

Trace metals in the open oceans: speciation modelling based on humic-type ligands

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Environmental context. Speciation of trace metals in the oceans is typically explained by invoking the concept of metal binding to specific organic ligands. Here, using a speciation model widely used for freshwaters, we assess the extent to which non-specific humic-type ligands found in the ocean may explain chemical speciation of cationic metals. We found that the model can give good fits in some cases, and that experimental results do not give consistent variation from the model. This has implications for the way that the availability of trace elements is considered in ocean environments.

Abstract. The speciation of trace metals in the oceans is typically explained by invoking the concept of metal binding to specific organic ligands, but a lack of detailed knowledge about the ligands has impeded the formulation of comprehensive models to predict speciation chemistry. The aim of our study was to shed further light on the possible role of humic-type ligands in trace metal complexation in the oceans by comparing published seawater (open ocean) speciation measurements with predictions obtained using a speciation model typically used for freshwater and soil systems (Windermere Humic Aqueous Model; WHAM). We show that in some cases, speciation of trace metals in seawater environments may be reasonably predicted using this model with its default parameter set, without any model fitting. The results support the idea that humic-type ligands may account for much of the observed organic binding at least in the cases of Fe, Cu and Pb. Although the model does not consistently provide agreement with the measured values, it provides a useful benchmark to compare different datasets and to examine variation in speciation as a result of varying levels of competing metal ion concentration and fulvic acid activity.

Introduction

Measurements of trace cation speciation in marine systems are typically performed using differential pulse adsorption stripping voltammetry (DPASV^[1,2]) or competitive ligand adsorptive cathodic stripping voltammetry (CL-AdCSV^[3]). These measurements enable calculation of a conditional ligand concentration and stability constant that probably represents a weighted average of a mixture of multiple ligands.^[4] From these data the fraction of metal in organic forms can be quantified. Such studies have been reported for analyses in the global oceans for the past 20 years. It is widely thought that the ligands responsible are specific chelators of biological origin,^[5,6] although their exact source is generally unknown, especially in the case of Fe, Ni, Zn, Co and Cd.^[5] There is a recognition that the lack of more detailed knowledge about the strong binding ligands in marine systems has impeded the formulation of comprehensive models to predict speciation chemistry.^[7]

Most of the dissolved organic matter (DOM) in the open ocean comprises exudates, cell lysis products, grazer mediated releases and excretions, and decomposition products from marine organisms.^[8] We assume that the more degraded material within this mixture contains a varied distribution of ligand

groupings forming binding sites for cations similar to those encountered in terrestrial and freshwater humic matter. Thus, marine DOM is likely to contain a continuum of ligands with a corresponding continuum of affinities for metal ions.^[9] For terrestrial systems there has been much interest in the development of speciation models parameterised using the extensive published laboratory data, obtained from binding experiments with humic substances isolated from DOM. Humic substances (HS) comprise humic acids (HAs) and fulvic acids (FAs), which are divided operationally on the basis of their solubility, as HAs precipitate at pH 1, whereas FAs are soluble.^[10] One of the reasons for the different approach in terrestrial systems is that comprehensive models are needed for freshwaters in order to predict the effects of their large variations in water chemistry, including major ions, pH and high aluminium concentrations in acidified waters. Examples of widely used comprehensive models are the Windermere Humic Aqueous Model VI (WHAM VI)^[11] and the Non-Ideal Competitive Adsorption (NICA–Donnan) model.^[12,13] In this work we use the terms marine DOM and humic-type ligands to refer to the non-specific organic material in the oceans, and reserve HS for terrestrial material.

Marine DOM is not conventionally thought to be important for binding of trace metals in seawater, largely as a result of the work of Mantoura et al.^[14] In their work HS were isolated from peat, freshwaters and coastal waters and they concluded that at most only 10% of Cu can be bound by isolated HS in seawater due to competitive binding by Ca and Mg. Other metals (Co, Ni, Zn and Cd) were found to exhibit weaker binding to organic ligands. The isolated humic substances (those adsorbed to Amberlite XAD-2 resin at pH 2.2) were assumed to be representative of marine DOM. However, this work was based on binding experiments carried out at low ionic strength (0.02 mol L^{-1}) and extrapolated to seawater ionic strength using a rudimentary model of metal-humic interactions. It has since been shown that the model greatly exaggerated the predicted competition effects of Mg and Ca in seawater, owing to an erroneous assumption about the electrostatic properties of HS.^[15] Additionally, high metal loadings onto the humic substances were used in the work of Mantoura and colleagues,^[14] thus the binding of metals to small numbers of strong binding sites is not considered. Low concentrations of trace metals in the oceans leads to low occupancy of binding sites, and thus, non-specific humic-type ligands may be important in these environments.

