

## PREDICTING SEDIMENT METAL TOXICITY USING A SEDIMENT BIOTIC LIGAND MODEL: METHODOLOGY AND INITIAL APPLICATION

DOMINIC M. DI TORO,\*†‡ JOY A. MCGRATH,‡ DAVID J. HANSEN,‡ WALTER J. BERRY,§ PAUL R. PAQUIN,‡  
ROONI MATHEW,‡ KUEN BENJAMIN WU,‡ and ROBERT C. SANTORE‡

†Department of Civil and Environmental Engineering, University of Delaware, Newark, Delaware 19716, USA

‡HydroQual, Mahwah, New Jersey 07430, USA

§U.S. Environmental Protection Agency, National Health and Environmental Effects Research Laboratory, Narragansett, Rhode Island 02882

(Received 18 August 2004; Accepted 17 March 2005)

**Abstract**—An extension of the simultaneously extracted metals/acid-volatile sulfide (SEM/AVS) procedure is presented that predicts the acute and chronic sediment metals effects concentrations. A biotic ligand model (BLM) and a pore water–sediment partitioning model are used to predict the sediment concentration that is in equilibrium with the biotic ligand effects concentration. This initial application considers only partitioning to sediment particulate organic carbon. This procedure bypasses the need to compute the details of the pore-water chemistry. Remarkably, the median lethal concentration on a sediment organic carbon (OC)–normalized basis,  $SEM_{x,OC}^*$ , is essentially unchanged over a wide range of concentrations of pore-water hardness, salinity, dissolved organic carbon, and any other complexing or competing ligands. Only the pore-water pH is important. Both acute and chronic exposures in fresh- and saltwater sediments are compared to predictions for cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) based on the *Daphnia magna* BLM. The  $SEM_{x,OC}^*$  concentrations are similar for all the metals except cadmium. For pH = 8, the approximate values ( $\mu\text{mol/gOC}$ ) are Cd- $SEM_{x,OC}^* \approx 100$ , Cu- $SEM_{x,OC}^* \approx 900$ , Ni- $SEM_{x,OC}^* \approx 1,100$ , Zn- $SEM_{x,OC}^* \approx 1,400$ , and Pb- $SEM_{x,OC}^* \approx 2,700$ . This similarity is the explanation for an empirically observed dose–response relationship between SEM and acute and chronic effects concentrations that had been observed previously. This initial application clearly demonstrates that BLMs can be used to predict toxic sediment concentrations without modeling the pore-water chemistry.

**Keywords**—Metal Toxicity Sediment Organic carbon

### INTRODUCTION

The simultaneously extracted metals/acid-volatile sulfide (SEM/AVS) method for evaluating the toxicity of the metals cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn) [1,2], and silver (Ag) [3] has proven to be quite successful at predicting the lack of toxicity in spiked and field-contaminated sediments [4,5]. It is based on the fact that these metals form insoluble metal sulfides by reacting with the iron sulfide (FeS) in sediments. Acid-volatile sulfides and SEMs are the measures used for reactive sulfide and reactive metal present in the sediment. If AVS exceeds the sum of the SEMs present ( $\Sigma\text{SEM} = \text{SEM}_{\text{Cd}} + \text{SEM}_{\text{Cu}} + \text{SEM}_{\text{Ni}} + \text{SEM}_{\text{Pb}} + \text{SEM}_{\text{Zn}}$ ), excess sulfide exists in the sediment, and all the metals are present as insoluble nontoxic metal sulfides.

However, because the  $\Sigma\text{SEM/AVS}$  method does not explicitly consider the other sediment phases that influence pore water–sediment partitioning, it was never intended to be used to predict the occurrence of toxicity. The proposed sediment quality criteria for metals [6]—now referred to as equilibrium partitioning (EqP)–derived sediment guidelines or equilibrium partitioning sediment benchmarks ([7]; [http://www.epa.gov/nheerl/publications/files/metalsESB\\_022405.pdf](http://www.epa.gov/nheerl/publications/files/metalsESB_022405.pdf))—were constructed as one-tailed guidelines. They can be used to predict the lack of toxicity but not its presence. Thus, the problem of predicting the onset of toxicity in metal-contaminated sediments remained to be solved. This is important for sediments in which the AVS concentration is small or zero.

The purpose of this article is to introduce an extension of

the SEM/AVS procedure that allows the prediction of effects in metal-contaminated sediments by accounting for partitioning to sediment particulate organic carbon as well as the effect of AVS. The partitioning is modeled using the Windemere Humic Aqueous Model (WHAM) [8], and toxicity is modeled using the biotic ligand model (BLM) [9]. In this article, the partitioning model is restricted to only sediment organic carbon because it is an important phase for metal sorption. And, unlike other phases that may be important (e.g., iron oxyhydroxide), its concentration is routinely measured. The *Daphnia magna* BLM is employed because it is available and because *D. magna* is among the most sensitive organisms to metals.

This article presents the methodology in detail, examines the behavior of the models, including some completely unexpected results, and compares the predictions to available toxicity data. It demonstrates that a sediment BLM model is feasible without needing to model detailed pore-water chemistry. It compares the predictions that are made without calibration to the sediment toxicity data. The data are within the range of the model prediction uncertainty that is primarily a consequence of the unknown pore-water pH levels of the tests.

### THEORY

The EqP model [10] gives the prescription for the development of causal sediment concentrations that predict both the toxicity and lack of toxicity in sediments. If the LC50 concentration  $C_W^*$ —the concentration that causes 50% mortality—for a specific chemical and test organism is known, then for a sediment exposure using the same test organism and the same test duration, the LC50 is predicted to occur at a pore-

\* To whom correspondence may be addressed (dditoro@ce.udel.edu).

water concentration  $C_{pw}^*$  that is equal to the water-only LC50 concentration

$$C_{pw}^* = C_w^* \quad (1)$$

The superscript (\*) is used to denote the effect concentration (e.g., the LC50 concentration) in any phase. The sediment LC50 concentration  $C_s^*$  is predicted to be that concentration that is in equilibrium—hence, EqP—with the pore-water concentration. Therefore, the application of the EqP model requires a prediction of the sediment concentration  $C_s^*$  that would be in equilibrium with the water-only LC50  $C_w^*$  at equilibrium

$$C_s^* \leftrightarrow C_w^* \quad (2)$$

If a linear partitioning model is appropriate for a class of chemicals—for example, neutral hydrophobic organic chemicals—the sediment concentration  $C_s$  can be predicted from the water concentration  $C_w$  using a linear partition coefficient  $K_p$

$$C_s = K_p C_w \quad (3)$$

then the sediment LC50 is predicted to be

$$C_s^* = K_p C_w^* \quad (4)$$

where  $C_s^*$  is the sediment LC50 concentration ( $\mu\text{mol/kg}$  dry wt),  $K_p$  (L/kg) is the partition coefficient between pore water and sediment solids, and  $C_w^*$  ( $\mu\text{mol/L}$ ) is the water-only LC50. For the derivation of a sediment quality criteria or guideline, the water-only effects concentration would be replaced by a water quality criteria concentration; for example, the U.S. Environmental Protection Agency Final Chronic Value  $FCV$  [10]

$$C_s^* = K_p FCV \quad (5)$$

A review of the predictive capability of the EqP model is available [11].

For application to metals (Cd, Cu, Ni, Pb, and Zn) that react with AVS to form insoluble metal sulfides, Equation 4 is no longer appropriate since the sediment concentration includes the concentration of metal sulfides as well as the concentration of metal that may be partitioned to other sediment solid phases. For the case in which the metal concentration exceeds the AVS, and if it is assumed that linear partitioning applies to the partitioned metal fraction, then Equation 4 becomes [1]

$$C_s^* = AVS + K_p C_w^* \quad (6)$$

where  $AVS$  is the sediment concentration of AVS ( $\mu\text{mol/kg}$  dry wt). Equation 6 states that since AVS can bind the metal as highly insoluble sulfides, the concentration of metal in a sediment that will cause toxicity is at least as great as the AVS that is present.

The sediment metal concentration  $C_s^*$  that should be used in Equation 6 is the SEM concentration, the metal concentration that is simultaneously extracted with the sulfide in the AVS extraction [2]. There are two reasons this is important. First, any metal that is bound so strongly that it is insoluble in the 1N hydrochloric acid used in the AVS extraction [12] is not likely to be bioavailable and, therefore, will not contribute to toxicity. Second, the metal sulfides, such as CuS and NiS, that are only partially soluble or that are not soluble in 1N HCl will not contribute to either the sulfide or the metal measurement, and so will be judged as inert and not contributing to toxicity [2].

Of course, this argument is based on the supposition that metals that are present as sulfides or that resist extraction in 1N HCl do not contribute to toxicity. Further, it is assumed

that there is no additional exposure due to transformations of the metal in the gut of sediment-ingesting organisms, or via exposure to contaminated food [13]. It is for this reason that so much effort has been expended to demonstrate experimentally that if AVS exceeds SEM, then no toxicity is observed [2,4,5,11, and the references cited below]. Therefore, using SEM in Equation 6 yields

$$SEM^* = AVS + K_p C_w^* \quad (7)$$

The basis for the SEM/AVS method is the observation that if the second term,  $K_p C_w^*$ , in Equation 7 is neglected, then the critical concentration is

$$SEM = AVS \quad (8)$$

and the boundary between toxicity and lack of toxicity is

$$SEM/AVS = 1 \quad (9)$$

or, equivalently

$$SEM - AVS = 0 \quad (10)$$

The failure of either the ratio condition  $SEM/AVS > 1$  (Eqn. 9) or the difference condition  $SEM - AVS > 0$  (Eqn. 10) to predict the occurrence of toxicity is due to the neglect of the partitioning term  $K_p C_w^*$  in Equation 7. Note that ignoring the term does not affect the prediction of lack of toxicity, because if AVS is in excess of SEM, the metal activity in the pore water is very small even for the most soluble (i.e., NiS) sulfide [2].

#### Partitioning and organic carbon-normalized excess SEM

The key to predicting toxicity is to include the partitioning term,  $K_p C_w^*$ , in Equation 6, rather than ignoring it. In a complete sediment BLM, the partitioning to all sediment phases (e.g., organic matter, iron, and manganese oxides, and other mineral components to which metal is partitioned [14]) would be considered. For this initial application, only sediment organic matter will be included. This choice is made for a number of reasons. First, it is well known that organic carbon is an important metal-partitioning phase for soils [15–18] and in surface-water particulate matter [19,20]. For many soils it is the dominant sorption phase [17,18]. Second, organic carbon is routinely measured in sediments [21]. Unfortunately, measurements of the quantities of the other sorption phases in toxicity tests are made either infrequently or not at all. Third, focusing on only one sediment sorption phase greatly simplifies the analysis of the modeling results and provides a great deal of insight into how the chemistry and toxicity interact.

For partitioning to organic carbon only, the partition coefficient  $K_p$  in Equation 7 is the product of the organic carbon-based partition coefficient  $K_{OC}$  (L/kg OC) and the fraction organic carbon in the sediment  $f_{OC}$  (kg OC/kg dry wt)

$$K_p = f_{OC} K_{OC} \quad (11)$$

This is the same formulation that is used for hydrophobic organic chemicals [10,22]. Using this expression in Equation 7 yields

$$SEM^* - AVS = f_{OC} K_{OC} C_w^* \quad (12)$$

where  $SEM^* - AVS$  is the excess SEM. The organic carbon-normalized SEM\* is

$$SEM_{x,OC}^* = \frac{SEM^* - AVS}{f_{OC}} = K_{OC} C_w^* \quad (13)$$

If both the  $K_{OC}$  and  $C_w^*$  were known, then Equation 13 could

Table 1. Sediment toxicity data

Organism tested		Metals	Reference
Acute exposure			
Marine amphipod	<i>Ampelisca abdita</i>	Cd, Cu, Ni, Pb, Zn	[4]
Marine amphipod	<i>Gammarus locusta</i>	Cu	[64]
Marine amphipod	<i>Chaetocorophium cf. lucasi</i>	Cd	[63]
Marine amphipod	<i>Leptocheirus plumulosus</i>	Zn	[66]
Marine amphipod	<i>Ampelisca abdita</i>	Cd	[77]
Marine polychaete	<i>Capitella capitata</i>	Cu, Pb, Zn	[67]
Marine polychaete	<i>Neanthes arenaceodentata</i>	Cd, Ni	[68]
Freshwater oligochaete	<i>Lumbriculus variegatus</i>	Cd	[69]
Freshwater snail	<i>Helisoma</i> sp.	Cd	[69]
Chronic exposure			
Marine amphipod	<i>Leptocheirus plumulosus</i>	Cd	[71]
Marine	Colonization	Cd	[74]
Freshwater	Colonization	Cd	[73]
Freshwater nematode <sup>a</sup>	<i>Caenorhabditis elegans</i>	Cd	[70]
Freshwater midge	<i>Chironomus tentans</i>	Zn	[72]
Marine	Colonization	Zn	[75]
Freshwater	Colonization	Zn	[76]

<sup>a</sup> Seventy-two-hour exposure, growth endpoint.

be used to predict toxicity. If  $SEM_{x,OC} > SEM_{x,OC}^* = K_{OC}C_W^*$ , then the LC50 for that sediment would be exceeded (Eqns. 4 and 12), and the sediment would be predicted to be toxic. An examination of this method of predicting sediment toxicity is presented below using the data sets described in the next section.

#### DATA SOURCES

The only way to be absolutely sure what is causing toxicity in a sediment is to add the chemical and compare the results to the unamended (control) sediment. This is, of course, the normal procedure in the scientific method. To be sure, there are artifacts with spiked sediment toxicity tests that have been examined and, one hopes, minimized [23]. The most convincing tests are long-term exposures in the field using spiked sediments.

An extensive literature search was made for articles that satisfied the following criteria: A single metal spiked into sediments; measured SEM, AVS, and  $f_{OC}$ ; and a measured endpoint, either mortality, growth, or, for colonization experiments, number of species present. Only studies for which the above information was reported or otherwise available were used. Studies with excessive control mortality were not included. The data sets are listed in Table 1. Both acute and chronic exposures in laboratory and field experiments employing single metal additions are considered in this article.

Experiments for which metal bioaccumulation was the endpoint were also not included. It has been known for some time that in certain cases the SEM/AVS model does not predict the presence or extent of metal uptake by sediment-dwelling organisms [24,25]. Ingestion has been indicated as the route of uptake [26]. If sediment processing in the gut changes the chemical form of the metal, then EqP no longer applies. If these processes contribute significantly to mortality, growth, or the number of species present in colonization experiments, then the EqP model should not be able to predict the effect of metal exposure. As shown below, this does not seem to be the case. For all cases examined—in particular the spiked sediment field exposure tests—the lack of toxicity is predicted correctly ([11] and Fig. 1 below).

