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DISSOLVED TRACE METAL SPECIATION IN ESTUARINE AND COASTAL WATERS: COMPARISON OF WHAM/MODEL VII PREDICTIONS WITH ANALYTICAL RESULTS

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Abstract: The authors apply the chemical speciation model WHAM/Model VII to investigate the distribution of metal species of Fe(III) and the divalent cations of Ni, Cu, Zn, Cd, Hg, and Pb, in the water column of estuaries and coastal areas. The authors compare, for the same locations, measured and modeled free ion and organically bound metal concentrations. The modeled free ion calculations show varying levels of agreement with experimental measurements. Where only natural organic matter is considered as the organic ligand, for Ni, Cd, and Pb, agreement within 1 order of magnitude is found in 122 of 128 comparisons. For Fe and Zn comparisons 12 of 34 (Fe) and 10 of 18 (Zn) agree to within 1 order of magnitude, the remaining modeled values being over 1 order of magnitude higher than measurements. Copper measurements agree within 1 order of magnitude of modeled values in 314 of 533 (59%) cases and are more than 1 order of magnitude lower than modeled values in 202 cases. There is a general tendency for agreement between modeled and measured values to improve with increasing total metal concentrations. There are substantial variations among different analysis techniques but no systematic bias from the model is observed across techniques. It would be beneficial to cross-validate the different analytical methods, in combination with further modeling. The authors also assessed the effect of including an anthropogenic organic ligand (ethylenediamine tetraacetic acid (EDTA)) in the modeling, given its known presence in some coastal environments. Except for Cd, all metals were sensitive to the presence of EDTA, even at a low concentration of 50 nM. *Environ Toxicol Chem* 2015;34:53–63.

Keywords: Chemical speciation Estuaries Saltwater Copper Modeling

INTRODUCTION

Many estuaries and coastal regions are important areas of economic activity. Wastewater treatment plants, heavy industry, refining and defense or merchant shipping can provide direct sources of contaminants into these areas, including from trace metals. In areas without industrial activity, contaminants may be caused indirectly by mixing of riverine transported material with seawater. Contaminants in estuaries, and subsequent human exposure via the food chain, have been of concern for over a century [1]. Early concerns focused on biological contamination of food sources, the effects of heavy metals on the health of benthic organisms had become of interest by the late part of the twentieth century [2]. Recent work has applied or adapted the biotic ligand model to saltwater environments with the aim of evaluating metal toxicity to organisms living in the water column, including the importance of chemical speciation to toxicity [3,4]. The biotic ligand model was developed to enable calculation of toxic effect concentrations of heavy metals based on local water chemistry. This concept requires that the distribution of chemical forms of the metal is taken into account, so that complexation by inorganic ligands (e.g., chloride, carbonate, sulfate) and natural organic matter decreases toxicity by decreasing the free ion activity [5]. The development of the biotic ligand model has been underpinned by efforts to model chemical speciation, including the binding to dissolved organic matter (DOM), within estuaries [6] and open ocean waters [7,8], including estimation of free ion concentrations.

Dissolved organic matter can play an important role in the chemical speciation of many trace metals through formation of DOM-metal complexes that may reduce the metal bioavailability. Indications that terrestrial fulvic and humic acids and marine humic acids bind Fe in a similar way [9] suggest that chemical speciation models used for freshwater environments may be suitable for marine systems. This suitability is supported by the closeness of fit between analytical and modeled data for Cu speciation calculated by Hiemstra and van Riemsdijk [7] and Stockdale et al. [8]. Koch et al. [10] suggest that there is a noticeable degree of similarity between elemental compositions and structural features of terrigenous and algal–derived organic matter when analyzed using Fourier transform ion cyclotron resonance mass spectrometry.

Direct analytical measurements on water samples from estuaries, coastal waters, and in open oceans have been undertaken for some time. Early work employed differential pulse anodic stripping voltammetry, which measures inorganic and potentially some highly labile organic species (e.g., [11]). Generally this method employs standard addition techniques where fixed quantities of the target metal are added to the primary sample and analyzed to allow back-calculation of the labile metal in the original sample; we refer to this technique as standard addition voltammetry. To target more directly the analysis of only inorganic or free ion concentrations the techniques of ion selective electrodes [12], hollow fiber – permeation liquid membrane [13], competitive ligand exchange adsorptive cathodic stripping voltammetry [14], and competitive ligand exchange solvent-solvent extraction [15] have been

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All Supplemental Data may be found in the online version of this article.
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utilized. Competitive ligand exchange adsorptive cathodic stripping voltammetry employs the same voltammetry principles as differential pulse anodic stripping voltammetry but within a different experimental framework. Data from competitive ligand exchange adsorptive cathodic stripping voltammetry and competitive ligand exchange solvent-solvent extraction (which we will collectively refer to as competitive ligand method) are used to derive metal–specific ligand concentrations and conditional stability constants for the ligands, valid under the specific experimental conditions. Typically, 2 classes of ligands are identified: L1 (stronger binding sites) and L2 (weaker binding sites). The ligand concentrations, conditional stability constants, and a side reaction coefficient can be used to obtain the organic, inorganic, and free ion concentrations of the metal (see Pesavento et al. [16] for a detailed description of the competitive ligand method; and Town and Filella [17] for a critical assessment of the L1, L2 approach). For a recent review of the experimental techniques employed in several of these studies we refer readers to Pesavento et al. [16].

If metal water quality standards for brackish and saltwater environments are to be formulated on a site-specific basis and based on chemical speciation concepts, then there is a need to test chemical speciation models specifically for these conditions. Accurate measurements of chemical species will aid the achievement of this goal by allowing direct comparisons with model predictions, under varying pH, DOM concentration, and in the presence of competing ions. For modeling chemical speciation in estuarine and coastal waters, some elements may not be subject to significant levels of organic complexation, and models exclusively considering inorganic speciation may be sufficient. Where trace metals complex strongly with organic ligands, DOM will exert a control on the free ion activity and therefore have a protective effect in terms of the exposure of organisms to potentially toxic metals [18,19]. Modeling of metal binding to DOM in freshwaters and the terrestrial environment almost always uses fulvic acid and/or humic acid to represent DOM. Two key modeling approaches have been developed for predicting DOM binding. These are the NICA-Donnan model [20] incorporated into the ECOSAT model and the humic ion binding models V, VI, and VII [21–23] incorporated into the WHAM model (http://www.ceh.ac.uk/products/software/wham/). These approaches assume that binding to DOM occurs at a heterogeneous array of binding sites, where complexation of a single cationic metal is controlled by competition for sites by major cations (e.g., Ca and Mg) and by other cationic trace metals and protons. The fitting of the models was performed using data from laboratory studies with fulvic acid and humic acid. For modeling, DOM in natural waters is assumed to have the same array of binding sites as these organic acids, but in addition the fraction of DOM that does not bind metal ions is accounted for.