Recent work by van den Berg and coworkers^[10,16] used isolated freshwater humic substances (IHSS fulvic and humic acids from Suwannee River; SRFA and SRHA) to investigate the DOM complexation of Fe within a seawater matrix, including the competitive effects of subsequent additions of competing metals. Strong binding of Cu to isolated terrestrial humic substances (also IHSS SRHA) in marine conditions was found by Voelker and Kogut^[17,18] Thus, it can be concluded that if marine DOM is analogous to terrestrial material then it may contain important ligands for these metals in seawater.^[16] Yang and van den Berg^[16] also concluded that the contribution of marine DOM to metal binding in seawater is likely to be significant, based on comparability in stability constants for ocean DOM and isolated freshwater HS added to UV treated seawater solutions, and assuming that marine DOM has similar properties to isolated SRHA and SRFA. Comparative measurements have shown that the iron binding capacity of humic substances in seawater can account for all of the ligands in samples from coastal and deep-sea origin.^[10] Hiemstra and van Riemsdijk,^[13] using the NICA-Donnan model, showed that the Fe-binding characteristics of marine DOM display the same type of chemical heterogeneity as that occurring in freshwater humic substances, suggesting that they may exhibit similar chemical binding properties.

The aim of our study was to shed further light on the possible role of humic-type ligands in trace metal complexation in the open oceans and the extent to which the humic-type ligands found in the ocean have characteristics that correspond to those in fresh water. We assume that marine DOM contains a wide range of ligand groupings forming binding sites for cations, similar to those encountered in terrestrial and freshwater humic matter, and represented in the WHAM model. This was achieved by comparing published open ocean seawater speciation measurements with predictions obtained using the WHAM^[19] model (incorporating Model VI^[11]). Our model predictions can be thought of as an indication of the background organic complexation in seawater, as humic-type ligands are likely to be present at some concentration throughout the oceans. Consequently the comparisons between predictions and speciation measurements should lead to a better assessment of

the occurrence of specific biological ligands, as their distributions will be more temporally and spatially restricted. We do not suggest that marine DOM is freshwater in origin, but that it may be represented in a similar way in that it contains a continuum of heterogeneous binding sites. WHAM VI also considers the competitive effects of other trace elements and major cations on metal binding. We explored these effects within the modelling exercise. More generally, we hope to provoke discussion amongst marine speciation scientists as to the significance of marine DOM as a source of important heterogeneous ligands in the oceans.

Theory

WHAM VI comprises two components: first the inorganic speciation code WHAM^[19]; and second the Humic Ion Binding Model VI.^[11] The Humic Ion-Binding Model VI was described in detail by Tipping^[11,20]; a concise description is given in Appendix A. The model uses a structured formulation of discrete, chemically-plausible, binding sites for protons, in order to allow the creation of regular arrays of bidentate and tridentate binding sites for metals. The multi-dentate sites are required to explain strong binding observed at low metal : humic ratios. It is these sites that are likely to be important for trace metal binding in the oceans. An important feature of the model is that divalent and trivalent cations and protons co-compete for complexation at humic binding sites. The degree of competitive effects is controlled by the binding affinities of metals and their concentrations.

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 (WHAM^[19]). Ionic strength effects on the inorganic reactions are discussed in the following section.

Methods

Data collation

Experimental data were collected from published studies^[2,21–40] that reported salinity and both dissolved metal concentrations and the concentration of either the free ion or inorganic fraction. Where inorganic concentrations were reported, we converted these to free ion concentrations using WHAM with zero DOM concentrations and with inorganic ligands accounted for. Table 1 lists the data sources including the ocean studied and the measurement technique employed (data from coastal waters and seas were not compiled as the DOM pool may include material from terrestrial sources). Fig. 1 shows the geographic locations of the sites and the metals analysed. In order to account for potential competitive binding effects by other trace metals, we used fixed estimates for their concentrations, based on mid-range values in Chester^[41] and Donat and Dryden,^[42] plus additional sources for Al.^[43,44] In making estimates of other (non-target) trace metals we recognise that these will vary with depth and geographical location, with many trace metals exhibiting nutrient type profiles where surface concentrations are depleted in relation to those at greater depths. It would be a huge undertaking to obtain data that are characteristic for each sampling site and depth. Therefore we have made single estimates for the concentrations of non-target trace elements applied to all sites. These estimates were 10, 1, 1, 0.02, 8, 2, 1, 0.1, 0.005 and 0.05 nmol L^{-1} for Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg and Pb respectively.

Data were modelled using the temperature and pH of the experimental procedures, which can differ from natural

Table 1. Experimental studies used for the comparison of modelled and experimental speciation results

Metal	Measurement technique	Ocean	Reference
Fe	CL-AdCSV	Southern	Boye et al. ^[21]
	CL-AdCSV	S & Equatorial Atlantic	Powell and Donat ^[22]
	CL-AdCSV	Southern	Croot et al. ^[23]
	CL-AdCSV	NE Atlantic	Boye et al. ^[24]
	CL-AdCSV	NE Atlantic	Boye et al. ^[25]
	CL-AdCSV	Southern ^A	Gerringa et al. ^[26]
	CL-AdCSV	Southern	Nolting et al. ^[27]
Co	CL-AdCSV	Southern	Ellwood et al. ^[28]
	CL-AdCSV	NE Atlantic	Ellwood and van den Berg ^[29]
	CL-AdCSV	N Atlantic	Saito and Moffett ^[30]
Ni	CL-AdCSV	Equatorial Pacific	Saito et al. ^[31]
Cu	CL-AdCSV	NW Pacific/Bearing Sea	Moffett and Dupont ^[32]
	CL-AdCSV	N Atlantic	van den Berg and Donat ^[33]
	DPASV titration	N Pacific	Coale and Bruland ^[34]
Zn	CL-AdCSV	NE Atlantic	Ellwood and van den Berg ^[35]
	DPASV titration	Central N Pacific	Bruland ^[36]
	DPASV titration	Sub-Antarctic	Ellwood ^[37]
	FF-ASV & CSV	N Atlantic	Jakuba et al. ^[38]
Cd	DPASV titration	Central N Pacific	Bruland ^[2]
	DPASV titration	Sub-Antarctic	Ellwood ^[37]
Pb	DPASV titration	Southern	Scarponi et al. ^[39]
	DPASV titration	N Pacific	Capoldaglio et al. ^[40]
	DPASV titration	Southern	Scarponi et al. ^[39]

^ASamples taken from near the Kerguelen Archipelago land mass.