#### GRAPHICAL ANALYSIS

The quantities needed to compute organic carbon-normalized SEM (Eqn. 9) are all available for the data sets listed in Table 1. It is interesting to examine the relationship between  $SEM_{x,OC}$  concentration and the observed effects for the acute and chronic data sets. All the acute data are presented in Figure 1A. The  $SEM_{x,OC}$  is plotted using a positive and negative log scale [27]. It appears that no acute toxicity occurs if  $SEM_{x,OC} < 100 \mu\text{mol/gOC}$ , regardless of metal identity. The chronic data for Cd and Zn are presented in Figure 1B. For Zn and Cd, the effect–no effect boundary also appears to be  $SEM_{x,OC} \approx 100 \mu\text{mol/gOC}$ . Note that this result also validates the prediction of lack of toxicity if  $SEM < AVS$ , for both acute and chronic tests.

This result—that the onset of chronic and acute toxicity occurs at  $SEM_{x,OC} \approx 100 \mu\text{mol/gOC}$ —had been noted previously [28] and forms the basis for the present guideline [7]. However, no explanation was available for the apparent independence of the effects boundary on metal identity other than to note the result implied (Eqn. 13) that  $K_{OC}C_W^* \approx 100 \mu\text{mol/gOC}$  is independent of metal identity. This indicates that there is an inverse relationship between partition coefficients to organic carbon  $K_{OC}$  and the water-only LC50s,  $C_W^*$  for the metals being considered.

However, without a method for calculating  $K_{OC}$  and  $C_W^*$  from more fundamental parameters, this observation was purely empirical—useful for estimating the lower boundary of sediment toxicity, but without a more fundamental basis. Therefore, it was not possible to determine the limitations of the method. In addition, it was unclear what the result of varying sediment chemical properties that affect both  $K_{OC}$  and  $C_W^*$  would be. With the development of the biotic ligand model, it is now possible to calculate these parameters explicitly and to evaluate the influence of pore-water chemistry, such as varying pH, hardness, and salinity.

#### DESCRIPTION OF THE SEDIMENT BIOTIC LIGAND MODEL

The sediment biotic ligand model (sBLM) is diagrammed in Figure 2. The methodology uses the EqP model of sediment

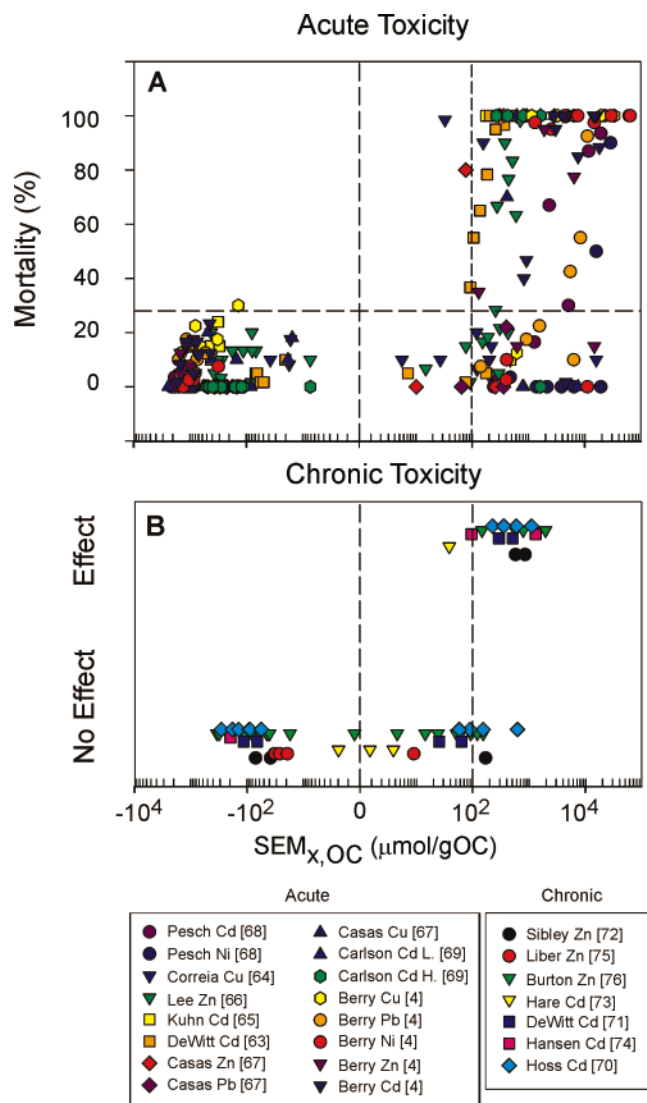


Fig. 1. Toxicity data (Table 1) versus organic carbon-normalized excess simultaneously extracted metals (SEM) concentration  $SEM_{x,OC}$ , plotted using a positive and negative log scale [27]. Tic marks at  $SEM_{x,OC} = 0, \pm 1, \pm 2, \pm 3, \dots, \pm 10, \dots, \pm 20, \dots, \pm 100, \dots$  (A) Mortality for acute exposures. (B) Chronic toxicity: Chronic data identified with either no effect or effect observed. Each chronic data set is displaced slightly to aid visualization.

toxicity [10] to relate the toxic sediment metal concentration to the toxic pore-water metal concentration (Eqn. 4). The BLM [9] is used to compute the LC50 concentration in the aqueous phase that results in a metal concentration at the site of action (the biotic ligand) that produces 50% mortality. It accounts for the varying bioavailability of dissolved metal due to metal complexation with inorganic anions, such as chloride ( $Cl^-$ ), bicarbonate ( $HCO_3^-$ ), and sulfide ( $HS^-$ ), and with dissolved organic carbon (DOC), by relating toxicity to the free metal ion activity. This is the free ion activity model of metal toxicity (see Morel [29], Morel and Herring [30], and Campbell [31] for reviews).

The BLM also accounts for the protective effects of the hardness cations  $Ca^{2+}$  and  $Mg^{2+}$  and the effect of pH as a competitive equilibrium at the biotic ligand following a model originally proposed by Pagenkopf [32] (see Paquin et al. [33] for a comprehensive review of the historical development of the BLM).

### Sediment Biotic Ligand Model sBLM

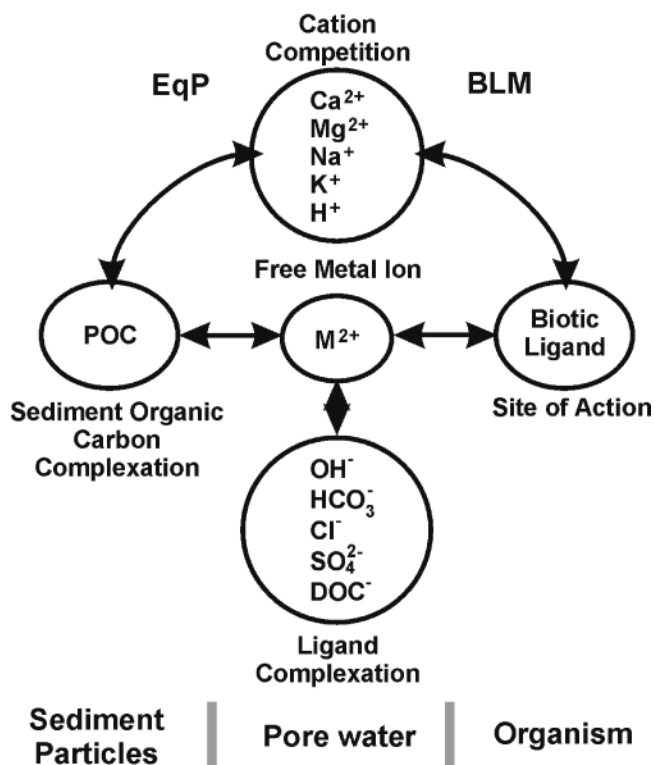


Fig. 2. Schematic diagram of the sediment biotic ligand model (sBLM) for computing sediment metal toxicity. Equilibrium partitioning (EqP) model for sediment toxicity [10] and the BLM for metal toxicity [9]. POC = particulate organic carbon; DOC = dissolved organic carbon;  $HCO_3^-$  = bicarbonate;  $OH^-$  = hydroxide;  $Cl^-$  = chloride;  $SO_4^{2-}$  = sulfate;  $DOC^-$  = dissolved organic carbon;  $HS^-$  = sulfide.

The metal speciation model used for both the dissolved ligands in the pore water and the sediment particulate organic carbon is WHAM, by Tipping and coworkers [34–36]. The model combines Humic Ion-Binding Model V with a simple inorganic speciation code for aqueous solutions. It is fully described, extensively calibrated, and the computer code is available [8]. The calculations are performed using the HydroQual implementation of the BLM, which is also publicly available ([37]; <http://www.hydroqual.com/blm/>). For simplicity, we refer to this version of WHAM as WHAM V, to distinguish it from the more recently developed WHAM VI [38]. The WHAM V rather than WHAM VI is used because the BLM has been calibrated using WHAM V, and it would be inconsistent to change the partitioning model and not the BLM calibration parameters.

The application of the BLM to sediment pore water (Fig. 2, right) is the obvious path to follow. However, this would require a complete characterization of the ligand concentrations that are present in pore water. These data are normally not available and are difficult to collect on a routine basis. Fortunately, these data are not necessary. Instead of using the computed pore-water metal LC50 activity  $\{M^{2+}\}^*$ , which is the metal ion concentration  $[M^{2+}]^*$  modified by the ionic strength correction, the metal concentration on the sediment particulate organic carbon  $[M^{2+} \equiv POC]^*$  is computed that is in equilibrium with the pore-water free metal ion activity  $\{M^{2+}\}^*$  and the biotic ligand  $[M^{2+} \equiv BL]^*$  concentration (Fig.

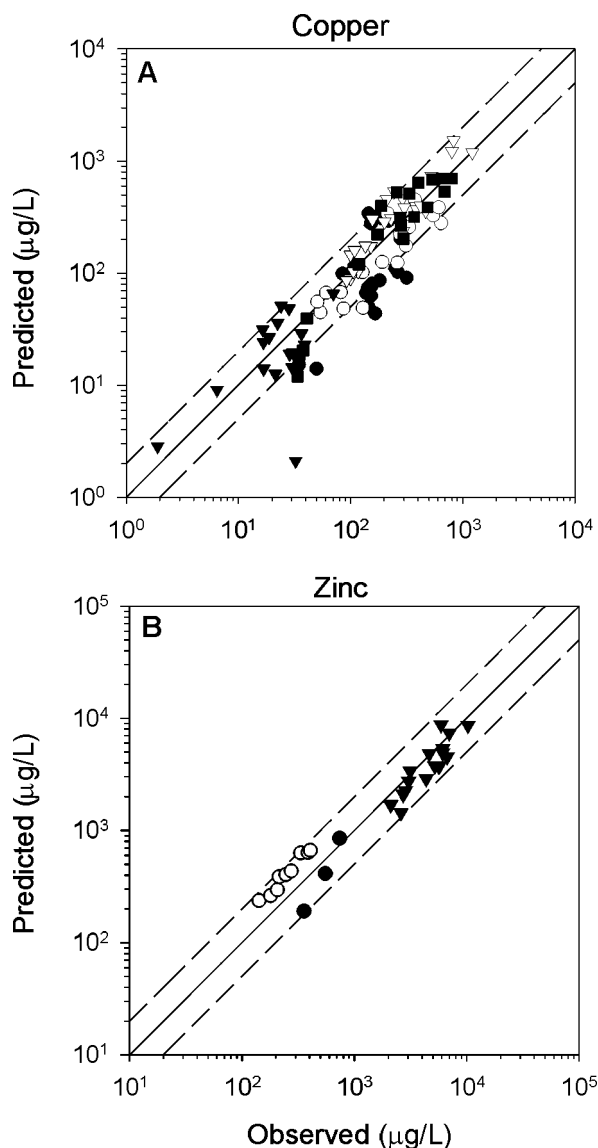
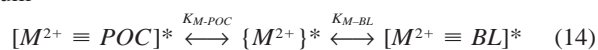


Fig. 3. Biotic ligand model calibration. Comparison of predicted and observed median lethal concentrations (LC50s) for *Daphnia magna* and *Ceriodaphnia dubia* (see Table 2 for test conditions). Line of perfect agreement (solid),  $\pm$  factor of two (dashed). (A) Cu:  $\nabla$  = [47];  $\blacksquare$  = [47];  $\circ$  = [49];  $\bullet$  = [50];  $\blacktriangledown$  = [81]. (B) Zn:  $\circ$  = [83];  $\bullet$  = [85];  $\blacktriangledown$  = [51];  $\nabla$  = [51].

2, left). The assumption is that the three phases are in equilibrium



where  $K_{M-POC}$  and  $K_{M-BL}$  are the equilibrium constants. The computed LC50 sediment metal concentration on particulate organic carbon is assumed to be equivalent to the measured organic carbon-normalized excess SEM concentration,  $SEM_{X,OC}^*$ . This is the fundamental idea. The extent to which pore-water processes affect the resulting concentration is addressed next.

#### Effect of pore-water complexation

It would appear, at first glance, that the pore-water concentrations of ligands that complex metals in the pore water (e.g., DOC,  $Cl^-$ ,  $HCO_3^-$ ,  $HS^-$ ) would be important since they form metal ligand complexes (e.g., a metal-bicarbonate

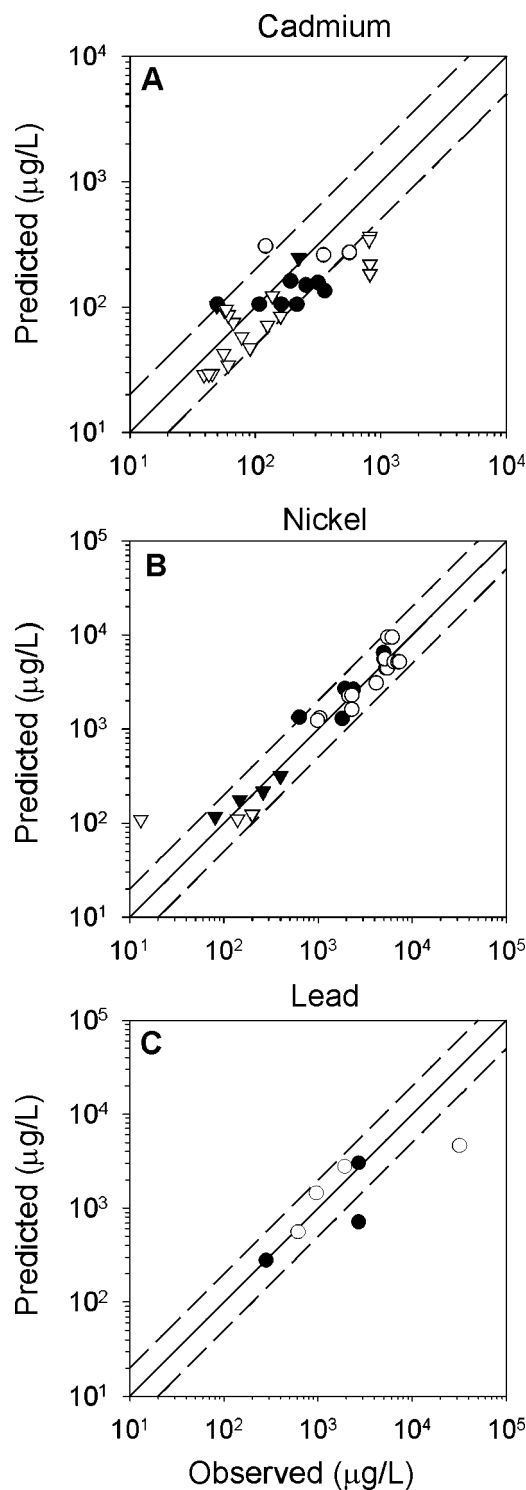


Fig. 4. Biotic ligand model calibration. Comparison of predicted and observed median lethal concentrations (LC50s) for *Daphnia magna* and *Ceriodaphnia dubia* (see Table 2 for test conditions). Line of perfect agreement (solid),  $\pm$  factor of two (dashed). (A) Cd:  $\bullet$  = [78];  $\circ$  = [79];  $\blacktriangledown$  = [80];  $\nabla$  = [52]. (B) Ni:  $\circ$  = [82];  $\bullet$  = [83];  $\nabla$  = [79];  $\blacktriangledown$  = [84]. (C) Pb:  $\circ$  = [83];  $\bullet$  = [79].

