approaches, matching sediment chemistry and biological effects data have been compiled and analyzed with several methods to determine the concentrations of trace metals associated with toxicity and other adverse biological effects in sediments [3-5,8]. Sediment quality guidelines derived using these approaches are premised upon the assumption that relationships between sediment chemistry and effects will emerge during analyses of large data sets compiled from many different locations. Such SQGs do not account for factors controlling bioavailability and are expressed on a dry weight-normalized basis. Some investigators [2] have encountered difficulty predicting toxicity with dry weight-normalized concentrations.

In a different approach, partitioning models have been developed to account for the factors that likely influence metal bioavailability in bed sediments [2,9]. Analyses of simulta-

neously extracted trace metals (SEM) in acid-volatile sulfides (AVS) have been proposed to account for the relative bioavailability of trace metals in anaerobic sediments [10]. In laboratory experiments, AVS has been shown to control the pore water concentrations and bioavailability of cadmium and nickel [10,11]. Based upon the results of these investigations, divalent metals in sediments would not be predicted to cause toxicity or bioaccumulation when the concentrations of SEM are lower than the concentrations of AVS. Criteria based on SEM are expressed on a molar basis for summed concentrations of cadmium, copper, nickel, lead, and zinc normalized to molar concentration of AVS. The SEM:AVS concentrations, whether expressed as ratios or differences, were intended to predict an absence of toxicity attributable to metals [2,9]. However, Hansen et al. [9] reported the incidence of toxicity in laboratory bioassays was 79% in samples in which SEM concentrations exceeded AVS concentrations in both laboratory and field samples and concluded that "... this approach is, therefore, very useful in identifying sediments of concern." Furthermore, Berry et al. [12] concluded "normalizations involving AVS can be used to predict toxicity in sediments contaminated with cadmium, copper, nickel, lead, or zinc across a wide range of sediment types."

This paper quantifies and compares the ability of the SQGs based upon dry weight concentrations and proposed criteria based upon molar SEM:AVS concentrations to correctly identify samples as either nontoxic or toxic. Data assembled by Hansen et al. [9] from five different saltwater locations where trace metals occurred at relatively high concentrations were used as the basis for the comparison.

METHODS

Data from 77 samples chosen to reflect large trace metals gradients were compiled by Hansen et al. [9]. They reported

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Table 1. Percent of samples that were toxic in which the probability of toxicity was lowest^a

	Toxicity (mortality >24%)		Nontoxicity (mortality <24%)	
	Count	Percent	Count	Percent
Samples with SEM:AVS ratios $\leq 1.00^b$	10/52	19.2	42/52	80.8
Samples with SEM-AVS differences <0.00	10/52	19.2	42/52	80.8
Samples with metals <AETs	1/31	3.2	30/31	96.8
Samples with metals <ERLs	0/6	0.0	6/6	100.0
Samples with metals <ERMs	0/28	0.0	28/28	100.0
Samples with mean ERM quotients <1.0	3/40	7.5	37/40	92.5

^a [9].

^b SEM = simultaneously extracted trace metal; AVS = acid-volatile sulfide; AET = apparent effects threshold; ERL = effects range low; ERM = effects range median.

both SEM:AVS ratios and the concentrations of total metals normalized to dry weight were reported in Table 1. The percentages of the samples that were toxic (i.e., mortality >24%) or nontoxic (mortality <24%) as defined by Hansen et al. in tests performed with *Ampelisca abdita* were calculated. Trace metals concentrations from Hansen et al. [9] were compared to the saltwater effects range low (ERL) and effects range median (ERM) values of Long et al. [4] and the marine apparent effects thresholds (AET) values of Washington state [8].