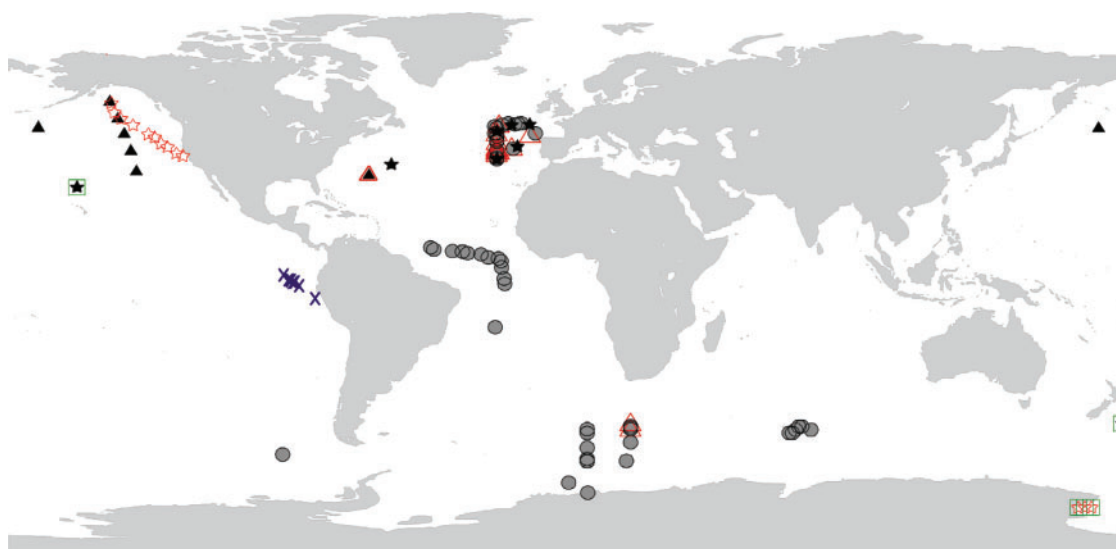


Fig. 1. Stations in the literature where samples for speciation measurements were collected. Many individual stations have multiple samples where depth ranges were investigated. The symbols represent: Co, open triangles; Ni, crosses; Fe, filled circles; Cu, filled triangles; Zn, filled stars; Cd, open squares; and Pb, open stars. Sources listed in Table 1.

conditions. For example, during speciation measurements Fe is buffered at pH conditions that are typical of surface waters (~8.0 to 8.1) meaning that measurements of deeper water samples generally have greater divergence from actual conditions than surface samples. Co measurements were performed at pH 9.1^[28,29] in order to improve the efficiency of the method. In contrast, the Cu studies used in our comparison^[32,34] were performed without buffering in order to yield results that were directly related to the in-situ conditions. To test the effects of

these variations the model was used to predict inorganic Fe in two contrasting surface ocean waters, for both in situ and experimental conditions. For a mid-Atlantic and a Southern Ocean site, the predicted inorganic concentrations at in-situ conditions were only 63 and 32% respectively of those under experimental conditions. This is a significant consideration for both modelling and experimental results. Temperature effects on Fe speciation were investigated briefly in the modelling of Hiemstra and van Riemsdijk.^[13]

Investigation of competition effects

In order to investigate the effect of other metals on competition for binding to humic-type ligands, we looked at additional scenarios where the estimated values were increased or lowered by a factor of 10 (unless this took them outside the range of values in the literature, in these cases the maximum or minimum was used). To investigate specifically the competitive effect of Cu on the binding of other metals we also modelled an additional scenario, where only Cu was lowered from the mid-range estimates. Minimum estimates were 1, 0.2, 0.1, 0.004, 2, 0.5, 0.1, 0.01, 0.0005 and 0.005 nmol L⁻¹ for Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg and Pb respectively. Maximum estimates were 40, 3, 3, 0.2, 12, 6, 1, 1, 0.01 and 0.15 nmol L⁻¹ for Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg and Pb respectively.