The primary objective of the present study is to apply the chemical speciation model WHAM/Model VII to investigate the distribution of metal species in the water column of estuaries and coastal areas. In doing this we compare, for the same field locations, modeled results with experimentally measured values from techniques that can give inorganic or free ion concentrations. The advantage of using a single model for a wide range of data sets is that it can help to identify whether there are consistent trends in activities obtained using different analytical methods, by comparison with a consistent set of predictions. Such comparisons have been performed on data for freshwater systems [24] and open oceans [8]. The target metals of the present study are those for which experimental inorganic or free ion data were available, namely Fe(III) and the divalent cations Ni, Cu, Zn, Cd, Hg, and Pb.

An additional consideration for estuarine and coastal areas is the potential presence of anthropogenic ligands such as ethylenediamine tetraacetic acid (EDTA). These ligands are found in the receiving waters of many industrial areas and can be extremely persistent in wastewater treatment plants and natural waters [25]. This chemical is widely used as an industrial detergent as well as in agriculture and the paper industry; it is also present in many household cleaning and cosmetic products [26]. Van den Berg and Dharmvanij [27] suggest that a better approximation of organic complexation is obtained if EDTA is used in model calculations of metal speciation in estuarine waters as EDTA provides a way to explain discrepancies where the free ion is modeled too high and organic complexation too low. To evaluate the potential for EDTA to influence the comparison between measurement and modeling we compare the results in the absence of EDTA to 2 scenarios where EDTA is present.

MATERIALS AND METHODS

WHAM/Model VII

WHAM VII comprises 2 components, firstly the inorganic speciation code WHAM [28] and secondly the humic ion binding model VII [22]. Model VII was described in detail by Tipping et al. [22], a concise description is given in Supplemental Data, Appendix A. The model uses a structured formulation of discrete, chemically plausible, binding sites for protons, to allow the creation of regular arrays of bidentate and tridentate binding sites for metals. The multidentate sites are required to explain strong binding observed at low metal: humic ratios. An important feature of the model is that cations and protons compete for complexation at all the binding sites.

The humic binding model is combined with an inorganic speciation model, the species list and constants for which were given in the description of the Windermere humic aqueous model [28]. Ionic strength effects on the inorganic reactions are discussed in the following section: *Ionic strength corrections*. We used the WHAM VII code to calculate chemical speciation in the estuarine and coastal waters, with measured total concentrations of solution components, and measured pH, as inputs. Concentrations of DOM were based on measured dissolved organic carbon (DOC), assuming that DOM comprises 50% carbon and that 65% of it is active with respect to cation binding and can be represented by fulvic acid [29]. For example, for a DOC concentration of $5\,\mathrm{mg\,L^{-1}}$, this corresponds to a fulvic acid concentration of $6.5\,\mathrm{mg\,L^{-1}}$ for modeling. The model predictions are those expected if DOM in natural waters behaves in the same way as extracted fulvic acid and humic acid used in laboratory experiments, taking into account competition effects and inorganic speciation.

Ionic strength corrections. In low ionic strength solutions, individual ion activities, required in the modeling of chemical speciation, are typically obtained using coefficients calculated from Davies or extended Debye-Hückel equations [30]. These equations relate the charge on an ion to an activity coefficient at a specified ionic strength. In the modeling of high ionic strength systems, such as estuarine and marine systems, it is usually recommended to use the "mean salt method" for calculating activity coefficients (γ), rather than the methods normally applied to lower ionic strength freshwater systems. The ion-pairing model described by Millero and Schreiber [31] incorporates the mean salt method with Pitzer's equations.

Using this approach, individual coefficients are calculated for each ion. We initially compared results for WHAM modeling using 2 approaches to the calculation of γ, the Pitzer equations, and the default method of WHAM, the extended Debye-Hückel equation. The model was applied to an inorganic system with typical concentrations for seawater of all major ions (Na, Mg, K, Ca, Cl, (bi)carbonate, sulfate) and several trace components (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, F, and nitrate; values from Chester [32] and references therein). Differences in the free ion activities calculated using the 2 methods were within ± 16%, with a mean difference of –1%. An exception was nitrate, where the free ion activity was 24% higher when the extended Debye-Hückel method was employed. These differences are small in comparison with the variations when comparing modeled and measured values of trace metal free ion concentrations. For our detailed estuarine/coastal modeling we exclusively used the default WHAM approach: extended Debye-Hückel. This is consistent with several other studies that have used universal relationships for all metals rather than metal specific relationships for activities in marine systems [33,34].

Chemistry data

Measured data, required as model inputs for speciation calculations, comprise salinity, pH, temperature, concentrations of DOC, and dissolved trace metals. Where concentrations of free ion or inorganic metals are also reported, comparison can be made with values calculated using WHAM/Model VII. Several studies were identified that reported the required model inputs and either inorganic or free ion trace metal. These data covered the trace metals, Fe, Ni, Cu, Zn, Cd, Hg, and Pb. Table 1 gives a summary of these studies, including the analysis method used and the study locations. The different techniques vary in their analytical windows. Several methods yield data (after varying levels of mathematical processing) that can be considered representative of only the inorganic or free ion concentrations, e.g., ion selective electrodes, hollow fiber-permeation liquid membrane, and most competitive ligand method studies. However, standard addition voltammetry will yield measurements that are representative of the inorganic metal, plus some contribution from labile organic complexes. This contribution is minimized when a thin mercury film – rotating glassy carbon disc electrode is used, compared with a hanging drop mercury electrode [35]. Use of the thin mercury film-rotating glassy carbon disc is reported in 2 of the 3 studies that we use in our comparison.