$[MHCO_3^+]$  and metal-DOC [ $M \equiv DOC$ ]) that reduce the free metal ion activity  $\{M^{2+}\}$ . This is, of course, true if the pore water is considered in isolation. However, if the entire system (sediment particulate organic carbon, pore water, and the biotic ligand) is considered as a whole (Fig. 2), then a different conclusion is reached.

Table 2. Biotic ligand model (BLM) data; see Figures 3 and 4 for reference

Metal	Organism	Description	Critical BL concn. <sup>a</sup>	Symbol	Reference
Cd	<i>Ceriodaphnia dubia</i>	Water effect ratio study	7.53	●	[78]
Cd	<i>C. dubia</i>	Reconstituted water	7.53	○	[79]
Cd	<i>C. dubia</i>	Reconstituted water	7.53	▼	[80]
Cd	<i>Daphnia magna</i>	Lake water	7.53	▽	[52]
Cu	<i>D. magna</i>	Alrich humic acid	0.500	▽	[47]
Cu	<i>D. magna</i>	Field-collected DOC	0.500	■	[47]
Cu	<i>D. magna</i>	Field-collected DOC	0.500	○	[49]
Cu	<i>D. magna</i>	Chronic, field DOC	0.069	●	[50]
Cu	<i>D. pulex</i>	Field-collected DOC	0.030	▼	[81]
Ni	<i>D. magna</i>		21.9	○	[82]
Ni	<i>D. magna</i>	Well water	21.9	●	[83]
Ni	<i>C. dubia</i>	Reconstituted water	0.21	▽	[79]
Ni	<i>C. dubia</i>	Reconstituted water	1.92	▼	[84]
Pb	<i>D. magna</i>	Well water	0.94	○	[83]
Pb	<i>C. dubia</i>	Reconstituted water	0.62	●	[79]
Zn	<i>D. magna</i>	Well water	0.33	○	[83]
Zn	<i>D. magna</i>	Pond water	0.33	●	[85]
Zn	<i>D. magna</i>	Field-collected samples	1.00	▼	[51]

<sup>a</sup> [M = BL] nmol/g wet weight. Values from the cited references.

This can be seen by considering a simplified model. The mass balance equation for total metal in the three phases is

$$\begin{aligned} \Sigma M_T = & V_S[M \equiv POC] \\ & + V_{PW}([M \equiv DOC] + [M \equiv L] + [M^{2+}]) \\ & + V_{BL}[M \equiv BL] \end{aligned} \quad (15)$$

where  $\Sigma M_T$  is total mass (not concentration) of metal in the sediment-pore water-organism system and  $V_S$ ,  $V_{PW}$ , and  $V_{BL}$  are the volumes of the sediment, pore-water, and biotic ligand phases, respectively. Metal is either bound to sediment particulate organic carbon [ $M \equiv POC$ ], pore-water dissolved organic carbon, [ $M \equiv DOC$ ], other pore-water ligands [ $M \equiv L$ ], or as free cation [ $M^{2+}$ ], and to the biotic ligand [ $M \equiv BL$ ]. In the usual situation, however, the amount of metal associated with the biotic ligand  $V_{BL}[M \equiv BL]$  and the pore-water  $V_{PW}([M \equiv DOC] + [M \equiv L] + [M^{2+}])$  are small relative to the mass of metal in the sediment  $V_S[M \equiv POC]$ . As a consequence, the mass balance Equation 15 becomes

$$\Sigma M_T \approx V_S[M \equiv POC] \quad (16)$$

and the concentration of metal  $\Sigma M_T/V_S = [M]_T$  in the sediment determines [ $M \equiv POC$ ] using Equation 16

$$[M \equiv POC] = \Sigma M_T/V_S \quad (17)$$

Table 3. Biotic ligand model (BLM) parameters for *Daphnia magna*<sup>a</sup>

	Cd	Cu	Ni	Pb	Zn
Critical BL concn. <sup>b</sup>	7.53	0.069	21.9	0.940	0.330
Gill site density <sup>b</sup>	8.0	30.0	1000.0	30.0	30.0
Equilibrium constants <sup>c</sup>					
Log $K_{M-BL}$	8.60	7.40	4.00	6.65	5.50
Log $K_{MOH-BL}$		6.22			
Log $K_{Ca-BL}$	4.50	3.60	4.00	4.00	4.80
Log $K_{Mg-BL}$	3.50	3.60		4.00	4.80
Log $K_{H-BL}$	6.70	5.40	6.70	4.00	6.70
Log $K_{Na-BL}$	3.00	3.00	3.00	3.80	

<sup>a</sup> Parameter values from references in Table 2.

<sup>b</sup> Concn. is measured in nmol/gm wet weight.

<sup>c</sup>  $K_{M-BL} = [M \equiv BL]/\{M\}[BL]$ .

Knowing the concentration of metal on sediment particulate organic carbon, the free metal ion concentration follows from the usual equilibrium equation

$$\frac{[M \equiv POC]}{\{M^{2+}\}[ \equiv POC]} = K_{M-POC} \quad (18)$$

or

$$\{M^{2+}\} = \frac{[M \equiv POC]}{K_{M-POC}[ \equiv POC]} \quad (19)$$

where  $K_{M-POC}$  is the equilibrium constant for the metal-POC binding (Eqn. 14) and  $[ \equiv POC]$  is the concentration of unbound POC sites. Therefore, the free metal activity in the pore water is determined only by the concentrations in the sediment particulate organic carbon  $\Sigma M_T/V_S = [M \equiv POC]$  and unbound POC sites  $[ \equiv POC]$  (Eqns. 17 and 19). It is not influenced by the concentrations of the complexing ligands in pore-water  $[DOC]_T$  and  $[L]_T$ . These influence the amount of complexed metal in pore water  $[M \equiv POC]$  and  $[M \equiv L]$  but not the free metal activity.

This important result can be understood by considering the case in which initially there are no complexing ligands in pore water. The free metal activity is determined by Equation 19. Now add a quantity of DOC to the pore water. The metal-DOC complex [ $M \equiv DOC$ ] forms and lowers the free metal activity  $\{M^{2+}\}$ . However, Equation 19 must be satisfied. This can happen in two ways. Either [ $M \equiv POC$ ] decreases in response to the lower  $\{M^{2+}\}$ , or metal from the sediment particulate organic carbon desorbs into the pore water and  $\{M^{2+}\}$  increases. Which of these processes occurs depends on the sizes of the sediment and pore-water phases. If the quantity of DOC added is large relative to the sediment POC, then [ $M \equiv POC$ ] decreases, since the mass balance Equation 15 must be satisfied. In this case, pore-water metal activity decreases. However, in the usual case the reverse is true. The added DOC is small relative to sediment POC. Hence, only a small fraction of the metal sorbed to POC desorbs to form the required quantity of [ $M \equiv POC$ ]. Therefore, the metal sorbed to sediment POC [ $M \equiv POC$ ] is essentially unchanged, and  $\{M^{2+}\}$  is unchanged as well. Hence, in the usual case in which Equation

Table 4. Windemere Humic Aqueous Model (WHAM) V metal equilibrium constants<sup>a</sup> ( $\log_{10}K_{M-L}$ )<sup>b</sup>

Metal (M)	Cd	Cu	Ni	Pb	Zn	Ca	Mg
Ligands (L)							
OH <sup>1-</sup>	3.92	6.48	4.14	7.60	5.04		
(OH) <sub>2</sub> <sup>2-</sup>	7.65	11.78	9.00	10.88	11.10		
(OH) <sub>3</sub> <sup>3-</sup>				13.94			
SO <sub>4</sub> <sup>2-</sup>	2.46	2.36	2.32	2.60	2.38	2.3	2.37
Cl <sup>1-</sup>	1.98	0.40	0.40	1.40	0.40		
Cl <sub>2</sub> <sup>2-</sup>	2.60			2.00			
CO <sub>3</sub> <sup>2-</sup>	3.50	6.75	2.41	6.40	4.76	3.22	2.98
HCO <sub>3</sub> <sup>1-</sup>	10.95	14.62	13.41	9.90	13.12	11.44	11.4
(CO <sub>3</sub> ) <sub>2</sub> <sup>4-</sup>		9.92					
Particulate organic carbon							
Log <sub>10</sub> K <sub>MHA</sub> <sup>c</sup>	2.7	1.5	2.7	1.7	2.3	3.2	3.3
A-sites <sup>d</sup>	1.32	2.52	1.32	2.32	1.72	0.82	0.72
Range	0.43, 2.21	1.63, 3.41	0.43, 2.21	1.43, 3.21	0.83, 2.61	-0.07, 1.71	-0.17, 1.61
B-sites <sup>e</sup>	7.05	7.75	7.15	7.65	7.25	6.35	6.35
Range	5.34, 8.77	6.04, 9.47	5.44, 8.87	5.94, 9.37	5.54, 8.97	4.64, 8.07	4.64, 8.07

<sup>a</sup> Constants from the WHAM V database [8].

<sup>b</sup>  $K_{M-L} = \{M \equiv L\} / \{M\}\{L\}$ .

<sup>c</sup>  $K_{MHA} = \{M \equiv A\}\{H^+\} / \{H^+ \equiv A\}\{M\}$ .

<sup>d</sup>  $K_{M-A} = [M \equiv A] / \{M\}[A]$ .

<sup>e</sup>  $K_{M-B} = [M \equiv B] / \{M\}[B]$ .

16 is true, the pore-water concentrations of complexing ligands do not affect the pore-water free metal activity  $\{M^{2+}\}$ .

#### Effect of pore-water competition

It is not true, however, that the concentrations of pore-water competing cations have no effect. The other term in Equation 19 that determines  $\{M^{2+}\}$  is  $\{ \equiv POC \}$ , the concentration of free POC sites. If pore-water cations also bind to POC, then they can have an effect. This can be seen from the mass balance for sediment POC binding sites

$$[POC]_T = [\equiv POC] + [M \equiv POC] + [C \equiv POC] \quad (20)$$

where  $[POC]_T$  is the concentration of sediment POC binding sites and  $[C \equiv POC]$  is the concentration of competing ligand  $C^{2+}$  (e.g.,  $Ca^{2+}$ ) bound to the sediment POC. The equilibrium equation is

$$\frac{[C \equiv POC]}{\{C^{2+}\}[\equiv POC]} = K_{C-POC} \quad (21)$$

or

$$[\equiv POC] = \frac{[C \equiv POC]}{\{C^{2+}\}K_{C-POC}} \quad (22)$$

where  $\{C^{2+}\}$  is the competing cation pore-water activity. Hence, pore-water concentrations of competing cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^{2+}$ , and  $H^+$ ) will affect the pore-water free metal activity by changing  $\{ \equiv POC \}$ , the concentration of free sediment POC sites.

This is what would be expected—competitive effects from competing cations. The remarkable result, shown below, is that the only pore-water competing cation that significantly affects the computed sediment organic carbon LC50,  $SEM_{xOC}^*$ , is the pore-water pH. The concentration of the other competing cations is much less important. The reasons for this unexpected result are also discussed below.

#### WATER COLUMN BLM

The BLM that will be used in the computations below differs from the simplified model presented above (Eqns. 19

and 22) in the representation of the sorption of the metal and competing cations to organic carbon. Rather than one sorption site  $[ \equiv POC ]$ , the WHAM V model [36] is used that incorporates a distribution of both weak and strong monodentate and bidentate sites at which protons, cations, and metal can bind. Also, electrostatic effects and activity corrections are explicitly taken into account. The end result is a set of conditional equilibrium constants  $K_{M-POC}$  and  $K_{C-POC}$  that apply at the pH, ionic strength, and other solution conditions for which the computation is made. These could be used in the simplified model equations above. However, since large variations in solution composition will be evaluated, the more general model is required. For the computations discussed below, the BLM that incorporates WHAM V [37] is used.

The BLMs in various stages of development are available for all the metals being considered [39–43]. Most of the available sediment toxicity data are for amphipods, which are crustaceans. Biotic ligand models are available for either the cladocerans *Daphnia magna* or *Ceriodaphnia dubia*, which are also crustaceans. A comparative sensitivity investigation of freshwater species using 48-h LC50s [44] demonstrates that for metals, *C. dubia* is the most sensitive species, and amphipods are a factor of two less sensitive than *D. magna*. Therefore, using the available BLMs for comparison to amphipod toxicity is not unreasonable for a feasibility calculation.

The relationship between freshwater and saltwater species sensitivity has also been investigated [45]. The ratio of the saltwater to freshwater HC5s are 1.08 (Cd), 2.07 (Pb), 4.31 (Cu), 9.03 (Ni), and 13.4 (Zn). These results indicate that saltwater species are less sensitive to metals than are freshwater species. However, these results are not directly applicable to evaluating the use of freshwater BLMs for predicting saltwater toxicity, since the LC50s used to make the HC5 analyses are dissolved metal concentrations rather than metal activities. Nevertheless, since the BLMs used to make the predictions are not specific to the sediment organisms being tested, the comparisons presented below should be viewed as a feasibility investigation rather than a definitive test.

The state of calibration of the BLMs for various metals is

Table 5. Solution composition

	Ca ( $\mu\text{M}$ )	Mg ( $\mu\text{M}$ )	Na ( $\mu\text{M}$ )	K ( $\mu\text{M}$ )	SO <sub>4</sub> ( $\mu\text{M}$ )	Cl ( $\mu\text{M}$ )	$\Sigma\text{CO}_2$ ( $\mu\text{M}$ )
Freshwater [86]	330	150	230	30	69	160	860
Seawater [86]	10,200	53,200	468,000	10,200	28,200	545,000	2,380
Hardness (mg/L) <sup>a</sup>	( $\mu\text{M}$ )	( $\mu\text{M}$ )	( $\mu\text{M}$ )	( $\mu\text{M}$ )	( $\mu\text{M}$ )	( $\mu\text{M}$ )	( $\mu\text{M}$ )
20	138	63	230	30	69	160	358
50	344	156	230	30	69	160	896
100	688	313	230	30	69	160	1,790
200	1,380	625	230	30	69	160	3,580
500	3,440	1,560	230	30	69	160	8,960
1,000	6,880	3,130	230	30	69	160	17,900
Salinity (g/L) <sup>b</sup>	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)
0	0.33	0.15	0.23	0.03	0.07	0.16	0.86
2	0.89	3.18	27.0	0.61	1.68	31.3	0.95
5	1.74	7.73	67.1	1.48	4.09	78.0	1.08
10	3.15	15.3	134	2.94	8.11	156	1.29
20	5.97	30.5	268	5.84	16.1	311	1.73
30	8.79	45.6	401	8.75	24.2	467	2.16
35	10.20	53.2	468	10.2	28.2	545	2.38

<sup>a</sup> Hardness (g/L) = 100.0([Ca] + [Mg]), Ca, Mg in mol/L. [Ca]/[Mg] = 2.20, [ $\Sigma\text{CO}_2$ ]/[Ca] = 2.61.