Sources for DOM data

DOM concentrations were derived from dissolved organic carbon (DOC) concentration data that were largely taken from papers cited in the review by Dafner and Wangersky^[45] together with several other sources.^[46–50] DOC values were estimated based on the available data closest to the metal water sample location and depth (estimates are tabulated in the Accessory publication). For the fraction of DOM that can be represented by fulvic acid (referred to here as the fulvic acid activity) we applied values used in recent studies, i.e. that DOM is 2 times the DOC and that it can be represented by fulvic acid (FA) with an activity of 65%; e.g. Tipping et al.^[51] To evaluate the sensitivity of FA activity, we modelled additional scenarios where activity was set at 30 and 100%, variations in speciation as a result of these activity ranges are shown as error bars in the plotted results. We note that any potential errors in the DOC concentration estimates will be well within this range of FA activities. Other modelling in marine systems has applied other values, including a fraction of humic acid (HA) in some cases.^[52] Hiemstra and van Riemsdijk^[13] assumed all DOM could be represented using FA, justified by studies showing that marine DOM is present to a greater extent in the smaller size fractions. As we sought to test the model in an a priori ‘default’ scenario without any fitting, we chose to present results for FA only. However, results using HA at an activity of 65% in place of FA do not substantially change the predicted binding characteristics and are within the uncertainty limits of the error bars shown for FA (this work, unpublished results). Lofts et al.^[53] calculated maximum theoretical limits for the binding of Fe to DOM from modelling of data for UK freshwaters. They predicted generic ratios of Fe^{III}:DOM (i.e. typical values for the ratio based on a large dataset) for a wide range of pH values, and at a typical seawater pH of ~8–8.1 this ratio is ~15 μmol g⁻¹.

For the Fe studies used in our comparison, the typical values for the concentration of measured ligands is ~1–5 nM. In order for such ligands to contribute significantly to DOM they would need to have very large molecular weight. For example, assuming a concentration of 1 nM and MW of 1000 (a reasonable assumption for some ligands) this only yields a contribution to the DOM of 0.004 mg L⁻¹.

Ionic strength corrections

In low ionic strength solutions, individual ion activities required in the modelling of chemical speciation, are typically corrected using coefficients calculated from Davies or Extended Debye–Hückel (EDH) equations.^[54] These equations relate the charge on an ion to an activity coefficient at a specified ionic strength.

In the modelling 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^[55] 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 modelling using two approaches to the calculation of γ values, the Pitzer’s equations and the default method of WHAM, the EDH equation. The model was applied to an inorganic system with typical values for seawater for all major ions (Na, Mg, K, Ca, Cl, (bi)carbonate, sulphate) and several trace components (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, F and nitrate; values from Chester^[39] and references therein). Differences in the free ion activities calculated using the two methods were within $\pm 16\%$. An exception was nitrate, where the free ion activity was 24% higher when the EDH method was employed. These differences are small in comparison to the variations when comparing modelled and measured values of trace metal free ion concentrations. For our detailed open ocean modelling we exclusively used the default WHAM approach, EDH. This is consistent with other studies that have used component independent relationships for activities in marine systems.^[56,57]

Results and discussion

Fig. 2 shows the comparison of modelled against measured concentrations of the metal bound to organic ligands. Figs 3 (Fe) and 4 (all other metals) show the modelled against measured free ion concentrations. To aid the reader in comparing the data, we have included in each plot, a shaded area that highlights the data that fall within one order of magnitude either side of the 1 : 1 line. Error bars on the free-ion concentration plot represent the ranges of modelled values when the fulvic acid activity is varied. Lower predicted free-ion concentrations represent calculations at higher fulvic acid activity and higher free-ion concentrations are observed when the activity is decreased. Where no error bars are included, there were no noticeable differences in concentrations over the ranges of the fulvic acid activity.

Small deviations in the amount of the inorganic fraction present as free ion may arise from differences in the way the inorganic speciation is considered between the model and measurements. Within WHAM the ratio between total inorganic and free ion (the side reaction coefficient) will be slightly different for each calculation as the exact salinity and pH of each measurement is considered and all calculations are performed using the same set of inorganic complexation constants. The mean and ranges of these values is the reciprocal of data showing the fraction of inorganic present as free ion in Table 2. In contrast, the electrochemical studies frequently use a fixed side reaction coefficient calculated from the different data compilations presented in Turner et al.^[58] or Byrne et al.^[57]; for Fe the value in Hudson et al.^[59] is commonly used. These differences are small, with an average discrepancy between the literature values and modelled values of 0.29 log units. Fig. A1 in the Accessory publication compares these coefficients. Furthermore, 12 of the 22 studies collated here report inorganic concentrations that are converted to free ion using the WHAM model.

Table 2 reports the means and ranges for measured total dissolved concentrations, the modelled fraction of organic speciation (summarising the Fig. 2 data in terms of the total dissolved concentration at each site) and the fraction of