Where experimental studies report free ion concentrations we use the values as reported. Where only inorganic metal is reported we calculate free ion using WHAM, excluding DOM from the calculation, these studies are identified in Table 1. Values for metal binding associated with organic matter were taken directly from the literature. Several studies reported only total metal and free ion concentrations, and thus results of these studies are only compared with modeled free ion concentrations.

Binding of any metal to DOM will be related to the concentration of other metals in solution, owing to competition at binding sites. The majority of the analytical studies in the present study's comparison solely report the total dissolved concentrations of the target metal(s) and not those of other metals that will be present. To address the effect of competition, we devised an approach for dealing with the model input concentrations for competing metals. In addition to the 6 metals of interest, we also included Al, Mn, and Co in the modeling so that competition could be properly considered. We estimated absent concentrations of these metals by reviewing the distribution of concentrations from the experimental studies of the target metals as well as several other sources ([36] Co, Ni, Cu, Cd, Pb; [37] Mn, Ni, Cu, Zn, Cd; [38] Mn, Fe; [39] Fe, Ni, Cu, Cd, Pb; [40,41] Al). We approximated concentration values to the nearest order of magnitude (half order for Cu). Our best estimates were $10^{-7}\,\mathrm{mol\,L^{-1}}$, $10^{-7}\,\mathrm{mol\,L^{-1}}$, $10^{-8}\,\mathrm{mol\,L^{-1}}$, $10^{-9}\,\mathrm{mol\,L^{-1}}$, $10^{-8}\,\mathrm{mol\,L^{-1}}$, $5\times10^{-8}\,\mathrm{mol\,L^{-1}}$, $10^{-8}\,\mathrm{mol\,L^{-1}}$, $10^{-10}\,\mathrm{mol\,L^{-1}}$, $10^{-12}\,\mathrm{mol\,L^{-1}}$, and $10^{-10}\,\mathrm{mol\,L^{-1}}$ for Al, Mn,

Table 1. Experimental studies used for the comparison of modeled and experimental speciation results[a]

Metal	Measurement technique[b]	Study location	Reference
Single metal studies			
Fe	CLM	*North Sea*[c]	[60]
Ni[d]	CLM	*UK, Beaulieu Estuary*	[49]
	CLM	*UK, Mersey Estuary*	[48]
Cu	CLM	US, Galveston Bay, TX	[44]
	CLM	US, San Francisco Bay, CA	[46]
	CLM	US, Cape Fear Estuary, NC	[61]
	ISE	Australia, Macquarie Harbour, Tasmania[c]	[51]
	ISE	Italy, Venice Lagoon[e]	[62]
	ISE	US, San Diego Bay, CA	[63]
	SAV	Croatia, Krka Estuary	[64]
	SAV	*UK, southern harbours*	[65]
Zn	CLM	*US, Cape Fear Estuary, NC*	[53]
Hg	CLM	US, Galveston Bay, TX	[55]
Multiple metal studies			
Ni, Cu, Cd, Pb	HF-PLM	Coastal Black Sea	[50]
Cu, Zn	CLM (Cu)/SAV (Zn)	Western Black Sea[c]	[66]
Cu, Zn, Cd, Pb	SAV	*US, Narragansett Bay, RI*[c]	[54]
Cu, Cd, Pb	CLM (Cu, Pb)/SAV (Cd)	UK, Firth of Clyde[c]	[67]

[a] Italicized study locations indicate the studies where free ion concentrations were calculated from reported inorganic data.

[b] Techniques are competitive ligand methods (CLM), standard addition voltammetry methods (SAV), ion selective electrode (ISE), and hollow fiber–permeation liquid membrane (HF-PLM).

[c] Dissolved organic matter (DOM) concentrations were not reported so were estimated from other studies as follows: Macquarie Harbour, Teasdale et al. [38]; pH also estimated from this study; Narragansett Bay, from the range of measurements reported in the other studies at similar salinities; Western Black Sea, Slaveykova et al. [50]; Firth of Clyde, Lønborg et al. [68]; North Sea, Suratman et al. [69]; and Reinthaler and Herndl [70].

[d] These studies report that some labile organic complexes may be measured by the analytical technique used.

[e] The pH was not reported so a single value was estimated from Chapman et al. [71].

Fe, Co, Ni, Cu, Zn, Cd, Hg, and Pb respectively (sensitivity to such estimates was quantitatively assessed by Stockdale et al. [8]). As would be expected for estuaries and coastal waters these values are higher than concentrations in the open oceans [32,42]. If temperature was not reported, we used a value of 20 °C as a reasonable approximation of laboratory temperature (as none of the analytical methods are field based). Reported salinities were used to calculate major ion concentrations (i.e., Na, Mg, K, Ca, Cl, (bi)carbonate, and sulfate) based on the values reported in Chester [31].

Although the potential influence of EDTA in estuarine and coastal environments is recognized [43], there are only limited data for estuarine and coastal waters. Of all the locations covered in our analysis, EDTA concentration data are available for only 2. These are Trinity River, a principal freshwater input to Galveston Bay, Texas (where Cu was measured by Tang et al. [44]) for which a mean EDTA concentration of $4.7 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$ (range, $0.6\text{–}20.1 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$) was reported by Jiann et al. [45] and wastewater entering San Francisco Bay, California (where Cu was measured by Buck and Bruland [46]) for which EDTA concentrations of up to $10^{-6}\,\mathrm{mol\,L^{-1}}$ have been observed [43,47]. In addition, EDTA concentrations as high as $2 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$ have been reported for the mouth of the Odiel River in Spain [26]. In examining the effect of EDTA we included this ligand in the modeling at 2 different concentrations, $5 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$ and $1 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$. These modeled results are compared with results obtained in the absence of EDTA.

RESULTS AND DISCUSSION

Figures 1 through 4 compare the experimental results and model-derived concentrations. A summary of both measured and modeled data (median and ranges) for each metal is shown in Table 2, which also includes the fractions of total metal present as organic species and as free ions. Figure 1 shows comparisons of the degree of loading of metals onto DOM, as represented by the ratio of organically bound to free metal ion concentrations. These data effectively represent site-specific partition coefficients. The stronger binding metals lay to the top right of the data, whereas the weaker binding metals lay to the bottom left. Model predictions of low levels of organic complexation tend to result in poorer agreements when comparing these site-specific partition coefficients with measurements, as observed for the weaker binding metals in Figure 1. As the chemical speciation is controlled by different factors for each metal we discuss them individually in relation to the data shown in the Figures and Table 2. Following the metal specific discussions, the subsequent sections discuss the potential effect of EDTA, and more general observations.