<sup>b</sup> For each cation/anion [C] = [C]<sub>Freshwater</sub>(1 - Salinity/35.0) + [C]<sub>Seawater</sub>(Salinity/35.0).

examined in Figure 3, which presents a comparison of the predicted and observed LC50s for Cu and Zn, and in Figure 4, there is a comparison for Cd, Ni, and Pb. The parameters used in the model—the biotic ligand (BL) equilibrium binding constants (e.g.,  $K_{M-BL}$  and  $K_{C-BL}$ ) and critical BL concentrations [ $M \equiv BL$ ]\*—the sources of data, and the plotting symbols are listed in Tables 2 through 4.

The biotic ligand binding constants  $K_{M-BL}$  and  $K_{C-BL}$  are not specific to *Daphnia* or *Ceriodaphnia*. The calibration of the original BLM for copper [9,39] was based on the supposition that the equilibrium constants for biotic ligand binding  $K_{M-BL}$  and  $K_{C-BL}$  were the same for all the organisms being considered. The rationale is that the mechanism of toxicity, and therefore the biotic ligand, is the same across the organisms. Only the critical biotic ligand concentration [ $M \equiv BL$ ]\* was varied to fit the observed LC50s for different organisms. For copper, the critical data set comprised Erickson's larval fathead minnow experiments [46]. These constants were then used to fit the *Daphnia* data that were available at the time. Subsequently, a direct analysis of *D. magna* toxicity data demonstrated that the *D. magna* and fathead minnow BLM binding constants are remarkably similar [47], supporting the use of universal BLM binding constants.

This strategy was adopted because extensive data sets with systematic variations in water chemistry were not—and are still not—available for many of the water column and benthic

organisms of interest. For the application of BLMs to criteria development, this will almost certainly be the case for the foreseeable future. Therefore, this procedure is continued. The BLM's binding constants are not specific to *Daphnia* or *Ceriodaphnia* but are rather the results of fitting the BLM to the full data set that includes fish species. Only the critical biotic ligand LC50 concentration, [ $M \equiv BL$ ]\*, is organism specific.

For copper (Fig. 3A), the original BLM calibration [9,39] is employed with one modification. The biotic ligand binding constant for Mg is assumed to be equal to the Ca binding constant, consistent with more recent data [47–49]. These data are included in Figure 3A as well. However, for very low DOC concentrations and for pH < 7, the original BLM model predictions start to deviate from these observations. Since the sediments being considered all contain significant quantities of POC, and because sediment pore-water pH is usually above pH = 7 [27], the data in Figure 3A are restricted to pH  $\geq$  7. In addition to acute data, in which the carbon sources are Alrich humic acid and natural organic matter, a set of chronic data are also included [50], which also are in reasonable agreement with the original Cu BLM parameterization. Of course, the biotic ligand binding constants could be adjusted to conform to the new data [47–50]. However, for the reasons given above, the original Cu BLM binding constants are used, and only the critical BL concentrations are varied (Table 2).

For zinc, the BLM [43] is modified in the same way as the

Table 6. Excess simultaneously extracted metals (SEM) concentration  $SEM_{x,OC}^*$  for varying pH<sup>a</sup>

pH	Cd ( $\mu\text{mol/gOC}$ )	Cu ( $\mu\text{mol/gOC}$ )	Ni ( $\mu\text{mol/gOC}$ )	Pb ( $\mu\text{mol/gOC}$ )	Zn ( $\mu\text{mol/gOC}$ )
6.0	20.2	80.6	537	834	265
6.5	21.1	187	525	1,065	357
7.0	40.7	450	642	1,530	787
7.5	66.2	684	830	1,972	1,075
8.0	97.1	905	1,057	2,716	1,368
8.5	132	1,089	1,301	3,421	1,659
9.0	162	1,210	1,523	3,857	1,927

<sup>a</sup> Hardness = 50 mg/L.

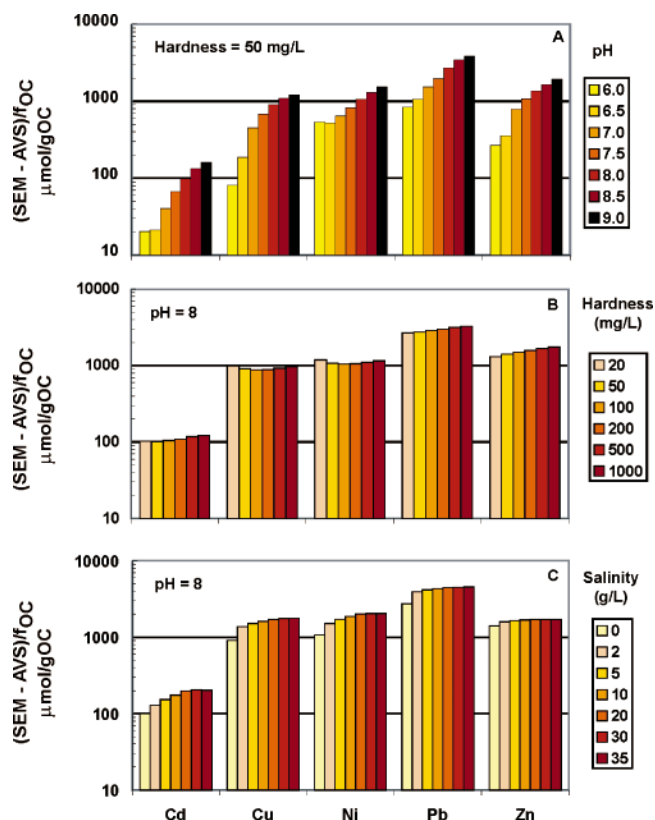


Fig. 5. Sediment median lethal concentrations (LC50s). Organic carbon-normalized excess simultaneously extracted metals ( $SEM_{x,OC}$ ) concentration  $SEM_{x,OC} = (SEM^* - AVS)/f_{OC}$  in equilibrium with the critical biotic ligand concentration for *Daphnia magna* LC50s for the listed metals. See Tables 3 and 4 for biotic ligand model parameters, Table 5 for pore-water solution composition. (A) Effect of pH variation. (B) Effect of hardness variation. (C) Effect of salinity variation. AVS = acid-volatile sulfide.

Cu BLM. The biotic ligand binding constant for Mg is assumed to be equal to the Ca binding constant. Figure 3B presents the original calibration data as well as more recent data [51]. The data for very low DOC concentrations are again excluded. The critical biotic ligand concentrations are listed in Table 2.

For cadmium (Fig. 4A), an additional data set [52] is included together with those used in the original calibration [42]. For the remaining metals, Ni (Fig. 4B) and Pb (Fig. 4C), the data for *Daphnia* and *Ceriodaphnia* used in the original calibrations are presented [40,41].

In general, the BLM predictions are within a factor of two of the observed LC50s, although there are some systematic deviations. The small data set that is available for Pb makes these predictions more uncertain.

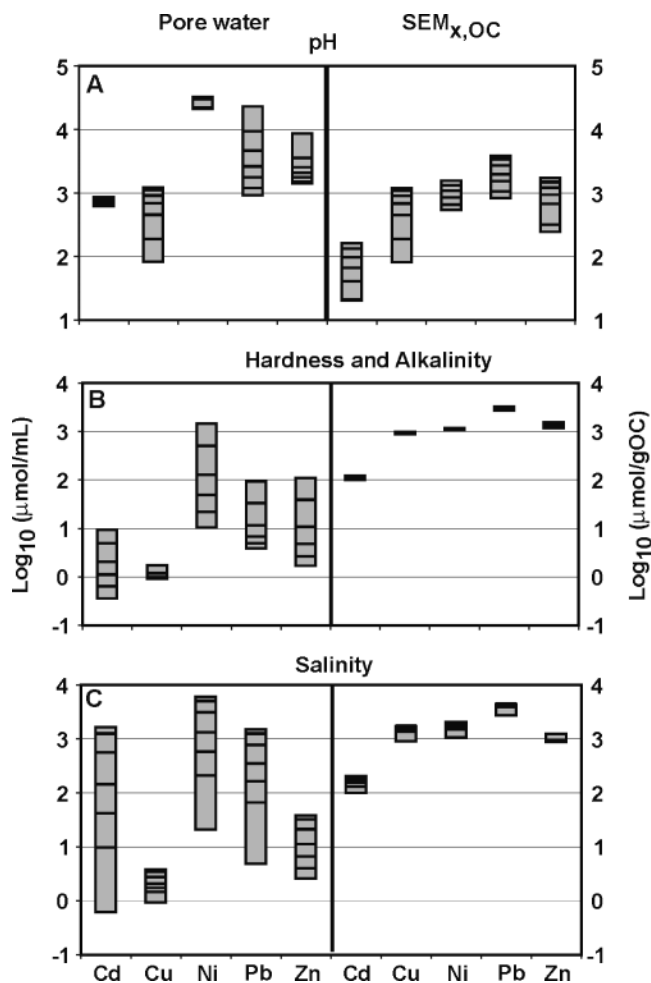


Fig. 6. Comparison of pore-water and sediment median lethal concentrations (LC50s). Concentrations of total dissolved metal in pore-water (left column) and sediment particulate organic carbon-normalized particulate metal concentrations (right column) in equilibrium with the critical biotic ligand concentration for *Daphnia magna* LC50s. The conditions (A–C) are the same as in Figure 5. The ranges correspond to the maximum and minimum concentrations and the lines within the bars correspond to the individual cases in Figure 5. SEM = simultaneously extracted metals.

#### SEDIMENT BLM

The sBLM is a straightforward extension of the water column BLM. Pore-water DOC is not considered, based on the analysis presented above (Eqns. 15–19). Instead, sediment POC is included. It is modeled as humic acid using WHAM V, following the procedure employed by Tipping and colleagues for predicting metal sorption to soils [53–57]. WHAM

Table 7. Excess simultaneously extracted metals (SEM) concentration  $SEM_{x,OC}^*$  for varying hardness and alkalinity<sup>a</sup>

Hardness (mg/L)	Cd ( $\mu\text{mol/gOC}$ )	Cu ( $\mu\text{mol/gOC}$ )	Ni ( $\mu\text{mol/gOC}$ )	Pb ( $\mu\text{mol/gOC}$ )	Zn ( $\mu\text{mol/gOC}$ )
20	102	991	1,188	2,683	1,157
50	101	910	1,071	2,747	1,252
100	104	880	1,046	2,856	1,332
200	109	882	1,057	2,989	1,414
500	118	921	1,104	3,164	1,517
1,000	122	967	1,153	3,281	1,591

<sup>a</sup> pH = 8.

Table 8. Excess simultaneously extracted metals (SEM) concentration  $SEM_{x,OC}^*$  for varying salinity<sup>a</sup>

Salinity (g/L)	Cd ( $\mu\text{mol/gOC}$ )	Cu ( $\mu\text{mol/gOC}$ )	Ni ( $\mu\text{mol/gOC}$ )	Pb ( $\mu\text{mol/gOC}$ )	Zn ( $\mu\text{mol/gOC}$ )
0	100	913	1,074	2,742	1,404
2	129	1,381	1,516	3,957	1,592
5	153	1,514	1,717	4,152	1,649
10	174	1,613	1,875	4,303	1,684
20	198	1,709	2,006	4,446	1,708
30	205	1,758	2,046	4,512	1,713
35	202	1,773	2,049	4,530	1,712

<sup>a</sup> pH = 8.

V is also used by Lofts and Tipping in their Surface Chemistry Assemblage Model for Particles model that has been applied to sorption to suspended solids in the water column [58,59]. Since sediment POC is formed by water column POC settling to the sediment, and a portion of water column POC is from soil runoff, modeling sediment POC as humic acid seems to be a reasonable assumption for a feasibility investigation. However, clearly direct confirmation that sediment POC can, in fact, be modeled as humic acid would be desirable.

The BLM is used to compute the LC50 for *Daphnia* in pore water. The pore-water concentrations of competing cations and pH are specified, together with the appropriate concentrations of anions needed to maintain electroneutrality and to contribute to the ionic strength. The concentration of metal sorbed to sediment POC per unit POC is equated to the organic carbon-normalized excess SEM

$$SEM_{x,OC}^* = \frac{[M \equiv POC]}{[POC]_T} \quad (23)$$

This is the sBLM prediction of the sediment LC50.

A series of representative cases (Table 5) are considered: An average freshwater with varying hardness and  $\Sigma\text{CO}_2$ , and freshwater-seawater mixtures with varying salinity. These cases do not necessarily represent actual sediment pore-water compositions, but rather provide a range of conditions to examine the behavior of the model.

Figure 5A and Table 6 present the results for varying pH values. The resulting LC50s ( $SEM_{x,OC}^*$ ), with the exception of Cd, are in the same range (100–2,000  $\mu\text{mol/gOC}$ ) as concentrations of organic carbon-normalized excess SEM that are associated with toxicity (Fig. 1). Although there are differences between the metals—the Cd LC50s are approximately an order of magnitude lower than the others—there is a remarkable similarity for the other metals. It is also apparent that pH has a direct impact on the computed sediment LC50s.

By contrast, varying the hardness and inorganic carbon by

keeping the ratio of inorganic carbon to calcium [ $\Sigma\text{CO}_2$ ]/[Ca] constant (Table 5)—this covariation contributes to the empirically observed effect of hardness on metal toxicity [60]—has essentially no effect on the result (Fig. 5B and Table 7). Varying only calcium produces the same result. This result, a consequence of the WHAM V and BLM calcium and magnesium binding constants that are independently determined, is quite unexpected.

The effect of salinity is examined in Figure 5C and Table 8. The composition is varied from freshwater to full-strength seawater. The critical concentrations,  $SEM_{x,OC}^*$ , vary by approximately a factor of two, whereas most of the cations and anions vary by almost three orders of magnitude. The reason for this unexpected and important result—the independence of the  $SEM_{x,OC}^*$  with respect to the concentration of the competing hardness and salinity cations—is discussed in the next section.

The BLM model also computes the total dissolved metal in the pore water that is in equilibrium with the sediment POC. The variation in pore-water and sediment metal concentrations corresponding to the results in Figure 5 are compared in Figure 6. For these illustrative calculations, a pore-water DOC = 1 mg/L of humic acid value is assigned. For pH variations, the concentrations in both phases vary by approximately the same degree. However, for hardness/alkalinity and salinity variations, the pore-water concentrations vary by orders of magnitude, whereas the sediment POC concentrations are within a factor of two.