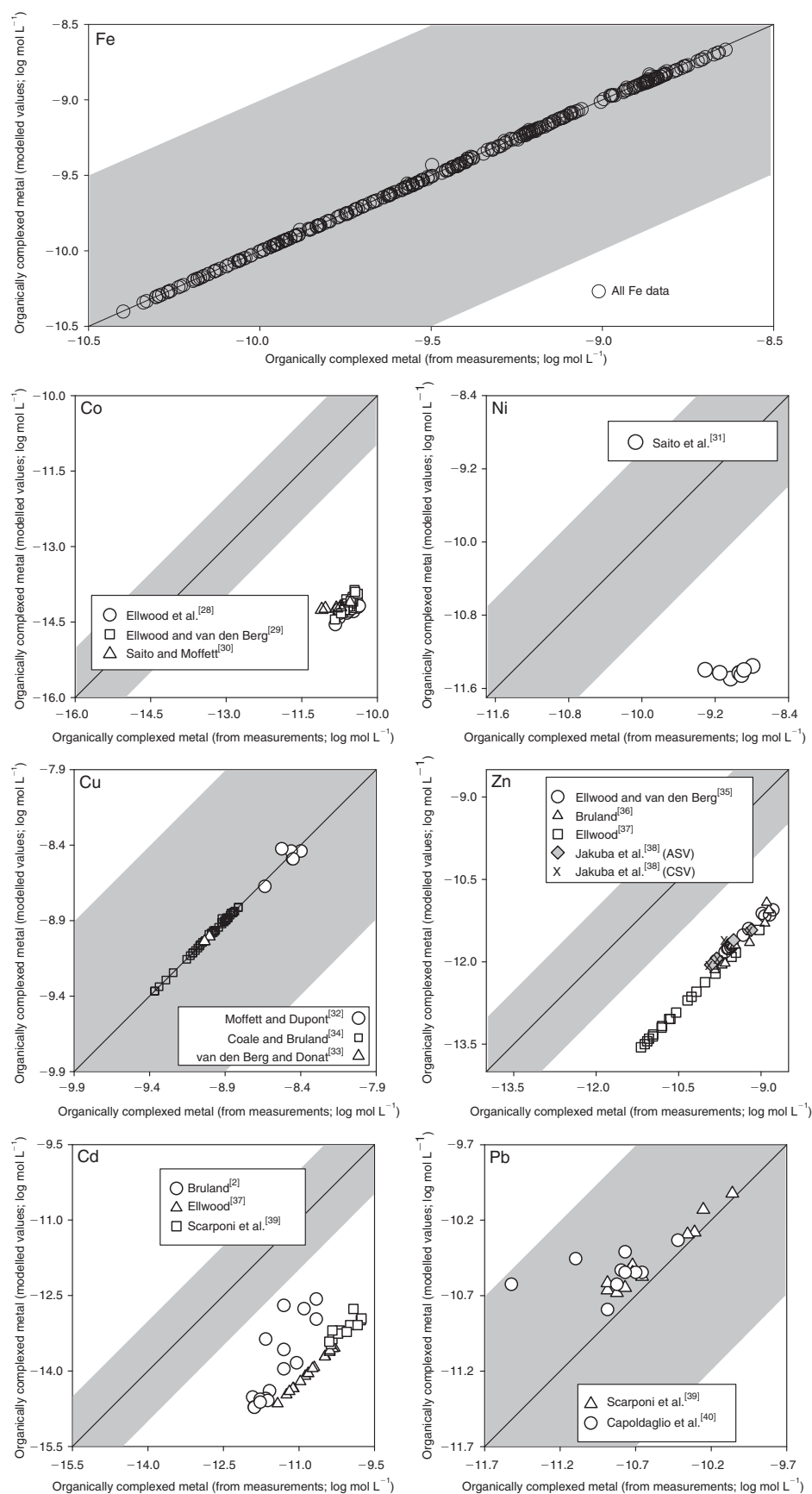


Fig. 2. Comparison of WHAM calculated concentrations of organically complexed metal and those derived from experimental data in the literature. Note the different scales for each metal. The solid line represents the 1 : 1 line. One point is omitted from the plots for Ni and Co as no organic speciation was detected and it cannot be plotted on these log-log plots.