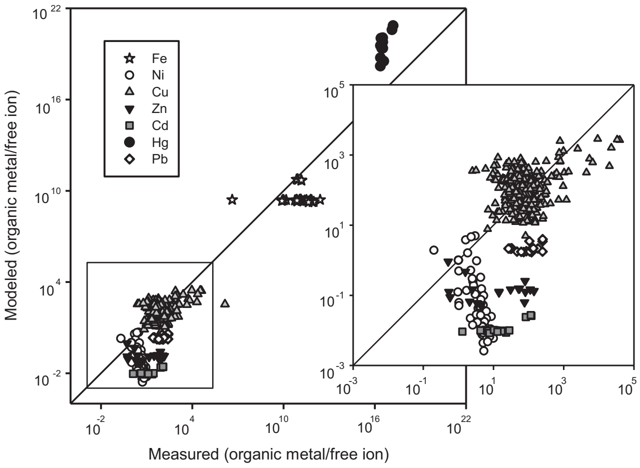

Figure 1. Comparisons of the degree of loading of metals onto dissolved organic matter (DOM), as represented by the ratio of organically bound to free metal ion concentrations. These data effectively represent site-specific partition coefficients.

Metal specific observations

Iron (III). The model predicts that Fe is strongly complexed with DOM and good agreement between measurement and modeling arises because nearly all of the metal is organically bound (Figures 1 and 2). Inorganic Fe is dominated by hydrolysis products making the free ion concentrations very low (Table 2). There is poorer agreement between the measured and WHAM modeled values for free ion (Figure 3), where agreement within 1 order of magnitude is obtained for 12 of 34 data. At 1 sub-location within the Fe study, measurements were performed at pH 8 as well as pH 6.9, which was the standard value for all other measurements. This was done to allow comparison with measurements performed at a pH closer to that of the in situ value. Agreement between measurements and modeling for free ion concentrations were within an order of magnitude for all measurements at this location for pH 8 compared with 1 of 6 measurements performed at pH 6.9.

Nickel. The model predicts weak binding of Ni by DOM (Table 2, Figure 1) except at low salinities where

Table 2. Median and ranges of the fractions of metal speciation measured and calculated by WHAM/Model VII for the data presented in Figures 1–4

	Fraction of total metal present as organic		Fraction of total metal present as Me^{x+}		
Metal	Measured	Modeled	Measured	Modeled	Salinity range
Fe	0.999 0.730–0.999	0.993 0.773–0.994	$10^{-11.1}$ $10^{-12.4}$–$10^{-6.8}$	$10^{-9.4}$ $10^{-10.9}$–$10^{-9.3}$	35
Ni	0.615 0.141–0.758	0.010 0.001–0.820	0.14 0.01–0.70	0.34 0.17–0.50	0.16–33
Cu	0.795 0.197–1.00	0.888 0.113–1.00	$10^{-2.6}$ $10^{-8.2}$–$10^{-0.9}$	$10^{-2.2}$ $10^{-6.6}$–$10^{-1.0}$	0–38
Zn	0.837 0.240–0.982	0.073 0.028–0.399	0.06 0.01–0.53	0.54 0.43–0.57	7–31
Cd	0.279 0.038–0.830	0.000 0.000–0.005	0.02 0.01–0.24	0.04 0.04–0.08	18–34
Hg	1.00 0.997–1.00	1.00 1.00–1.00	$10^{-16.5}$ $10^{-17.2}$–$10^{-16.4}$	$10^{-19.5}$ $10^{-20.9}$–$10^{-18.2}$	0.1–27
Pb	0.689 0.423–0.937	0.055 0.052–0.176	0.01 0.00–0.03	0.03 0.01–0.05	18–34