This result—that  $SEM_{x,OC}^*$  is approximately constant as the concentrations of major cations and anions vary with hardness or fraction of seawater—has important consequences for the development of a sediment BLM. A straightforward application of a BLM to sediment pore water, following the precepts of EqP, requires a reasonably complete characterization of the pore-water chemistry: The concentrations of the cations and anions in Tables 3 and 4, DOC, and total dissolved metal.

Table 9. Excess simultaneously extracted metals (SEM) concentration  $SEM_{x,OC}^*$  for seawater and varying pH

pH	Cd ( $\mu\text{mol/gOC}$ )	Cu ( $\mu\text{mol/gOC}$ )	Ni ( $\mu\text{mol/gOC}$ )	Pb ( $\mu\text{mol/gOC}$ )	Zn ( $\mu\text{mol/gOC}$ )
6	31.2	181	769	2,187	513
6.5	53.1	377	1,044	2,813	799
7	93.1	625	1,353	3,579	1,095
7.5	145	916	1,697	4,072	1,398
8	200	1,242	2,048	4,530	1,712
8.5	254	1,536	2,326	5,137	2,022
9	302	1,763	2,507	5,836	2,333

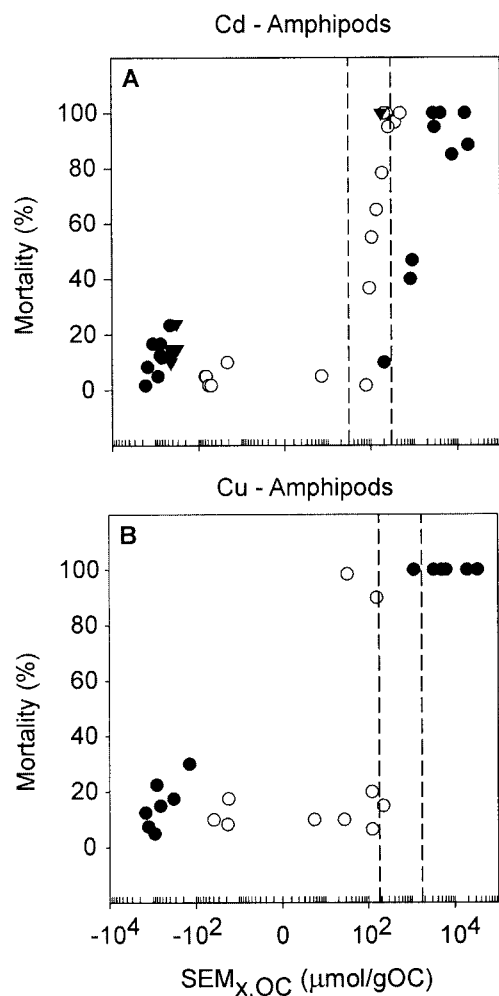


Fig. 7. Comparisons between observed mortality and excess organic carbon-normalized simultaneously extracted metals (SEM),  $SEM_{x,OC}^* = (SEM^* - AVS)/f_{OC}$  plotted using a positive and negative log scale [27] for marine amphipods in acute sediment toxicity tests. (A) Cadmium [4], ●; [63], ○; [65], ▼. (B) Copper [4], ●; [64], ○. The vertical lines span the range of computed median lethal concentrations (LC50s) for pH = 6 to 9 (Table 9). AVS = acid-volatile sulfide.

However, if the BLM is applied to sediment POC, then only the pore-water pH is required, in addition to the usual solid phase measurements SEM, AVS, and  $f_{OC}$ . The need to avoid pore-water measurements was a major motivation for developing sediment quality criteria/guidelines/benchmarks [10,61,62] in the first place, and the sediment BLM continues in this tradition.

#### Effect of competing cations

The fact that  $SEM_{x,OC}^*$  is approximately constant as the concentrations of major cations and anions vary with hardness or fraction seawater (Fig. 5B and C), but not with variations in pH (Fig. 5A), is an important result that merits a careful analysis. As discussed above, the competing cations affect both the metal binding to sediment POC (Eqn. 22) and to the biotic ligand (Fig. 2, top). It would be expected, therefore, that increasing the calcium concentration, for example, would decrease the quantity of metal binding to the biotic ligand [ $M \equiv BL$ ] and to sediment organic carbon [ $M \equiv POC$ ]. If the strength of binding were the same in each phase, it would be expected that the effect of the competing cation would ap-

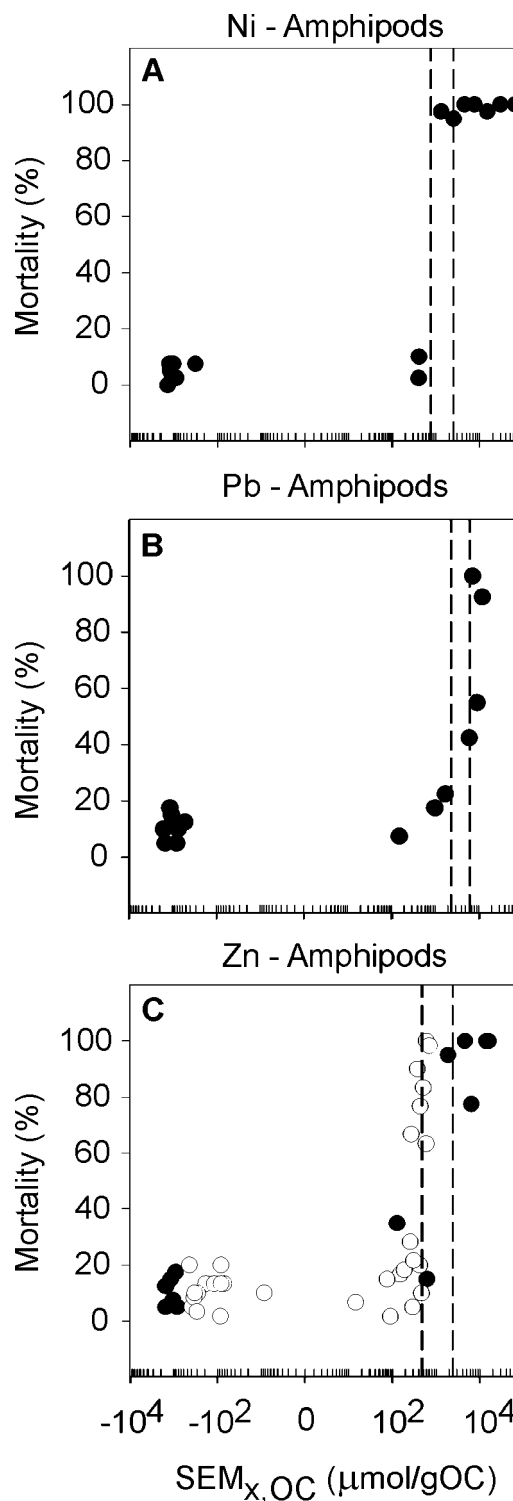


Fig. 8. Comparisons between observed mortality and excess organic carbon-normalized simultaneously extracted metal (SEM),  $SEM_{x,OC}^* = (SEM^* - AVS)/f_{OC}$  plotted using a positive and negative log scale [27], for marine amphipods in acute sediment toxicity tests. (A) Nickel [4], ●. (B) Lead [4], ●. (C) Zinc [4], ●; [66], ○. The vertical lines span the range of computed median lethal concentrations for pH = 6 to 9 (Table 9). AVS = acid-volatile sulfide.

proximately balance out. However, the reason for this independence is not due to similar binding strengths, as was initially suspected. Rather, it is due to the saturation of the sites on sediment organic carbon. An analysis is presented in the Appendix.

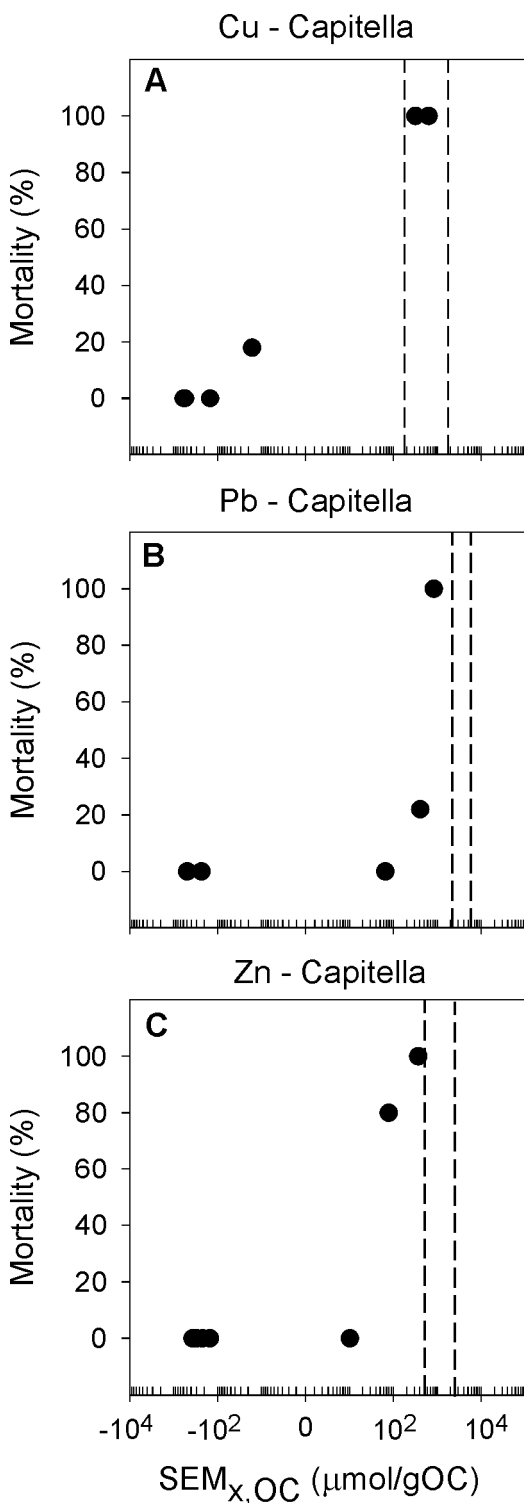


Fig. 9. Comparisons between observed mortality and excess organic carbon-normalized simultaneously extracted metal (SEM),  $SEM_{x,OC}^* = (SEM^* - AVS)/f_{OC}$  plotted using a positive and negative log scale [27], for the marine polychaete *Capitella capitata*. (A) Copper, ●. (B) Lead, ●. (C) Zinc, ●, [67]. The vertical lines span the range of computed median lethal concentrations for pH = 6 to 9 (Table 9). AVS = acid-volatile sulfide.

#### SPIKED SEDIMENT TOXICITY TESTS

The analysis of the spiked sediment toxicity tests using the sediment BLM is complicated by the following circumstances. The endpoint used for the BLM is for the water column or-

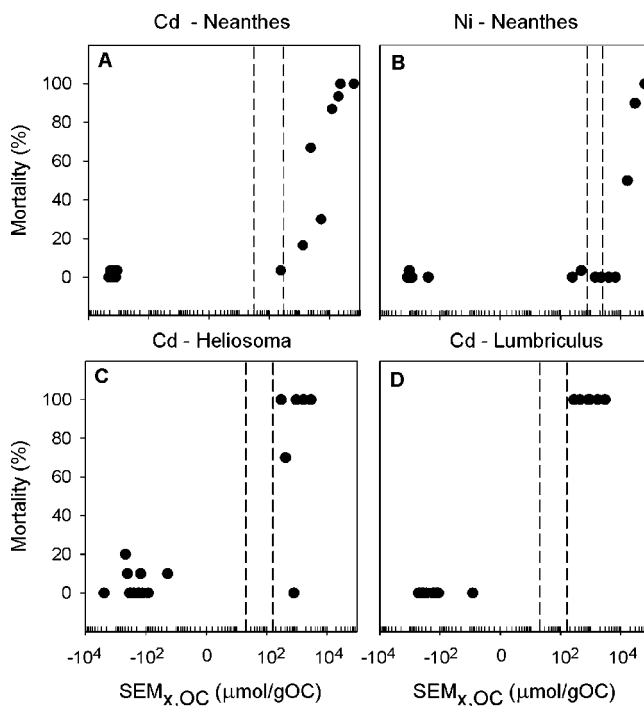


Fig. 10. Comparisons between observed mortality and excess organic carbon-normalized simultaneously extracted metal (SEM),  $SEM_{x,OC}^* = (SEM^* - AVS)/f_{OC}$  plotted using a positive and negative log scale [27], for the marine polychaete *Neanthes arenaceodentata*. (A) Cadmium, ●. (B) Nickel, ●, [68]. (C) Cadmium for the freshwater snail *Heliosoma*, ●. (D) Cadmium for the freshwater oligochaete *Lumbriculus variegatus*, ●, [69]. The vertical lines span the range of computed median lethal concentrations for pH = 6 to 9 (Tables 6 and 9). AVS = acid-volatile sulfide.

ganism *D. magna*. The sediment experiments employed various benthic and epibenthic organisms (Table 1). Therefore, the comparisons do not, strictly speaking, conform to the requirements of the EqP model that predicts the sediment toxicity based on water-only exposures to the same organism. Comparing the observed toxicity in sediment exposures to the BLM computations assumes that the organisms being tested have a sensitivity similar to that of *Daphnia*. Also, it is implicitly assumed that the BL binding constants that are derived from the responses of the organisms employed in the calibration are applicable to the organisms tested in sediments.

For the marine organism tests, there is an additional difficulty. The BLMs are calibrated using freshwater organisms exclusively. This is also the case for metal partitioning to DOC using WHAM V. Therefore, the application to marine tests requires that both the BLM binding constants and the partitioning to sediment POC computed by WHAM V are applicable to marine organisms and seawater chemistry, respectively.

Finally, the pH of the pore waters for the sediment toxicity experiments examined below is unknown and is not likely to be constant. Adding substantial quantities of metal will lower the pH due to metal hydrolysis. Therefore, it is difficult to be specific about the actual pHs of the experiments. Measuring the pore-water pH should be an important part of future sediment toxicity tests.

Therefore, these comparisons are not definitive tests of the sediment BLM model, but rather are more on the order of a feasibility investigation. Can the model predict concentrations in the right order of magnitude of those observed?