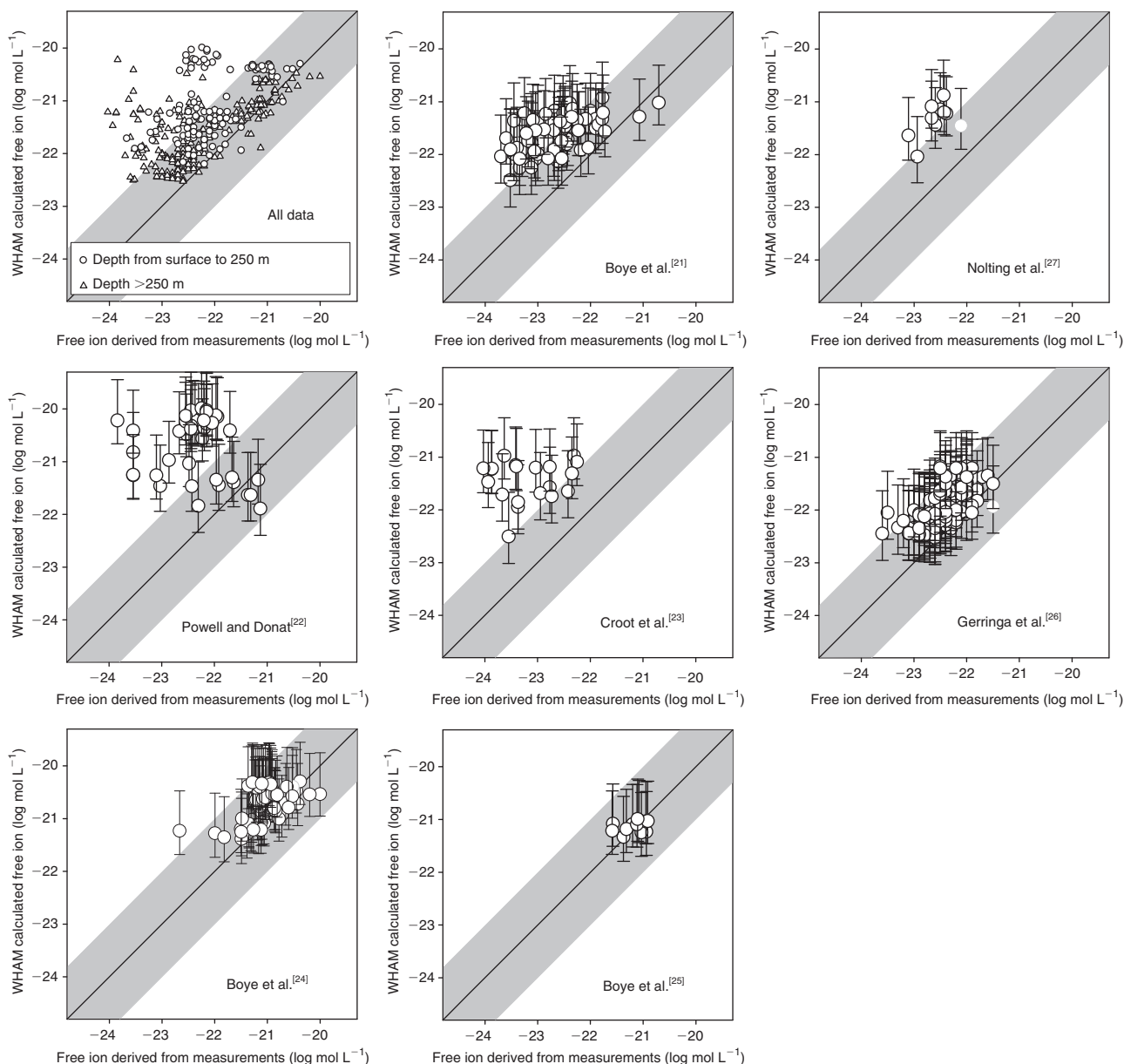


Fig. 3. Free ion activities of Fe^{III} . Comparison of WHAM calculated free ion concentrations and free ion concentrations for iron determined experimentally. The solid line represents the 1 : 1 line and the shaded area represents one order of magnitude either side of the 1 : 1 line. Error bars show the range of WHAM calculated free ion concentrations given upper and lower values for the fulvic acid activity.

inorganic present as free ion. Also reported are the modelled amounts of metal bound to fulvic acid ($\nu, \text{nmol g}^{-1}$). Total dissolved concentrations for some metals can vary by orders of magnitude, when all oceans and depth ranges are considered. Model predicted fractions of organic bound and free ion concentrations (Table 2; columns 5 and 6) cover a narrow range, owing to only small variations in pH, DOC and salinity. As the chemical speciation is controlled by different factors for each metal we discuss them individually in relation to the data shown in Figs 2–4, and Table 2. More general observations are then discussed in the following section. The calculations performed here put all the available data into a consistent framework, enabling different datasets (from different locations, surveys, methods, etc.) to be compared. The terms correlation and agreement are used to define two different relationships between the measured and modelled data; correlation is used to describe where the general trends in concentration tend to be related

between model and measurements, but not necessarily following the 1 : 1 line; agreement is used to describe where the data are close to the 1 : 1 line but not necessarily correlated.

Broadly speaking, WHAM speciation calculations produce two patterns. For metals strongly complexed by humic-type material, nearly all the metal is complexed, agreement with measured bound metal is therefore good, and the important comparison is between measured and observed free ion concentration. For metals weakly complexed by humic-type material, an appreciable amount of the total metal is in inorganic forms, and so free ion concentrations can agree fairly well despite differences in the measured and modelled bound concentrations. For example if 50% of the total concentration is measured to be organically complexed, but the model predicts little organic complexation, measured and modelled free-ion concentrations will differ by 0.3 log units. If 90 or 99% organic complexation is measured, the difference will still only be 1 or 2 log units.

Table 2. Mean and ranges of total dissolved concentrations and the fractions of metal speciation calculated by WHAM VI for the data presented in Figs 2–4
Data were calculated at the experimental pH values. Salinity across all the data was $34.5 \pm 2.5\text{‰}$

Metal	Number of data	Total dissolved concentrations (pmol L ⁻¹)	Fraction of total metal present as organic as reported in the studies included in this work	Fraction of total metal present as organic as calculated by WHAM	Fraction of inorganic present as free ion (WHAM calculated)	WHAM calculated cation bound to FA (v, nmol g ⁻¹)
Fe	330	558 (40–2290)	0.992 (0.838–1.000)	0.978 (0.937–0.994)	$10^{-10.2}$ ($10^{-10.4}$ – $10^{-10.1}$)	642 (51–2751)
Co	47	31.2 (14.4–55.2)	0.775 (0.000–1.000)	$10^{-3.7}$ ($10^{-3.6}$ – $10^{-3.8}$)	0.187 (0.185–0.190)	0.007 (0.003–0.013)
Ni	8	3390 (2880–3950)	0.271 (0.000–0.410)	0.001 (–)	0.36 (–)	3.46 (2.95–4.04)
Cu	53	1360 (430–4200)	0.98 (0.708–1.000)	0.982 (0.887–0.999)	0.064 (0.038–0.093)	1645 (375–6029)
Zn	53	524 (7.19–4770)	0.884 (0.266–0.987)	0.005 (0.003–0.007)	0.52 (0.50–0.54)	2.74 (0.03–19.3)
Cd	45	104 (2.00–780)	0.63 (0.000–0.994)	0.001 (0.000–0.001)	0.043 (0.041–0.043)	0.064 (0.002–0.433)
Pb	22	40.4 (17.0–114)	0.577 (0.120–0.778)	0.886 (0.832–0.948)	0.045 (0.038–0.051)	42.8 (14.1–135)