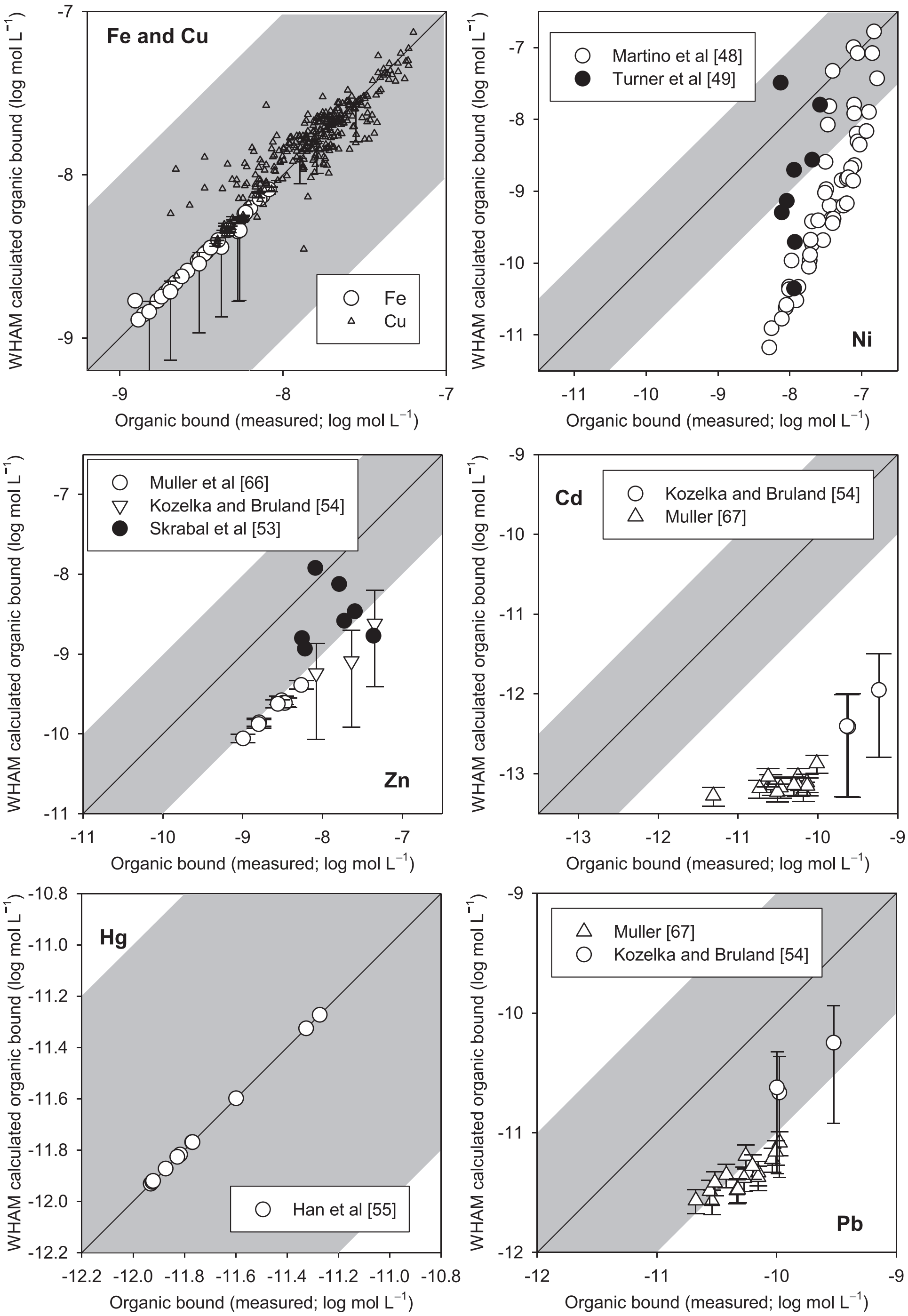

Figure 2. Comparison of WHAM/Model VII calculated and measured concentrations of organically bound metal. Note the different scales for each metal. Data from separate studies are shown as different symbols, except Cu where all available data are shown. See Table 1 for the analytical methods used. The solid line represents the 1:1 line and the shaded area represents 1 order of magnitude either side of the 1:1 line. Where data include error bars these represent points where dissolved organic matter (DOM) concentrations have been estimated. The ranges represent concentrations calculated from scenarios where DOM concentrations are at the upper and lower estimates (where variations are small, the bars appear as a solid line behind the data symbol). Several studies only report total concentration and free ion, these studies are not included in these plots.

there is less competition by major ions. The difference between measurements and modeling is linearly related to salinity, with greater divergence at the highest salinity values ($R^2 = 0.95$). In Figures 2 and 3 those data at higher free ion concentrations are for the lower salinity locations, with concentrations (modeled and measured) falling as the salinity increases. Free ion and organic bound Ni concentrations fall as the salinity increases due to increasing complexation with major anions in seawater. Model predictions of free ion concentrations give agreement within 1 order of magnitude of measured values in 60 of 64 data. On average inorganic Ni concentrations represent approximately 99% of the total for modeling and 38% for measurements (Table 1). The mean difference between modeling and measurements for free ion concentrations is approximately 2.5 (or less than a half an order of magnitude variation) and the closeness of agreement for Ni (as well as Cd, and Pb) is largely related to there being a significant proportion of the metal being present in inorganic forms. Good