In these comparisons, we assumed the probabilities of toxicity would be lowest among samples in which AVS concentrations equaled or exceeded SEM concentrations (i.e., SEM:AVS ratios were ≤ 1.0 or SEM-AVS differences were <0.0), if the concentrations of all five metals were less than ERL, ERM, or AET values, or if the mean of the quotients calculated by dividing the five trace metals concentrations by the ERM concentrations ("mean ERM quotients") was <1.0 (Table 1). In contrast, we assumed that the probabilities of toxicity would be greater among samples in which there was an excess of SEM relative to AVS (i.e., SEM:AVS ratios >1.0 or SEM-AVS differences ≥ 0.0), if one or more of the metals exceeded the SQG values, or if the mean metals:ERM quotients were >1.0 (Table 2). The predictive abilities of both SEM:AVS ratios and SEM-AVS differences, as described by Hansen et al. [9], were calculated.

In addition, the relative efficiency and sensitivity of each set of guidelines were compared using metrics previously applied to the development of the AETs [8]. Sensitivity was calculated as the percent of the 17 samples in the database that were toxic in which chemical concentrations exceeded the SQGs or criteria (e.g., 16 of 17 [94%] for the AETs). Efficiency was calculated as the percent of samples predicted to be toxic

(i.e., exceeded the SQG) that were actually toxic (e.g., seven of 25 [28%]; data from Table 2).

RESULTS AND DISCUSSION

Based upon our calculations, 19% of 52 samples with SEM:AVS ratios ≤ 1.0 were toxic and 81% were nontoxic (Table 1). The same result (81% nontoxic) was observed among samples with SEM-AVS differences of <0.0. In comparison, 97% of the samples were nontoxic when the five metals concentrations were less than the lowest Washington AETs. None of the samples was toxic when these concentrations were less than the ERLs or the ERMs. Furthermore, 93% of the samples were nontoxic when the mean ERM quotients for the five metals were <1.0.

Toxicity was more likely in samples that had very high metals concentrations. Seven of the 25 saltwater samples (28%) with SEM:AVS ratios >1.0 and SEM-AVS differences ≥ 0.0 were toxic (Table 2). Hansen et al. [9] reported that 31 of 79 samples (39.2%) from both marine and freshwater studies combined were toxic with SEM:AVS ratios >1.0. The incidence of toxicity increased to 40% (six of 15) among saltwater samples with SEM:AVS ratios >2.0 and to 50% (four of eight) with SEM:AVS ratios >5.0. In comparison, 34.8 or 34.7% of samples were toxic in which at least one AET or ERM, respectively, was exceeded. Also, 38 and 67% of the samples were toxic in which the means of five metals:ERM quotients were ≥ 1.0 and ≥ 10.0 , respectively. Toxicity in these samples may have been attributable to the presence of organic compounds, and/or unmeasured substances, as well as the metals quantified in the analyses [9].

The SEM:AVS ratios, AETs, ERMs, and mean ERM quotients were similar in efficiency: i.e., correctly predicting toxicity in 28 to 38% of the samples (Fig. 1). However, their

Table 2. Percent of samples that were toxic in which the probability of toxicity was highest^a

	Toxicity (mortality >24%)		Nontoxicity (mortality <24%)	
	Count	Percent	Count	Percent
Samples with SEM:AVS ratios >1.00 ^b	7/25	28.0	18/25	72.0
Samples with SEM:AVS ratios >2.00	6/15	40.0	9/15	60.0
Samples with SEM:AVS ratios >5.00	4/8	50.0	4/8	50.0
Samples with SEM-AVS differences ≥ 0.00	7/25	28.0	18/25	72.0
Samples with at least one metal >AET	16/46	34.8	30/46	65.2
Samples with at least one metal >ERM	17/49	34.7	32/49	65.3
Samples with mean ERM quotients ≥ 1.0	14/37	37.8	23/37	62.2
Samples with mean ERM quotients ≥ 10.0	6/9	66.7	3/9	33.3

^a [9].

^b See footnote to Table 1 for all abbreviations.