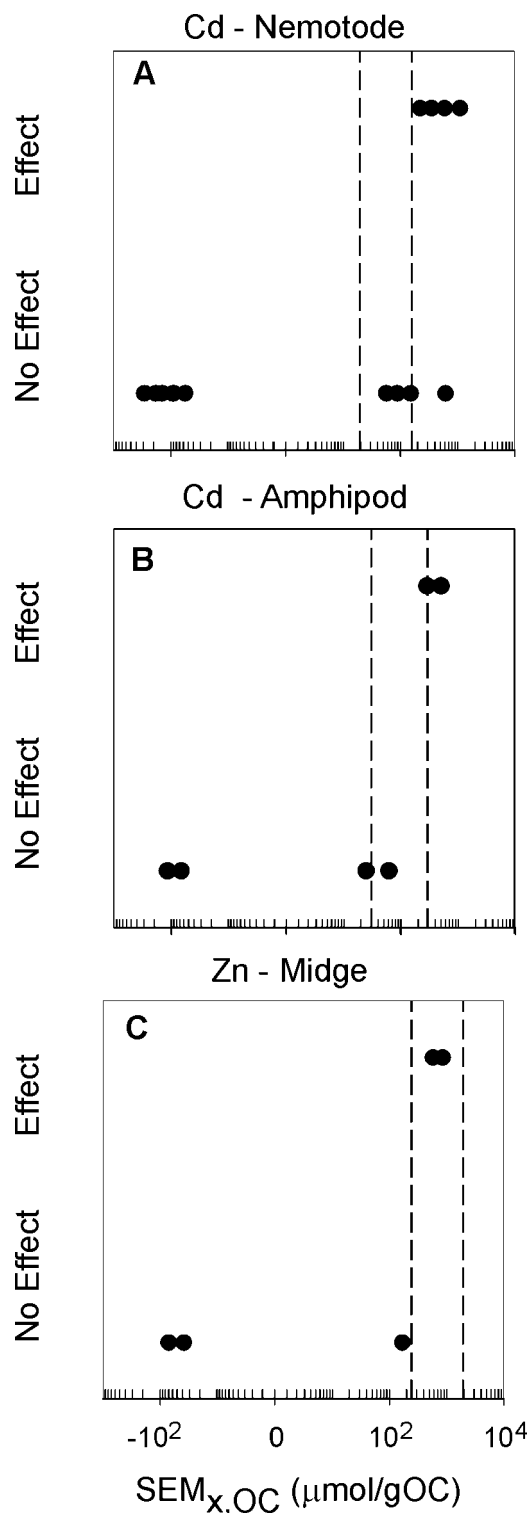


Fig. 11. Chronic toxicity for single organisms. Comparisons between observed no-effect/effects and excess organic carbon-normalized simultaneously extracted metal (SEM),  $SEM_{x,OC}^* = (SEM^* - AVS)/f_{OC}$  plotted using a positive and negative log scale [27]. (A) Cadmium: 72-h growth test with the freshwater nematode *Caenorhabditis elegans* [70], ●—included as effect/no effect data. (B) Cadmium: 28-d life cycle test with the marine amphipod *Leptocheirus plumulosus* [71], ●. (C) Zinc: 56-d test with the freshwater midge *Chironomus tentans* [72], ●. The vertical lines span the range of computed median lethal concentrations for pH = 6 to 9 (Tables 6 and 9). AVS = acid-volatile sulfide.

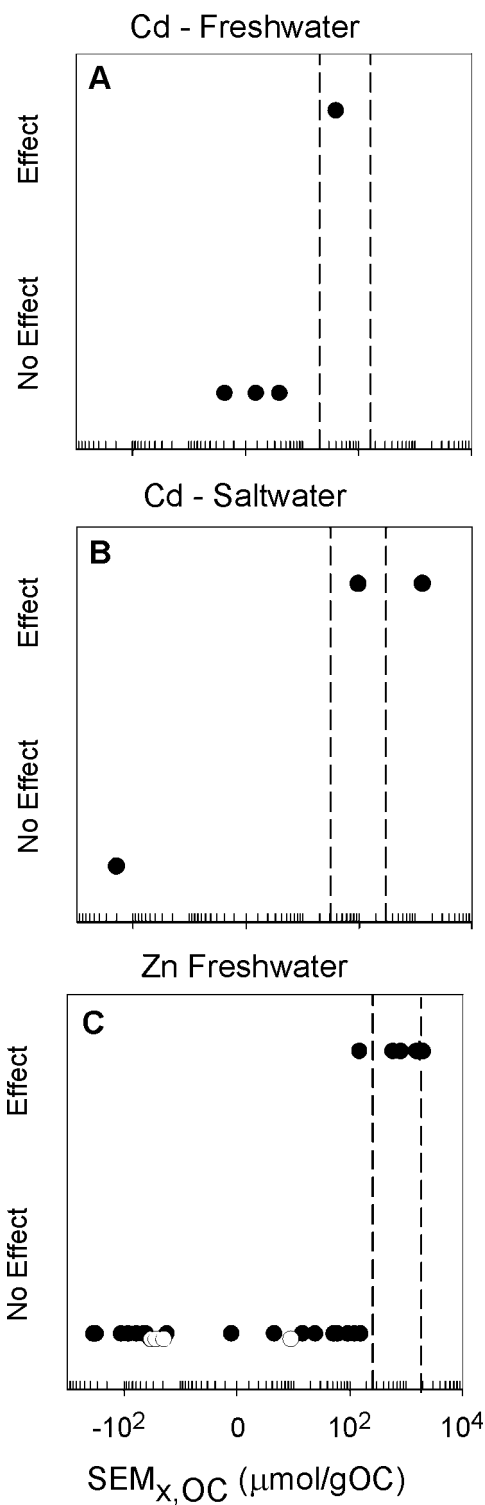


Fig. 12. Chronic toxicity employing multiple organisms. Comparisons between observed no-effect/effects and excess organic carbon-normalized simultaneously extracted metal (SEM),  $SEM_{x,OC}^* = (SEM^* - AVS)/f_{OC}$  plotted using a positive and negative log scale [27]. (A) Cadmium: 14-month lake colonization experiment in a low-acid volatile sulfide (AVS = 0.5  $\mu\text{mol/g}$ ) freshwater lake [73], ●. (B) 117-d laboratory marine chronic colonization experiment [74], ●. (C) 349-d freshwater lake field colonization experiment, ○, [75], and a 9-month multilocation lake and stream field colonization experiment, ●, [76]. The vertical lines span the range of computed median lethal concentrations for pH = 6 to 9 (Tables 6 and 9). AVS = acid-volatile sulfide.

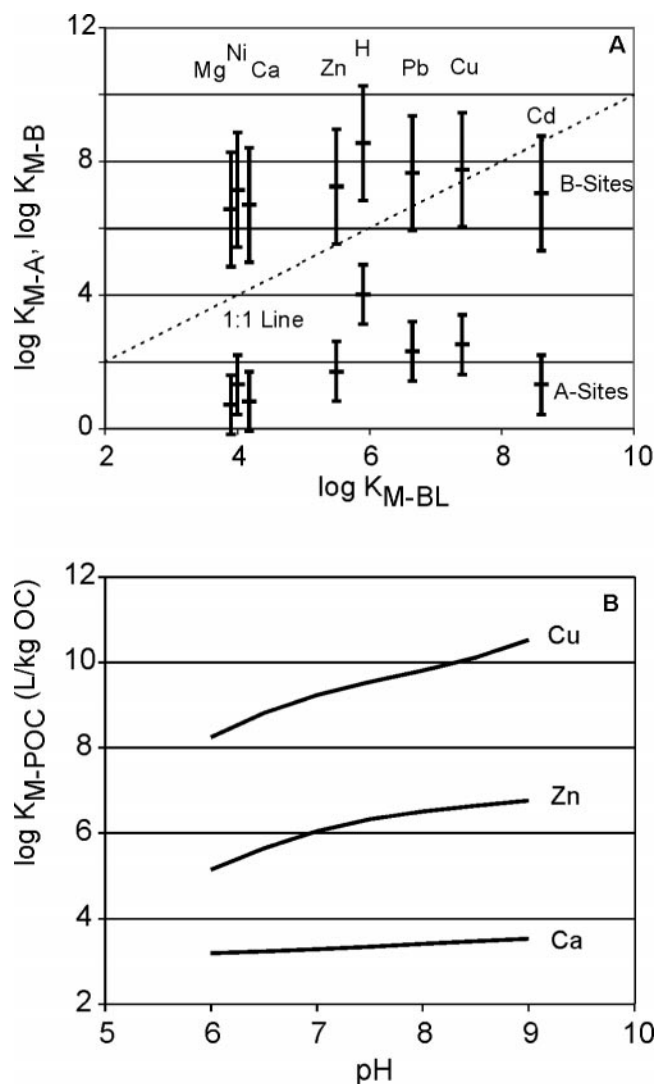


Fig. 13. (A) Mean and range of metal-A site  $\log K_{M-A}$  and metal-B site  $\log K_{M-B}$  equilibrium constants (Table 4) versus metal-biotic ligand equilibrium constants  $\log K_{M-BL}$  (Table 3). For Mg and Ca, the average  $\log K_{M-BL}$  is used. (B) Conditional  $\log K_{M-POC}$  versus pH for Ca, Zn, and Cu for the solution conditions used in Figure 5A; hardness = 1,000 mg/L (Table 5). POC = particulate organic carbon.

#### Acute toxicity

Figures 7 and 8 present the comparisons between observed mortality and excess organic carbon-normalized SEM,  $SEM_{xOC}$ , for marine amphipods in acute sediment toxicity tests [4,63–66]. The  $SEM_{xOC}$  is plotted using a positive and negative log scale [27]. The vertical lines span the range of computed LC50s for pH = 6 to 9 for full-strength seawater (Table 9). The region of uncertainty in prediction between the two vertical lines is due to the unknown pHs. No mortality is predicted to the left of the band, and mortality is predicted to the right.

For Cd (Fig. 7A), one set of observations conforms to the predictions (open symbols) and one set (filled symbols) appears to exhibit less toxicity. We have no explanation for this difference. For Cu (Fig. 7B), the results are essentially consistent with the predictions, with one exception. For Ni (Fig. 8A), the results are essentially consistent with the predictions. For Pb (Fig. 8B), mortality is predicted at lower concentrations than observed, although Pb has the highest predicted  $SEM_{xOC}^*$ . For Zn (Fig. 8C), the largest data set is at the pH =

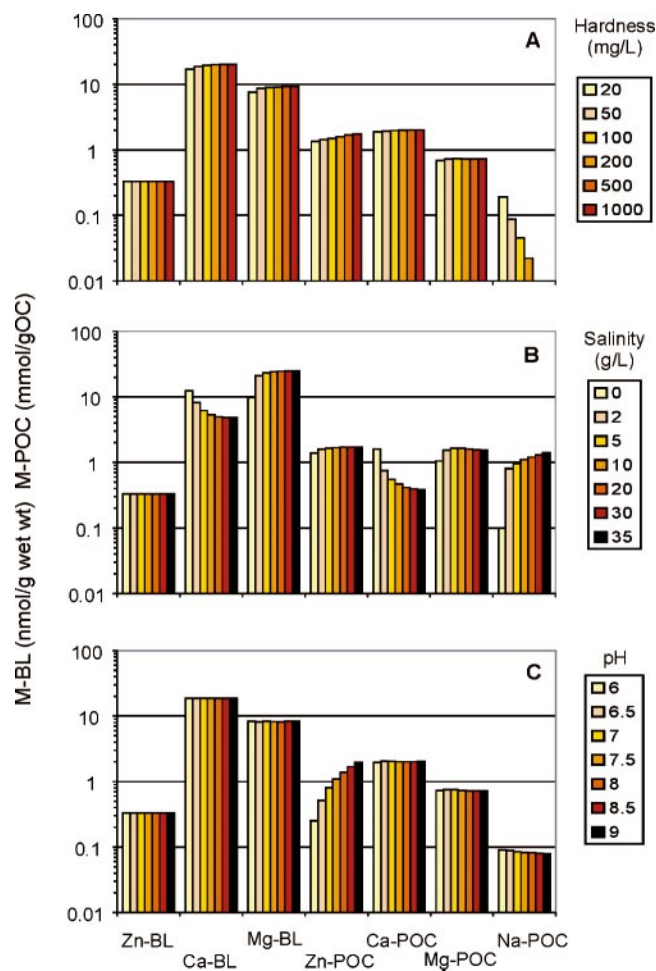


Fig. 14. Biotic ligand (BL) and particulate organic carbon (POC) concentrations for Zn, Ca, Mg, and Na for the varying hardness (A), salinity (B), and pH (C) cases presented in Figure 5. See Table 5 for solution composition.

6 boundary, indicating that either the pore-water pH is in fact low or that the predictions are inconsistent. The other data set conforms to predictions, with one exception.

Figure 9 is a similar presentation for sediment tests using the marine polychaete *Capitella capitata* [67]. The results for Cu (Fig. 9A) are essentially consistent with predictions. However, for Pb and Zn, the observed toxicity is at lower concentrations than predicted. Either *Capitella* is more sensitive than the predictions based on *Daphnia*, or the chemistry computations for seawater are inaccurate.

Figure 10 presents two sets of data. The marine polychaete *Neanthes arenaceodentata* [68] is apparently much less sensitive to Cd (Fig. 10A) and Ni (Fig. 10B). The freshwater oligochaete *Lumbriculus variegatus* [69] is apparently of similar sensitivity to *Daphnia* to Cd (Fig. 10D), whereas the snail *Helisoma* [69] appears to be less sensitive (Fig. 10C).

#### Chronic toxicity and other endpoints

The comparisons to tests employing chronic exposures are presented in Figures 11 and 12. Treatments are identified as either having no observed effect (no effect) or an observed effect (effect). Experiments that employed a single organism are shown in Figure 11. The data for the three experiments were as follows: A 72-h growth test for Cd with the freshwater nematode *Caenorhabditis elegans* [70] (Fig. 11A)—included

because the endpoint is not mortality; a 28-d life-cycle test for Cd with the marine amphipod *Leptocheirus plumulosus* [71] (Fig. 11B); and a 56-d test for Zn with the freshwater midge *Chironomus tentans* [72] (Fig. 11C). The results are correctly classified, with one exception (Fig. 11A).

Tests employing multiple organisms are presented in Figure 12. For Cd, two tests are included: A 14-month lake colonization experiment in a low-AVS ( $=0.5 \mu\text{mol/g}$ ) freshwater lake [73] (Fig. 12A), and a 117-d laboratory marine chronic colonization experiment [74] (Fig. 12B). For Zn, there are also two tests, plotted on the same graph (Fig. 12C) since they are both freshwater sediments: A 349-d freshwater lake field colonization experiment [75] and a nine-month multilocation lake and stream field colonization experiment [76]. Essentially all the tests conform to the predictions within the range of uncertainty due to the unknown pH.

### CONCLUSION

It appears that a sBLM can be successfully formulated that avoids the complications of explicitly modeling the pore-water chemistry. For the feasibility investigation presented above, the sediment concentrations are computed by assuming an equilibrium between the critical metal concentration on the biotic ligand and sediment POC. This concentration is compared to the sediment metal concentration in excess of AVS, normalized to the organic carbon concentration of the sediment ( $SEM^* - AVS$ )/ $f_{OC}$ . The computations presented above employ metal BLMs calibrated to water column organisms and freshwater chemistry. They use the critical BLM concentrations for *Daphnia magna* to compute the critical concentrations. The only sediment-partitioning phase is sediment organic carbon, modeled as humic acid.