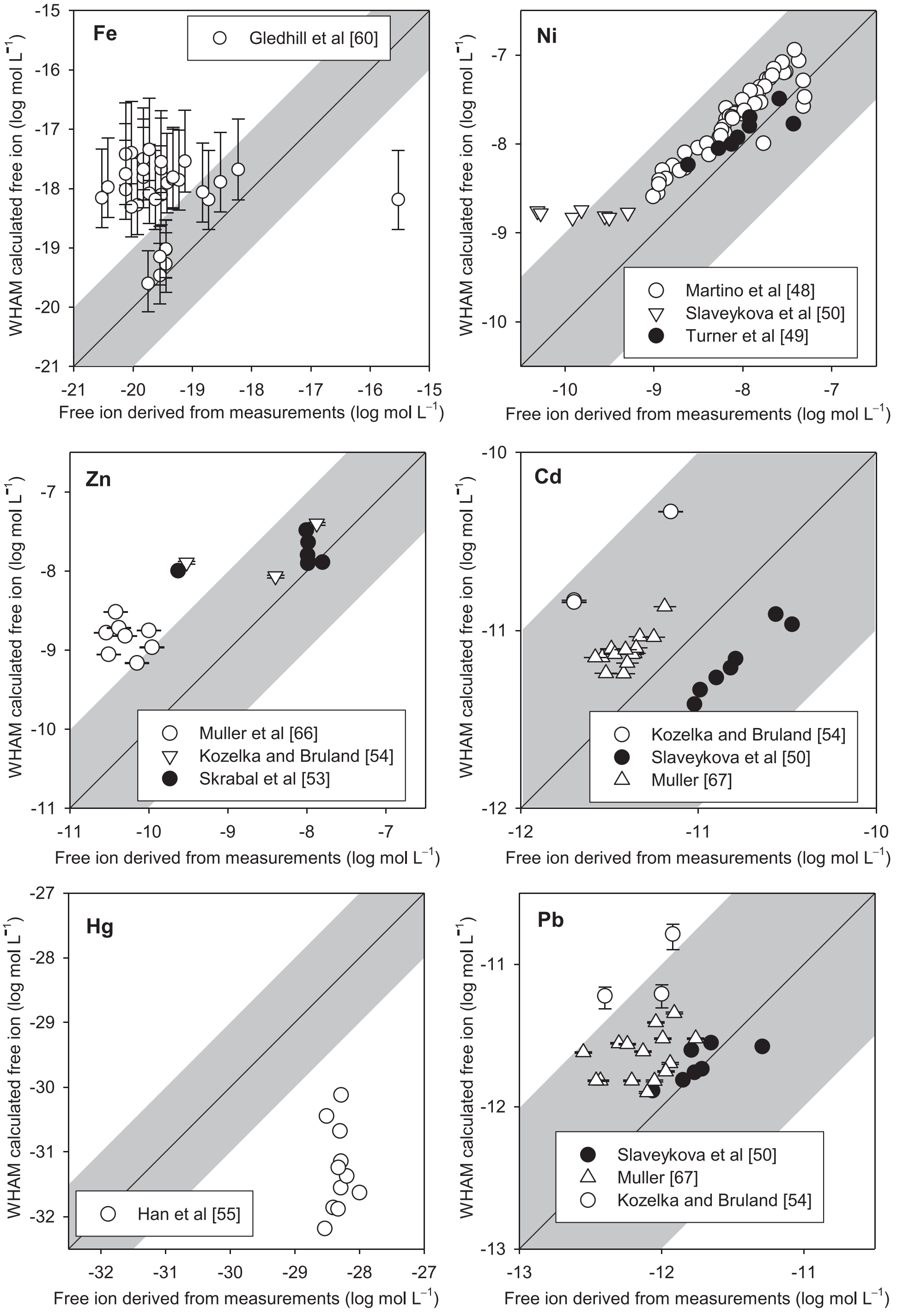

Figure 3. Comparison of WHAM/Model VII calculated free ion concentrations and free ion concentrations determined experimentally. Note the different scales for each metal. Data from separate studies are shown as different symbols. See Table 1 for the analytical methods used. The solid line represents the 1:1 line and the shaded area represents 1 order of magnitude either side of the 1:1 line. Where data include error bars these represent points where dissolved organic matter (DOM) concentrations have been estimated. The ranges represent the free ion concentrations calculated from scenarios where DOM concentrations are at the upper and lower estimates (where variations are small, the bars appear as a solid line behind the data symbol).

correlation is seen for the competitive ligand method studies (Martino et al. [48] and Turner et al. [49]) but not for the hollow fiber-permeation liquid membrane study of Slaveykova et al. [50].

Copper. Modeled results are compared with measurements in Figures 1, 2, and 4. Copper shows strong organic complexation (Table 2, Figure 1), with additional significant complexation of inorganic metal (Table 2). The model consistently predicts free ion concentrations higher than those measured in cases where the measured values fall below approximately $10^{-12}\,\mathrm{mol\,L^{-1}}$. Agreement is better at higher concentrations, which are most likely to be of interest when considering metal toxicity. Agreement between modeled and measured free-ion concentrations varies significantly between analytical methods. The single study using hollow fiber-permeation liquid membrane has data from 4 of 7 locations that agree within 1 order of magnitude, for the remaining locations model predictions are over 1 order of magnitude lower

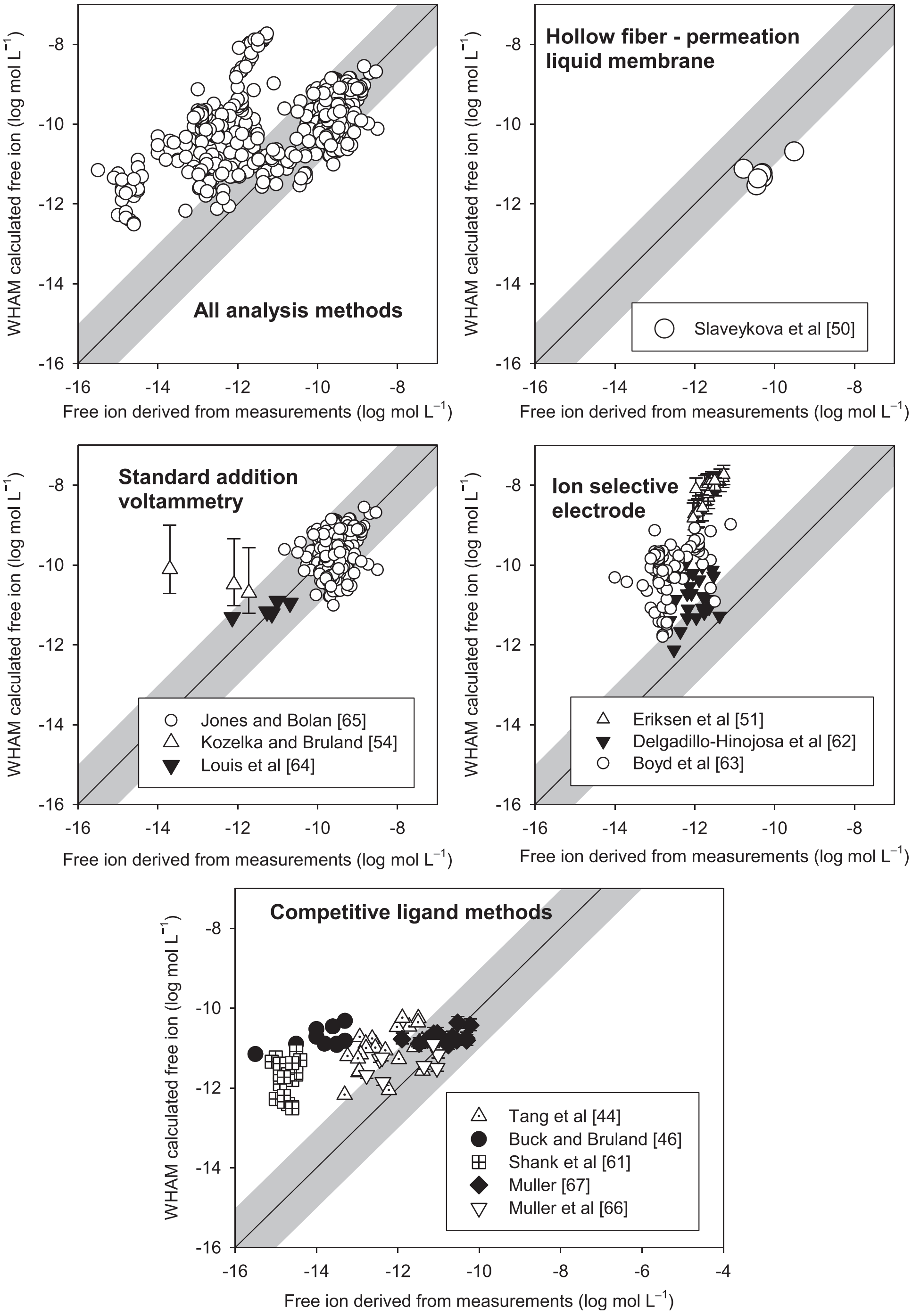

Figure 4. Comparison of WHAM/Model VII calculated Cu free ion concentrations and free ion concentrations determined experimentally. Measurements from studies using the same technique are grouped together. The solid line represents the 1:1 line and the shaded area represents 1 order of magnitude either side of the 1:1 line. Where data include error bars these represent points where dissolved organic matter (DOM) concentrations have been estimated. The ranges represent the free ion concentrations calculated from scenarios where DOM concentrations are at the upper and lower estimates.

than measurements. Standard addition voltammetry yields the closest agreements, with data from 276 of 292 measurements being within 1 order of magnitude of modeled concentrations. For ion selective electrodes analyses, 10 of 152 data fall within 1 order of magnitude of modeled concentrations, the remaining 142 data yield modeled concentrations over 1 order of magnitude greater those measured. The competitive ligand method data yield modeled concentrations over 1 order of magnitude greater those measured in 56 of 82 cases, with the remaining analyses falling within 1 order of magnitude of each other. When comparing the modeled and measured site-specific partition coefficients (Figure 1) there is no tendency of under- or over-prediction of these values for Cu.