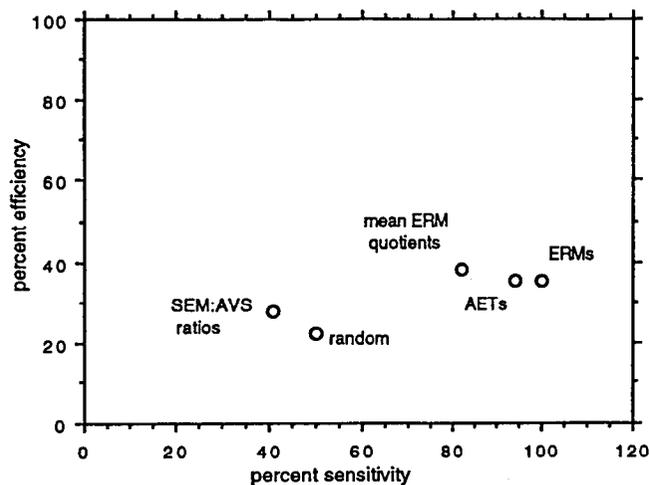


Fig. 1. Relative efficiency and sensitivity of four sediment quality guidelines for metals in predicting toxicity (>24% mortality) in laboratory toxicity tests in 77 saltwater, field-collected samples [9].

efficiency only slightly exceeded the outcome of repeated tosses of a coin (i.e., random chance is $[17/2]/[77/2] = 22\%$). The SEM:AVS ratios had considerably lower sensitivity than the ERMs and AETs; only seven of the 17 toxic samples (41%) exceeded SEM:AVS ratios of 1.0. By random chance, sensitivity would be 50% (8.5 of 17). The ERMs, mean ERM quotients, and AETs had sensitivities of 82 to 100%.

The results of these analyses do not support the conclusion of Hansen et al. [9] that AVS-normalized SEM concentrations are superior to dry weight-normalized concentrations in predicting the nontoxicity or toxicity of sediment-associated metals. To the contrary, these data suggest that in comparison with the SEM:AVS criteria, the SQGs based upon total dry weight-normalized metals concentrations were equally, if not more, accurate in correctly predicting both nontoxicity and toxicity in these selected data sets. The SQGs were considerably more sensitive than the SEM:AVS ratios. Hansen et al. [9] observed increased accuracy in predicting nontoxicity when data from pore-water analyses were included and when data from samples apparently contaminated with organic substances were eliminated from the analyses. Accuracy in predicting toxicity may improve among samples with extremely high metals concentrations, as observed in sediment spiking experiments [12], but it was not possible to quantify this possibility in the field with the present database.

The SEM:AVS tool cannot account for the presence and possible toxicity of metals other than the five divalent elements for which these criteria were developed. Because these criteria were not derived from field studies of mixtures of toxic substances, they may be less pertinent to data from field surveys of complex contaminant mixtures than SQGs derived from empirical approaches. Also, measurements of SEM are not compatible with reference element techniques that facilitate identification of the anthropogenic origin of sediment-associated metals [1]. However, it has been reported that the SEM:AVS approach "... is based on sound theory and has been verified by considerable experimental evidence" [13]. Factors that control bioavailability, such as AVS, are clearly important in understanding causality and the risks of sediment-associated toxicants. Nevertheless, more research is needed to understand

critical levels of SEM:AVS that cause no adverse effects, the roles of other factors (binding phases) that may influence bioavailability of metals, and the role of SEM in contributing to toxicity in complex mixtures of toxic substances.

Numerical guidelines or criteria based upon different approaches, assumptions, strengths, and weaknesses can be used for different purposes and management decisions. The weight of evidence necessary to make management decisions must be related to the significance (and costs) of the decisions. Both the U.S. EPA Science Advisory Board [13] and participants in a recent SETAC Pellston workshop [14] recommended that numerical guidelines based upon different approaches should be used together to categorize sediment quality, perhaps in tiered assessments [13]. Based upon the results of this comparative analysis, we recommend that prospective users consider the predictive capability of any numerical guidelines or criteria for assessing sediment quality. In addition, it is important to consider the compatibility of guidelines and criteria to other tools in the sediment quality assessment process.

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