In spite of these approximations, and without knowing the pore-water pH, the computations are not inconsistent with observations in acute and chronic, freshwater and marine sediment tests employing sensitive organisms. It is remarkable that this degree of agreement—within approximately one order of magnitude—is possible using models independently calibrated to freshwater organisms (*D. magna* or *C. dubia* BLMs) and chemistry (WHAM V) that considers partitioning only to sediment organic carbon modeled as humic acid. This indicates that an sBLM can be successfully developed. It should use critical BL concentrations appropriate to sediment organisms. The partition model should consider the additional sediment partitioning phases as necessary. It should be compared to toxicity data that include measured pore-water pH and the concentrations of the other partitioning phases, as appropriate. However, it is clear that detailed pore-water chemistry is not required.

**Acknowledgement**—The portion of this work that resulted in the empirical relationships was supported by the U.S. Environmental Protection Agency (U.S. EPA), Office of Water. We wish to thank our project officers, Mary Reiley and Heidi Bell (U.S. EPA), for their support, and our colleague Dave Mount (U.S. EPA) for his insightful comments. The development of the BLMs was supported by the International Copper Association (Christopher Lee and Robert Dwyer), the International Lead Zinc Research Organization (Andrew Green), the Water Environment Research Foundation (Pat Hadden), and the U.S. EPA (Cindy Roberts). The BLM computations and the preparation of the article were supported by the National Institute of Environmental Health Superfund Basic Research Program grant P42ES10344 and the U.S. EPA Center for the Study of Metals in the Environment at the University of Delaware.

### REFERENCES

- Di Toro DM, Mahony JD, Hansen DJ, Scott KJ, Hicks MB, Mayr SM, Redmond MS. 1990. Toxicity of cadmium in sediments: The role of acid volatile sulfide. *Environ Toxicol Chem* 9:1487–1502.
- Di Toro DM, Mahony JD, Hansen DJ, Scott KJ, Carlson AR, Ankley GT. 1992. Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environ Sci Technol* 26:96–101.
- Berry WJ, Cantwell M, Edwards P, Serbst J, Hansen DJ. 1999. Predicting the toxicity of sediments spiked with silver. *Environ Toxicol Chem* 18:40–48.
- Berry WJ, Hansen DJ, Mahony JD, Robson D, Di Toro DM, Shipley B, Rogers B, Corbin J, Boothman W. 1996. Predicting the toxicity of metals-spiked laboratory sediments using acid volatile sulfide and interstitial water normalizations. *Environ Toxicol Chem* 15:2067–2079.
- Hansen DJ, Berry WJ, Mahony JD, Boothman W, Di Toro DM, Robson D, Ankley GT, Ma D, Yan Q, Pesch C. 1996. Predicting the toxicity of metals-contaminated field sediments using interstitial concentrations of metal and acid volatile sulfide normalizations. *Environ Toxicol Chem* 15:2080–2094.
- Ankley GT, Di Toro DM, Hansen DJ, Berry W. 1996. Technical basis and proposal for deriving sediment quality criteria for metals. *Environ Toxicol Chem* 15:2056–2066.
- U.S. Environmental Protection Agency. 2005. Procedures for the derivation of equilibrium partitioning sediment Benchmarks (ESBs) for the protection of benthic organisms: metal mixtures (cadmium, copper, lead, nickel, silver, and zinc). EPA-600-R-02-011. U. S. Environmental Protection Agency, Washington, DC.
- Tipping E. 1994. WHAM—A computer equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. *Computers Geosci* 20:973–1023.
- Di Toro DM, Allen HE, Bergman H, Meyer J, Paquin PR, Santore RC. 2001. A biotic ligand model of the acute toxicity of metals. I. Technical basis. *Environ Toxicol Chem* 20:2383–2396.
- Di Toro DM, Zarba CS, Hansen DJ, Berry WJ, Swartz RC, Cowan CE, Pavlou SP, Allen HE, Thomas NA, Paquin PR. 1991. Technical basis for the equilibrium partitioning method for establishing sediment quality criteria. *Environ Toxicol Chem* 11:1541–1583.
- Di Toro DM, Berry WJ, Burgess R, Mount D, O'Connor T, Swartz RC. 2005. The predictive ability of sediment quality guidelines derived using equilibrium partitioning. In Wenning RJ, Ingersoll CG, eds, *Use of Sediment Quality Guidelines and Related Tools for the Assessment of Contaminated Sediments*. SETAC, Pensacola, FL, USA.
- Allen H, Gongmin F, Deng B. 1993. Analysis of acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) for estimation of potential toxicity in aquatic sediments. *Environ Toxicol Chem* 12:1441–1453.
- Meyer J, Adams W, Brix K, Luoma S, Mount D, Stubblefield W, Wood C. 2005. *Toxicity of Dietborne Metals to Aquatic Organisms*. SETAC, Pensacola, FL, USA.
- Jenne E. 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentration in soils and water: The significant role of hydrous Mn and Fe oxides. In Baker RA, ed, *Trace Inorganics in Water*. Advances in Chemistry Series 73. American Chemical Society, Washington, DC.
- Fu G, Allen HE, Cao Y. 1992. The importance of humic acids to proton and cadmium binding in sediments. *Environ Toxicol Chem* 11:1363–1372.
- Sauve S, Hendershot W, Allen HE. 2000. Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. *Environ Sci Technol* 34:1125–1131.
- Weng L, Temminghoff EJM, van Riemsdijk WH. 2001. Contribution of individual sorbents to the control of heavy metal activity in sandy soil. *Environ Sci Technol* 35:4436–4443.
- Gustafsson JP, Pechová P, Berggren D. 2003. Modeling metal binding to soils: The role of natural organic matter. *Environ Sci Technol* 37:2767–2774.
- Lee S, Allen H, Huang C, Sparks D, Sanders PF, Peijnenburg W. 1996. Predicting soil-water partition coefficients for cadmium. *Environ Sci Technol* 30:3418–3424.
- Tipping E, Lofts S, Lawlor A. 1998. Modelling the chemical speciation of trace metals in the surface waters of the Humber system. *Sci Total Environ* 210:63–77.

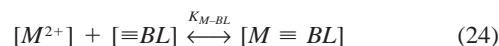
21. Ryba S, Burgess R. 2002. Effects of sample preparation on the measurement of organic carbon, hydrogen, nitrogen, sulfur, and oxygen concentrations in marine sediments. *Chemosphere* 48: 139–147.
22. Karickhoff SW, Brown DS, Scott TA. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res* 13:241–248.
23. American Society for Testing and Materials. 1995. Guide for conducting 10-day static sediment toxicity tests with marine and estuarine amphipods. E 1367-92. In *Annual Book of ASTM Standards*, Vol 11.05. Philadelphia, PA, pp 767–792.
24. Ankley GT. 1996. Evaluation of metal/acid-volatile sulfide relationships in the prediction of metal bioaccumulation by benthic macroinvertebrates. *Environ Toxicol Chem* 15:2138–2146.
25. Lee B, Lee J, Luoma S, Choi H, Koh C. 2000. Influence of acid volatile sulfide and metal concentrations on metal bioavailability to marine invertebrates in contaminated sediments. *Environ Sci Technol* 34:4517.
26. Lee B, Griscom S, Lee J, Choi H, Koh C, Luoma S, Fisher N. 2000. Influences of dietary uptake and reactive sulfides on metal bioavailability from aquatic sediments. *Science* 287:282.
27. Di Toro DM. 2001. *Sediment Flux Modeling*. John Wiley, New York, NY, USA.
28. Di Toro DM, McGrath JA, Hansen DJ, Berry WJ. 2002. Predicting the acute and chronic toxicity of metals in sediments using organic carbon normalized SEM and AVS. Technical Report. HydroQual, Mahwah, NJ, USA.
29. Morel FMM. 1983. *Principles of Aquatic Chemistry*. John Wiley, New York, NY, USA.
30. Morel FMM, Hering J. 1993. *Principles and Applications of Aquatic Chemistry*. John Wiley, New York, NY, USA.
31. Campbell PG. 1995. Interactions between trace metals and aquatic organisms: A critique of the free-ion activity model. In Tessier A, Turner DR, eds, *Metal Speciation and Bioavailability in Aquatic Systems*. John Wiley, New York, NY, USA, pp 42–102.
32. Pagenkopf G. 1983. Gill surface interaction model for trace-metal toxicity to fishes: Role of complexation, pH, and water hardness. *Environ Sci Technol* 17:342–347.
33. Paquin PR, Gorsuch WJ, Apte S, Batley GE, Bowles KC, Campbell PGC, Delos CG, Di Toro DM, Dwyer RL, Galvez F, Gensmer RW, Goss GG, Hogstrand C, Janssen CR, McGeer JC, Naddy RB, Playle RC, Santore RC, Schneider U, Stubblefield WA, Wood CM. 2002. The biotic ligand model: A historical overview. *Comp Biochem Physiol* 133:3–35.
34. Tipping E, Hurley M. 1992. A unifying model of cation binding by humic substances. *Geochim Cosmochim Acta* 56:3627–3641.
35. Tipping E. 1993. Modeling the competition between alkaline earth cations and trace metals species for binding by humic substances. *Environ Sci Technol* 27:520–529.
36. Tipping E. 2002. *Cation Binding by Humic Substances*. Cambridge University Press, Cambridge, UK.
37. HydroQual. 2002. Biotic ligand model. Mahwah, NJ, USA.
38. Tipping E. 1998. Humic ion-binding model Model VI: An improved description of the interactions of protons and metal ions with humic substances. *Aquat Geochem* 4:3–48.
39. Santore RC, Di Toro DM, Paquin PR, Allen HE, Meyer J. 2001. A biotic ligand model of the acute toxicity of metals. II. Application to acute copper toxicity in freshwater fish and *Daphnia*. *Environ Toxicol Chem* 20:2397–2402.
40. HydroQual. 2002. Phase I Development of a biotic ligand model for nickel. NIPERA0010. Technical Report. Mahwah, NJ, USA.
41. HydroQual. 2002. Phase I Development of a biotic ligand model for Pb. ILZRO0020. Technical Report. Mahwah, NJ, USA.
42. HydroQual. 2003. Phase I Development of a biotic ligand model for cadmium. Bat1106. Technical Report. Mahwah, NJ, USA.
43. Santore RC, Mathew R, Paquin PR, Di Toro DM. 2002. Application of the biotic ligand model to predicting zinc toxicity to rainbow trout, fathead minnow, and *Daphnia magna*. *Comp Biochem Physiol C* 113:271–286.
44. von der Ohe P, Liess M. 2004. Relative sensitivity distribution of aquatic invertebrates to organic and metal compounds. *Environ Toxicol Chem* 23:150–156.
45. Wheeler J, Leung K, Morrirt D, Sorokin N, Rogers H, Toy R, Holt M, Whitehouse P, Crane M. 2002. Freshwater to saltwater toxicity extrapolation using species sensitivity distributions. *Environ Toxicol Chem* 21:2459–2467.
46. Erickson R, Benoit D, Mattson VHN Jr, Leonard E. 1996. The effects of water chemistry on the toxicity of copper to fathead minnows. *Environ Toxicol Chem* 15:181–193.
47. De Schampelaere KAC, Heijerick D, Janssen CR. 2002. Refinement and field validation of a biotic ligand model predicting acute copper toxicity to *Daphnia magna*. *Comp Biochem Physiol C* 133:243–258.
48. De Schampelaere KAC, Janssen CR. 2002. A biotic ligand model predicting acute copper toxicity for *Daphnia magna*: The effects of calcium, magnesium, sodium, potassium, and pH. *Environ Sci Technol* 36:48–54.
49. De Schampelaere KAC, Vasconcelos FM, Tack FMG, Allen HE, Janssen CR. 2004. Effect of dissolved organic matter source on acute copper toxicity to *Daphnia magna*. *Environ Toxicol Chem* 23:1248–1255.
50. De Schampelaere KAC, Janssen CR. 2004. Effects of dissolved organic carbon concentration and source, pH, and water hardness on chronic toxicity of copper to *Daphnia magna*. *Environ Toxicol Chem* 23:1115–1122.
51. Heijerick D, De Schampelaere KAC, Janssen CR. 2002. Predicting acute zinc toxicity for *Daphnia magna* as a function of key water chemistry characteristics: Development and validation of a biotic ligand model. *Environ Toxicol Chem* 21:1309–1315.
52. Penttinen S, Kostamo A, Kukkonen V. 1998. Combined effects of dissolved organic material and water hardness on toxicity of cadmium to *Daphnia magna*. *Environ Toxicol Chem* 17:2498–2503.
53. Tipping E, Berggren D, Mulder J, Woof C. 1995. Modeling the solid-solution distributions of protons, aluminum, base cations, and humic substances in acid soils. *Eur J Soil Sci* 46:77–94.
54. Tipping E, Woof C, Kelly M, Bradshaw K, Rowe J. 1995. Solid-solution distributions of radionuclides in acid soils—Application of the WHAM chemical speciation model. *Environ Sci Technol* 29:1365–1372.
55. Tipping E. 1996. Hydrochemical modelling of the retention and transport of metallic radionuclides in the soils of an upland catchment. *Environ Pollut* 94:105–116.
56. Tipping E, Smith E, Lawlor A, Hughes S, Stevens P. 2003. Predicting the release of metals from ombrotrophic peat due to drought-induced acidification. *Environ Pollut* 123:239–253.
57. Tipping E, Rieuwerts JGP, Ashmore M, Lofts S, Hill M, Farago M, Thornton I. 2003. The solid-solution partitioning of heavy metals Cu, Zn, Cd, Pb, in upland soils of England and Wales. *Environ Pollut* 125:213–225.
58. Lofts S, Tipping E. 1998. An assemblage model for cation binding by natural particulate matter. *Geochim Cosmochim Acta* 62:2609–2625.
59. Lofts S, Tipping E. 2000. Solid-solution metal partitioning in the Humber rivers: Application of WHAM and SCAMP. *Sci Total Environ* 251–252, 381–399.
60. Meyer J. 1999. A mechanistic explanation for the Ln (LC50). vs. Ln (hardness) adjustment equation for metals. *Environ Sci Technol* 33:908–912.
61. U.S. Environmental Protection Agency. 2002. Equilibrium partitioning sediment guidelines ESGS for the protection of benthic organisms: Metal mixtures (cadmium, copper, lead, nickel, silver and zinc). [Draft] EPA 822-R-02-045. Washington, DC.
62. U.S. Environmental Protection Agency. 2003. Procedures for the derivation of equilibrium partitioning sediment benchmarks ESBs for the protection of benthic organisms: Endrin. EPA 600-R-02-009. Washington, DC.
63. Dewitt T, Hickey C, Morrisey D, Nipper M, Roper D, Williamson R, van Dam L, Williams E. 1999. Do amphipods have the same concentration-response to contaminated sediment in situ as in vitro? *Environ Toxicol Chem* 18:1026–1037.
64. Correia A, Costa M. 2000. Effects of sediment geochemical properties on the toxicity of copper-spiked sediments to the marine amphipod *Gammarus locusta*. *Sci Total Environ* 247:99–106.
65. Kuhn A, Munns W, Serbst J, Edwards P, Cantwell M, Gleason T, Pelletier M, Berry WJ. 2002. Evaluating the ecological significance of laboratory response data to predict population-level effects for the estuarine amphipod *Ampelisca abdita*. *Environ Toxicol Chem* 21:865–874.
66. Lee J-S, Lee B-G, Luoma S, Yoo H. 2004. Importance of equilibration time in the partitioning and toxicity of zinc in spiked sediment bioassays. *Environ Toxicol Chem* 23:65–71.
67. Casas A, Creclius E. 1994. Relationship between acid volatile

sulfide and the toxicity of zinc, lead and copper in marine sediments. *Environ Toxicol Chem* 13:529–536.