For the results of Eriksen et al. [51] measured using ion selective electrodes, we calculate a larger deviation from the 1:1 line than at other sites. This may be due to Cu concentrations at these sites being approximately 10 times higher than in other estuary studies, as a result of leaching from historical mining activity in the area [51]. The lower range of WHAM/Model VII calculated organically bound Cu in Table 2 reflects the inability of DOM to complex the high Cu concentrations. An earlier study of the same harbor [52] had suggested that copper complexing capacities (a function of DOM concentration) less than the total reactive concentration of copper may lead to the possibility of elevated free ion activities and potential toxicity. This is seen in the WHAM predicted concentration but not the experimental measurements. However, it has been suggested that much of the measured dissolved Cu may be in colloidal form, associated with manganese or iron hydroxide colloids [51]. Across the studies used in the present study's comparison it is possible for there to be colloidal oxides present, and potentially in a thermodynamically unstable form, given the short residence times of some water bodies. However, in the absence of additional measurements at these sites it is not possible to quantify the potential effects of colloidal metal oxides on the chemical speciation of trace metals.

Zinc. The model predicts that Zn is weakly complexed with DOM (Figure 2, Table 2), and show predictions, on average, 1 order of magnitude lower than measured concentrations. The major inorganic species is the free ion (Table 2). There is a better agreement with experimental results at higher measured concentrations, as seen from data from the competitive ligand method (Skrabal et al. [53]) and the standard addition voltammetry data of Kozelka and Bruland [54].

Cadmium. The model predicts that Cd has a very low level of complexation with organic matter (Figure 2), whereas the measurements suggest that DOM complexes represent on average 28% of the total metal across all of the field sites (Table 2). The dominance of inorganic forms in the speciation of Cd is reflected in the comparison of modeled and measured free ion concentrations, where all data agree within 1 order of magnitude. Inorganic Cd is predicted to be almost entirely present as chloride complexes (the sites modeled all have salinities higher than 18%), with a low fraction of the total inorganic metal present as free ion. The modeled free ion concentrations agree to within half an order of magnitude with the values obtained by standard addition voltammetry and hollow fiber-permeation liquid membrane.

Mercury. Han et al. [55] calculated concentrations for the organic ligand and conditional stability constants from experimental data, and used the modeling program MINEQL to calculate the equilibrium distributions of Hg species based on these data (together with stability constants for inorganic speciation reactions). Both the WHAM/Model VII and Han et al. [55] models predict very strong complexation by organic matter. WHAM/Model VII calculations of the extremely low free ion concentrations are 2–4 orders of magnitude lower than those measured.

Lead. For organically bound Pb, model calculations are approximately 1 order of magnitude lower than measured data (Table 2, Figure 2). There is a good agreement for the comparison of free ion hollow fiber-permeation liquid membrane data (measurement data are not available from this technique to compare with modeled concentrations for organic bound metal), and agreement generally within 1 order of magnitude of standard addition voltammetry method measurements. Inorganic Pb is almost entirely present as chloride and carbonate complexes (the sites modeled all have salinities higher than 18%) therefore a low fraction of the total is present as free ion irrespective of organic complexation.

Potential effects of anthropogenic ligands

Estuaries and coastal seas for which data have been collected are often likely to be contaminated with anthropogenic ligands such as EDTA. This is not likely to be the case for open oceans, nor for many of the freshwater locations where chemical speciation has been measured or modeled. Thus, it is constructive to assess the effect of these ligands in coastal and estuarine environments. Figure 5 shows the ratio between the modeled and measured metal free ion concentrations in the absence of EDTA and where it is present at of 5×10^{-8} mol L^{-1} and 1×10^{-6} mol L^{-1} (see the *Materials and Methods* section for why these values were selected). Except Cd, which is dominated by inorganic complexes, all metal free ion concentrations are predicted to be lower in the presence of EDTA at these concentrations. Nickel has markedly lower predicted free ion concentrations at the higher EDTA concentration, compared with the other metals. EDTA is likely to be present in several of the locations used in the present studies comparison and may have an observable effect on the measurements of organic complexation and free ion concentrations in these environments. In such cases there is a need to include data on the concentrations of anthropogenic ligands to improve model predictions of metal speciation. Two locations in this comparison have EDTA data in the published literature. The mean ratio between the modeled and measured copper free ion concentrations for sampling sites within Galveston Bay, Texas, and San Francisco Bay, California, is 48 (1 standard deviation range, 5.6 to 421) in the absence of EDTA. If EDTA is included in the modeling at concentrations of 5×10^{-8} mol L^{-1} and 1×10^{-6} mol L^{-1} this improves the mean ratio to 21.6 (range, 1.5 to 307) and 1.1 (range, 0.06 to 23.2) respectively. Figures showing model predictions for free ion concentrations in the presence of the 2 different EDTA concentrations are included in the Supplemental Data (Figures S1–S4). At the greater EDTA concentration, modeled values for Cu and Pb free ion concentrations tend to be "flattened" compared with where EDTA is absent. This is likely to be caused by significant complexation with this ligand resulting in a lessening in the variation, in absolute terms, of speciation by other ligands (including DOM).