Metal specific observations

Fe

Model results (Figs 2, 3; Table 2) show that Fe is strongly complexed with organic matter, with these complexes accounting on average for ~98% of the total dissolved concentrations. Organic speciation shows good agreement between measurements and the model owing to high predicted and observed affinities for organic binding sites. Differences between the approaches are more clearly observed in the free-ion data (Fig. 3). This is owing to sensitivity in small deviations in the organic fractions at such high organic loadings (i.e. if the modelled and measured organic fractions were 0.999 and 0.990 respectively, this yields an order of magnitude difference in the free-ion concentrations). Inorganic Fe is dominated by hydrolysis products, resulting in very low free ion concentrations (Table 2). For the free-ion data there is some agreement between the measured and WHAM modelled values, with 72% of the 330 data points falling within the shaded area. Two of the seven datasets (Powell and Donat,^[22] and Croot et al.^[23] datasets) give poor agreement with the modelled values. There is a general tendency for the model to over-predict free ion concentrations and this may be due to under-prediction of organic matter binding or inaccuracies in the estimates for the competing metals (this aspect is discussed further in a subsequent section).

Recent work showing relationships between dissolved organic carbon^[60] or humic-type fluorescence^[61,62] and dissolved or soluble Fe suggests that Fe^{III} solubility may primarily be as a result of complexation with natural organic ligands, such as marine dissolved humic substances. This is consistent with the modelling results where organic binding can be well predicted considering DOM as humic-type ligands.

In order to examine if there was any depth dependency in agreements between modelled and measured data, the top left panel of Fig. 3 shows all of the Fe data (330 points) separated for those samples from 0 to 250 m and those at depths greater than 250 m. Discrepancies between these two depth ranges may indicate the presence of additional strong ligands, or effects caused by the relative age of deep and surface DOM, however, no trends in agreements were observed.

Co

Results for the comparison of measured and WHAM modelled concentrations are shown in Figs 2 and 4. The poor agreement arises because WHAM predicts little binding to organic matter at all locations. Thus, modelled concentrations of Co²⁺ are largely a function of the total dissolved concentrations. Of all the metals considered, predicted Co²⁺ has by far the largest deviations from measured values (up to 5 orders of magnitude difference in free ion concentration). It is highly unlikely that the deviations could be explained through uncertainty over the binding properties of marine DOM. Although specific biological ligands have been suggested as the reason for strong binding of cobalt, it has also been hypothesised^[28,31] that it may be present in the Co³⁺ form, which may result in stronger binding to organic ligands. Speciation may also be affected by Co being present as chelated complexes in vitamin B12.^[63] However, further work is required to fully determine the redox states of this metal and the factors causing changes in the redox state.

Ni

Modelling results for Ni show no significant binding to organic matter (Fig. 2; Table 2). There is very good agreement