68. Pesch C, Hansen DJ, Boothman W, Berry WJ, Mahony JD. 1995. The role of acid volatile sulfide and interstitial water metal concentrations in determining bioavailability of cadmium and nickel from contaminated sediments to the marine polychaete *Neanthes arenaceodentata*. *Environ Toxicol Chem* 14:129–141.
69. Carlson A, Phipps G, Mattson V, Kosian P, Cotter A. 1991. The role of acid-volatile sulfide in determining cadmium bioavailability and toxicity in freshwater sediments. *Environ Toxicol Chem* 10:1309–1319.
70. Hoss S, Henschel T, Haitzer M, Traunspurger W, Steinberg CEW. 2001. Toxicity of cadmium to *Caenorhabditis elegans* (nematoda) in whole sediment and pore water—The ambiguous role of organic matter. *Environ Toxicol Chem* 20:2794–2801.
71. DeWit T, Swartz RC, Hansen DJ, McGovern D, Berry WJ. 1996. Bioavailability and chronic toxicity of cadmium in sediment to the estuarine amphipod *Leptocheirus plumulosus*. *Environ Toxicol Chem* 15:2095–2101.
72. Sibley P, Ankley GT, Cotter A, Leonard E. 1996. Predicting chronic toxicity of sediments spiked with zinc: An evaluation of the acid volatile sulfide model using a life cycle test with the midge *Chironomus tentans*. *Environ Toxicol Chem* 15:2102–2112.
73. Hare L, Carignan R, Huerta-Diaz M. 1994. A field study of metal toxicity and accumulation by benthic invertebrates: Implication for the acid-volatile sulfide (AVS) model. *Limnol Oceanogr* 39:1653–1668.
74. Hansen DJ, Mahony JD, Berry WJ, Benyi S, Corbin J, Pratt S, Di Toro DM, Able M. 1996. Chronic effect of cadmium in sediments on colonization by benthic marine organisms: An evaluation of the role of interstitial cadmium and acid volatile sulfide in biological availability. *Environ Toxicol Chem* 15:2126–2137.
75. Liber K, Call D, Markee T, Schmude K, Balcer M, Whiteman F, Ankley GT. 1996. Effects of acid volatile sulfide on zinc bioavailability and toxicity to benthic macroinvertebrates: A spiked-sediment field experiment. *Environ Toxicol Chem* 15:2113–2125.
76. Burton G, Nguyen L, Janssen CR, Baudo R, McWilliam R. 2005. Field validation of sediment zinc toxicity. *Environ Toxicol Chem* 24:541–553.
77. Kuhn A, Lussier S. 1987. Results from acute and life-cycle tests with *Mysidopsis bahia* exposed to phenanthrene. Memorandum to David J. Hansen. U.S. Environmental Protection Agency, Narragansett, RI.
78. Diamond J, Gerardi C, Leppo E, Miorelli T. 1997. Using a water-effect ratio approach to establish effects of an effluent-influenced stream on copper toxicity to the fathead minnow. *Environ Toxicol Chem* 16:1480–1487.
79. Schubauer-Berigan M, Dierkes J, Monson P, Ankley GT. 1993. pH-dependent toxicity of Cd, Cu, Ni, Pb, and Zn to *Ceriodaphnia dubia*, *Pimephales promelas*, *Hyalella azteca*, and *Lumbriculus variegatus*. *Environ Toxicol Chem* 12:1261–1266.
80. Hockett J, Mount D. 1996. Use of metal chelating agents to differentiate among sources of acute aquatic toxicity. *Environ Toxicol Chem* 15:1687–1693.
81. Dunbar L. 1996. *Derivation of a Site-Specific Dissolved Copper Criteria for Selected Freshwater Streams in Connecticut*. Connecticut Department of Environmental Protection, Water Toxics Program, The Department of Environmental Protection, Hartford, CT, USA.
82. Bossuyt B, Cornelis B, Janssen CR, Allen HE, Di Toro DM, Paquin PR. 2001. Bioavailability and ecotoxicity of nickel: Effects of water quality characteristics. Study ET-2001-03-15. Laboratory of Environmental Toxicology and Aquatic Ecology, Ghent University, Ghent, Belgium.
83. Chapman G, Ota S, Recht F. 1980. Effects of water hardness on the toxicity of metals to *Daphnia magna*. Technical Report. U.S. Environmental Protection Agency, Corvallis, OR.
84. Keithly J, Brooker J, DeForest D, Brix K, Ortego L, Paquin PR, Wu K. 2004. Acute and chronic toxicity of nickel to a cladoceran (*Ceriodaphnia dubia*) and amphipod (*Hyalella azteca*). *Environ Toxicol Chem* 23:691–696.
85. Paulaskis J, Winner R. 1988. Effects of water hardness and humic acid on zinc toxicity to *Daphnia magna* Straus. *Aquat Toxicol* 12:273–290.
86. Stumm W, Morgan JJ. 1970. *Aquatic Chemistry*. John Wiley, New York, NY, USA.

## APPENDIX

The reason that competing cations do not affect  $SEM^*_{x,OC}$  (simultaneously extracted metals) but pH does can be understood as follows. The equilibrium constant  $K_{M-BL}$  for metal binding to the biotic ligand (BL) is defined by the reaction

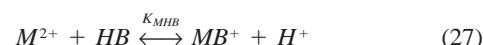
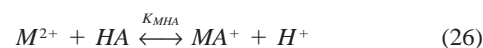


where  $≡BL$  is the uncomplexed biotic ligand and  $[M ≡ BL]$  is the biotic ligand–metal complex. The equilibrium constant  $K_{M-BL}$ , defined as

$$K_{M-BL} = \frac{[M ≡ BL]}{\{M^{2+}\}[≡BL]} \quad (25)$$

is an intrinsic constant that applies for any pH and competing cation concentrations.

In the Windemere Humic Aqueous Model (WHAM) V, there are two intrinsic constants that determine the relative binding strength of the various metal cations: The equilibrium constants  $K_{MHA}$  and  $K_{MHB}$  for the metal–proton exchange reactions



where  $HA$  and  $HB$  refer to the protonated A-sites and B-sites, representing the organic matter carboxylic and phenolic sites, respectively [36]. A direct comparison of the strength of binding can be made by determining the intrinsic metal–organic matter binding constants



that are analogous to the intrinsic metal–biotic ligand equilibrium constants (Eqn. 24). This requires the proton binding constants



The relationship is

$$\log K_{M-A} = \log K_{MHA} + \log K_{H-A} \quad (32)$$

WHAM V treats the heterogeneity of proton and metal binding sites by specifying a mean  $pK_{H-A}$ ,  $pK_{H-B}$  and range  $\Delta pK_{H-A}$ ,  $\Delta pK_{H-B}$  for the A and B sites, where  $pK_{H-A} = -\log_{10} K_{M-A}$ , etc. [36]. Since metal and proton binding are related via the metal–proton exchange reactions (Eqns. 26–27) the metal binding constants are also specified as means  $pK_{M-A}$ ,  $pK_{M-B}$  and ranges  $\Delta pK_{M-A}$ ,  $\Delta pK_{M-B}$  for the A and B sites. The comparison to the biotic ligand binding constants is shown in Figure 13A. The symbol represents the mean and range of  $\log K_{M-A}$  and  $\log K_{M-B}$  (Eqns. 28–29). Both the metal and proton (H) constants are shown. For  $pH > pK_{H-A} + \Delta pK_{H-A} \approx 5$  all the A sites are deprotonated and available for metal binding. As pH increases from 6 to 9 the B sites deprotonate as well. Hence, at a specific pH there is not one metal binding site with its equilibrium constant but a whole range of binding sites with their individual site densities and equilibrium constants—the y-axis in Figure 13A. By comparison the biotic ligand has only one binding site and equilibrium constant—the x-axis in Figure 13A. Therefore, the hardness and salinity cations do not have

the same binding constant to both the biotic ligand and sediment organic carbon. The latter vary with pH as the various strength sites deprotonate.

The mechanism responsible for keeping  $[M \equiv POC]^*$  and therefore  $SEM^*_{x,OC}$  (Eqn. 23) constant as hardness and salinity cations vary can be understood by examining the equilibrium equations. The relationship between the critical biotic ligand concentration  $[M \equiv BL]^*$  and the critical pore water metal activity  $\{M^{2+}\}^*$  is (Eqn. 25)

$$[M \equiv BL]^* = K_{M-BL}\{M^{2+}\}^*[\equiv BL] \quad (33)$$

This equation is true for all conditions since  $K_{M-BL}$  is an intrinsic constant. The critical particulate organic carbon (POC) concentration  $[M \equiv POC]^*$  is (Eqn. 19)

$$[M \equiv POC]^* = K_{M-POC}\{M^{2+}\}^*[\equiv POC] \quad (34)$$

However, because of the variation of equilibrium constants with pH,  $K_{M-POC}$  is a conditional equilibrium constant that applies only for a specific pH. This can be seen in Figure 13B where  $K_{M-POC}$  for Ca, Zn, and Cu for the solution conditions in Figure 5A are displayed. Substituting Equation 34 for  $\{M^{2+}\}^*$  in Equation 33 yields

$$[M \equiv BL]^* = K_{M-BL}[\equiv BL] \frac{[M \equiv POC]}{K_{M-POC}[\equiv POC]} \quad (35)$$

or

$$\frac{[M \equiv POC]^*}{[M \equiv BL]^*} = \frac{K_{M-POC}[\equiv POC]}{K_{M-BL}[\equiv BL]} \quad (36)$$

The equations for a competing cation are analogous to Equations 33 to 34

$$[C \equiv BL] = K_{C-BL}\{C^{2+}\}[\equiv BL] \quad (37)$$

$$[C \equiv POC] = K_{C-POC}\{C^{2+}\}[\equiv POC] \quad (38)$$

Using Equations 37 and 38 to solve for the free ligand concentrations yields

$$[\equiv BL] = \frac{[C \equiv BL]}{K_{C-BL}\{C^{2+}\}} \quad (39)$$

$$[\equiv POC] = \frac{[C \equiv POC]}{K_{C-POC}\{C^{2+}\}} \quad (40)$$

and substituting these relationships into Equation 36 yields

$$\frac{[M \equiv POC]^*}{[M \equiv BL]^*} = \frac{K_{C-BL} K_{M-POC} [C \equiv POC]}{K_{M-BL} K_{C-POC} [C \equiv BL]} \quad (41)$$

Therefore, the ratio  $[M \equiv POC]^*/[M \equiv BL]^*$  is determined by ratios of equilibrium constants and competing cation concentrations.

Consider, first, the cation concentrations. As an example, Figure 14 presents the biotic ligand and POC concentrations for Zn, Ca, Mg, and Na for the varying pH, hardness, and

salinity cases presented previously (Fig. 5). Since these are concentrations at the critical biotic ligand concentration, the  $[Zn \equiv BL]$  is constant in all cases, corresponding to the critical concentration  $[M \equiv BL]^*$ . The  $[Zn \equiv POC]$  concentration varies only slightly as hardness (A) and salinity (B) vary. This is the unexpected result that needs to be explained.

For the varying hardness (Fig. 14A) and pH (Fig. 14C) cases, note that  $[Ca \equiv BL]$  and  $[Ca \equiv POC]$  are both the highest concentration relative to the other competing cations and that they are approximately constant as hardness varies from 20 to 1,000 mg/L or as pH varies from 6 to 9. For the varying salinity case (Fig. 14B), it is  $[Mg \equiv BL]$  and  $[Mg \equiv POC]$  that are the highest concentrations and approximately constant for salinity  $>2$  g/L.

The reason that the Ca or Mg concentrations are constant is that both the biotic ligand and the POC are saturated with Ca or Mg, even at the lowest Ca or Mg concentration corresponding to 20 mg/L hardness or 2 g/L salinity, respectively. For Zn the biotic ligand site density is 30 nmol/gm wet wt and the POC deprotonated site density is 7.85 mmol/g OC at pH = 8. Increasing the pore water Ca or Mg concentrations, does little to change the Ca or Mg bound to the biotic ligand and to POC since all the available sites are already occupied. This is the reason that the competing cation ratios  $[Ca \equiv POC]/[Ca \equiv BL]$  and  $[Mg \equiv POC]/[Mg \equiv BL]$  are constant.

The other terms in the right hand side of Equation 41 are ratios of the equilibrium constants. The biotic ligand equilibrium constants  $K_{M-BL}$  and  $K_{C-BL}$  are intrinsic constants and do not vary and so their ratio  $K_{C-BL}/K_{M-BL}$  is constant. However, the POC equilibrium constants  $K_{M-POC}$  and  $K_{C-POC}$  are conditional constants that are constant only at a constant pH. This is due to the variation in available binding sites as pH varies as discussed above (Fig. 13). They also vary slightly with changes in competing cations but not significantly. Hence, since  $K_{Ca-BL}/K_{Zn-BL}$  or  $K_{Mg-BL}/K_{Zn-BL}$  are constant at constant pH, the ratio of zinc bound to POC and the biotic ligand  $[Zn \equiv POC]^*/[Zn \equiv BL]^*$  is also constant as hardness and salinity vary. Therefore,  $SEM^*_{x,OC} = [Zn \equiv POC]^*$  is constant for constant pH.

Changing the pH changes  $[Zn \equiv POC]^*/[Zn \equiv BL]^*$  because the ratio of the conditional constants  $K_{M-POC}/K_{C-POC}$  changes (Eqn. 41). The equilibrium constants for Ca ( $K_{Ca-POC}$ ), Zn ( $K_{Zn-POC}$ ), and Cu ( $K_{Cu-POC}$ ) versus pH are shown in Figure 13C for the solution conditions used in Figure 5A (Table 5). Note that the Cu and Zn constants change significantly but Ca less so. Hence, the ratios  $K_{Zn-POC}/K_{C-POC}$  and  $K_{Cu-POC}/K_{C-POC}$  for  $C = Ca$  and Mg are changing and, therefore, so is  $[Zn \equiv POC]^*/[Zn \equiv BL]^*$  and  $[Cu \equiv POC]^*/[Cu \equiv BL]^*$ . Note also that the change in Cu concentration is larger than the change in Zn concentration (Fig. 5A) due to the greater variation in  $K_{Cu-POC}$  relative to  $K_{Zn-POC}$  (Fig. 13C). This variation in the conditional equilibrium constants is a consequence of the WHAM V description of cation binding to POC as a series of monodentate and bidentate sites with varying  $K_{M-A}$  and  $K_{M-B}$ .