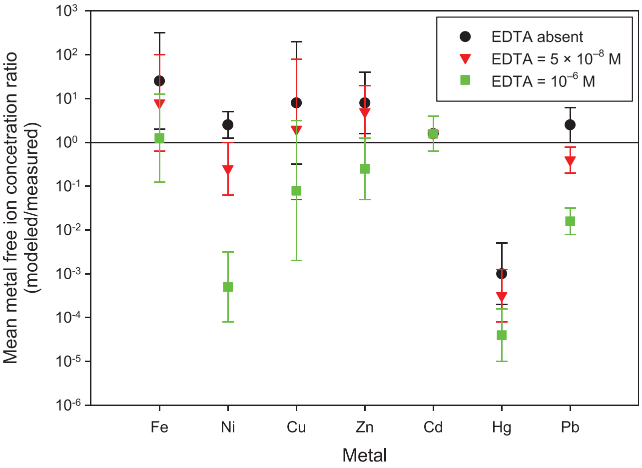

Figure 5. Mean ratios of modeled to measured metal free ion concentrations under different concentrations of ethylenediamine tetraacetic acid (EDTA). The solid horizontal line indicates the point at which measurements and modeling agree. Points above the line are where modeled concentrations are greater than measurements, points below the line are where modeled values are lower than those measured. Error bars represent 1 standard deviation from the mean.

Sulfur containing ligands may also be present in effluents and receiving waters, although fewer data exist on their nature and concentration. Sulfur functional groups may be found on organic ligands in both reduced (e.g., sulfide, thiol) or as oxidized species (e.g., sulfonate, sulfate) [56]. To date work has tended to focus of their interaction with Hg, [57] which has a strong affinity for reduced sulfur ligands. Further work is required to determine their potential impact on other trace metals.

Comparisons with previous model evaluations on freshwater and open ocean measurements

Two previous comparisons of modeling and measurements have been performed. Lofts and Tipping [24] used WHAM/Model VII to assess data for freshwaters and Stockdale et al. [8], used WHAM/Model VI to assess data for open ocean environments. Data for Fe were compared for open oceans by Stockdale et al. [8] where 330 data from 7 surveys were compared. Both modeled and measured free ion Fe concentrations were approximately 2–3 orders of magnitude lower than those reported in the present study for estuaries and coastal regions. For the open oceans, there was a general tendency for predictions to be greater than measurements; this is also seen in our single dataset for a coastal area. For Cu, Zn, and Cd the open ocean datasets were largely consistent with the present study, where better agreement was observed at higher concentrations, and lower measured concentrations tended to deviate more from modeled values, which are higher than measurements. Lead is the metal with the greatest deviation between the 2 comparisons. For coastal/estuarine waters we generally observe greater modeled values than those measured, for open oceans the opposite trend was observed.

For freshwaters [24] the metal concentrations tend to extend to greater values than those seen for the open ocean and coastal/estuarine datasets. Nickel free ion concentration comparisons were similar to the present study, where modeled values correlated with, but were slightly greater than, measured values and greater divergence between measurements and modeling was seen for free ion values below approximately 10^{-9} mol L^{-1}. Cadmium and Pb free ion concentrations in freshwaters followed a similar trend to Ni. For the coastal/estuarine data, Cd and Pb span much narrower free ion concentration ranges than freshwaters, and tend to be at the high end of the concentration range where better agreement is observed. For Zn the coastal/estuarine data extend to lower concentrations than for freshwaters and the deviations at low concentrations seen for Ni, Cd, and Pb in freshwaters are seen for Zn in coastal/estuarine data. A notable feature of the Cu data in both comparisons is the similarity in the competitive ligand method data. Both studies show a narrow range of modeled free ion concentrations in contrast to a wide range of measured values, a pattern that is not observed for other measurement techniques.

General observations

The modeled free ion calculations show a range of different levels of agreement. Iron free ion concentrations are higher than measurements, Hg predictions are lower, Ni, Zn, and Pb give closer agreement but a tendency to be greater than measurements, and Cd gives good agreements and correlation with no consistent under or over prediction compared with measurements. In cases where anthropogenic organic contaminants such as EDTA are known to be present, better agreement between modeled and measured concentration may be achieved for Fe, Ni, Cu, Zn, and Pb by inclusion of these ligands within the modeling. When differences in the ranges of free ion concentrations are taken into consideration, our results are largely consistent with those using WHAM/Model VI for open oceans [8] and WHAM/Model VII for freshwaters [24]. The fact that the model gives closer agreement with measurements at higher free ion concentrations means that it may be applicable in the assessment of toxic effects, which tend to occur under such conditions.

The comparison of the different techniques for Cu measurements (Figure 4) indicates that agreement may be dependent on the analytical method. The differences for Cu suggest that different measurement techniques give different results. However, this cannot be tested as different methods have yet to be applied to the same samples. The model provides a suitable yardstick for the comparison of experimental techniques. Given that neither multiple studies have been used for the same site, nor are there analytical methods that clearly stand out as giving a larger bias than other, then it is not possible to evaluate which may be the optimum techniques. There is a pressing need to cross-validate the different analytical methods used to measure speciation in estuarine, coastal, and marine systems. This type of comparison has already been done for freshwaters [58] and model comparisons have been done as part of the same study [59], although on very limited datasets. Both models and measurements are uncertain, and to date measurements have not been subjected to sufficient cross-comparison. To make progress, a concerted multi-institutional cross-comparison exercise, using multiple analysis techniques and modeling to investigate trace metal speciation on the same freshwater, estuarine, and marine sites is needed. Further validation of the model, through comparisons such as that presented in the present study, can give useful information to those who wish to use the humic ion binding models in ecotoxicological modeling.

CONCLUSIONS

Generally, the best agreements between modeled and measured values were for Ni, Cd, and Pb, where measured and modeled free ion concentrations were within 1 order of magnitude for 122 of 128 comparisons. For Zn 10 of 18 data give agreement within 1 order of magnitude, 8 values being over 1 order of magnitude higher than measurements.

Copper free ion measurements agree within 1 order of magnitude of modeled values in 314 of 533 of cases and are more than 1 order of magnitude lower than modeled values in 202 cases. Several datasets are compared for Cu and there is a general tendency for modeled free ion values to exceed those measured. There are large variations between different analysis techniques with standard addition voltammetry yielding the greatest fraction of data agreeing within 1 order of magnitude (274 of 292 data).

Agreements for organically bound and free ion concentrations tend to improve for the majority of metals at higher total concentration values. Although the model and measured values do not consistently agree, equally, the measured values do not give a consistent discrepancy compared with the model. There is a pressing need to cross-validate the different analytical methods. Ligands derived from anthropogenic activities also need to be taken into account where natural waters contain contamination from industrial or wastewater sources.

SUPPLEMENTAL DATA

Appendix A1, Table A1. (132 KB DOC).
Figures S1–S4. (905 KB DOC).

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