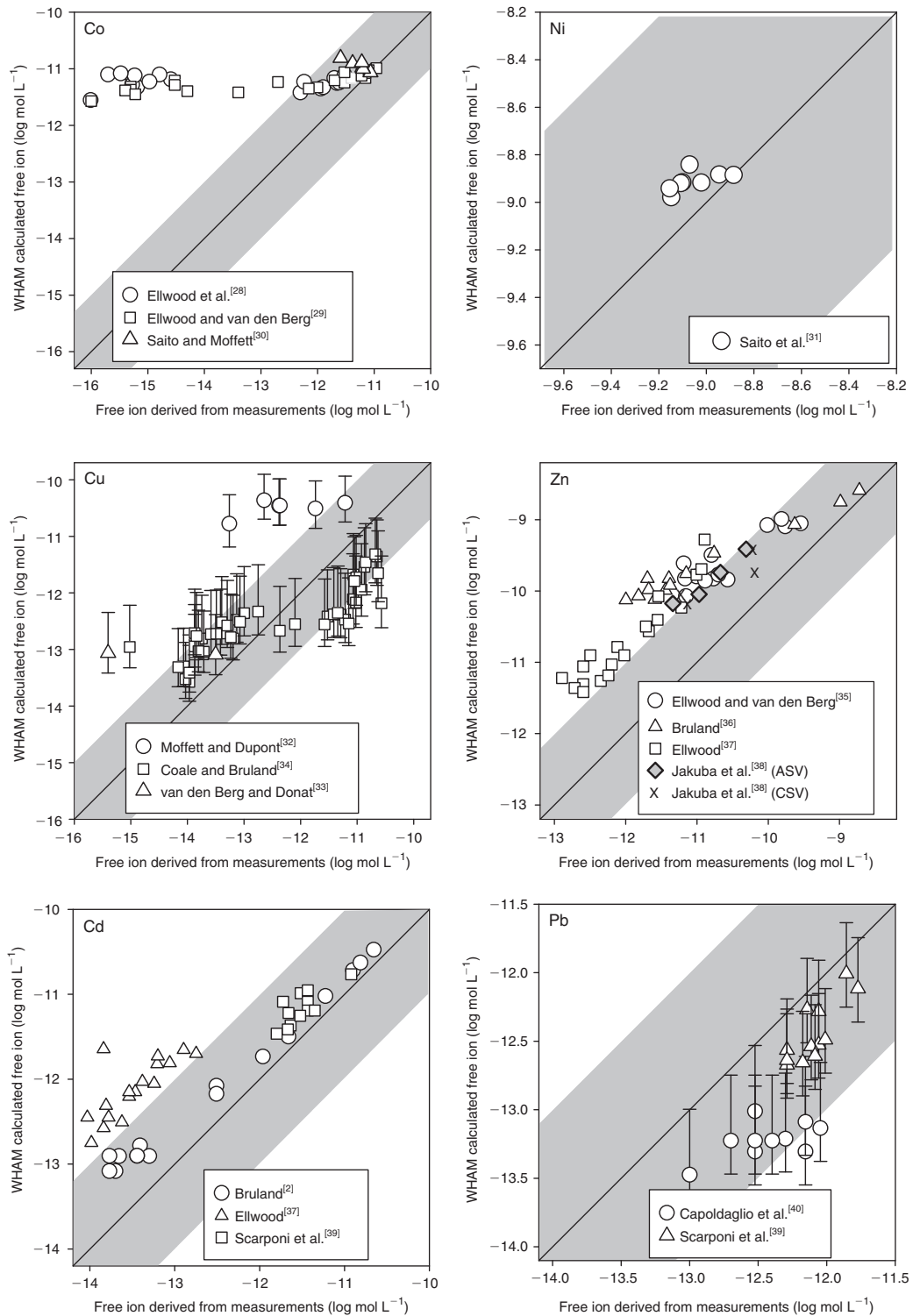


Fig. 4. Comparison of WHAM calculated free ion concentrations and free ion concentrations derived from experimental data in the literature. Note the different scales for each metal. Error bars show the range of WHAM calculated free ion concentrations given upper and lower values for the fulvic acid activity. See Table 1 for the analytical methods used. The solid line represents the 1 : 1 line and the shaded area represents one order of magnitude either side of the 1 : 1 line.

in Ni concentrations between the modelled and measured values for free ion concentrations, although few data were available for comparison. The reason for the discrepancies in organic concentrations and similarity in the free ion are related to intermediate levels of organic matter binding, as stated in the general discussion above. One point is omitted from the Ni plot for

organic species as no organic speciation was detected at this location. Our results are largely in agreement with the data of Achterberg and van den Berg,^[64] who measured Ni in a large number of samples collected from the Mediterranean. They found only small differences in the concentrations of electrochemically labile and total dissolved metal. Given that at several

sites labile concentrations were measured to be higher than the total dissolved and that these differences were of a similar order to those sites where labile concentrations were lower, this suggests there was little organic binding at the sites studied.

Cu

Comparison of the modelled data with those from different studies and measurement techniques are shown in Figs 2 and 4. As with Fe, organic complexation is generally well predicted. The model predicts ~98% organic complexation, consistent with the average observed for measurements (Table 2, columns 4 and 5). Significant Cu complexation is also seen by inorganic ligands (Table 2, column 6). For the Coale and Bruland^[34] data there is no consistent trend in over or under prediction of free ion concentrations, with two discrete groups of data either side of the 1:1 line. The majority of data fall within the shaded area, although, the smaller datasets^[32,33] give poorer agreement to model predictions. Better agreement is observed for the dataset that used the DPASV titration than those using CL-AdCSV. Although too few data exist to draw conclusions about the individual methods, it does highlight how deployment of different techniques for the same water sample and comparison with modelled values to give a consistent framework may give useful insight into the analytical windows of the techniques.

Zn

Model results (Fig. 2; Table 2) predict that Zn is weakly complexed. This is possibly due to underestimation of the organic binding by the model. The major inorganic species is the free ion (Table 2, column 6). There is a good correlation with experimental results, but poorer agreement stems from model predictions of weak organic binding relative to measurements. There is general consistency across the different datasets in the correlations with modelled free ion data. For the organically complexed Zn there is general agreement between all the measurements.

Cd

The model results show that Cd has a very low level of complexation with organic matter (Fig. 2; Table 2). Cd concentrations are generally correlated between the model predictions and measurements, but, as observed for Zn, weaker agreement stems from predictions of low levels of organic complexation. Inorganic Cd is almost entirely present as chloride complexes; therefore, a low fraction of the total inorganic metal is present as free ion. Amongst the different studies there is agreement between the Scarponi et al.^[39] and Ellwood et al.^[37] datasets, with less agreement with the Bruland^[2] data.

Pb

Reasonable agreement is seen for both datasets between the model calculated and measured values for both the organically bound and free ion concentrations, with few data falling outside the shaded area. There was a slight tendency for the model to underestimate the free ion compared to measurements, owing to higher levels of organic complexation predicted by the model compared to observations (Fig. 2; Table 2). There is also a general parallel trend of decreasing model predictions with decreasing measured values for the Scarponi et al.^[39] dataset. Model results predict that Pb has a high level of complexation with organic matter. Inorganic Pb is almost entirely present as chloride and carbonate complexes, therefore, a low fraction of

the total inorganic is present as free ion. It is worth noting that specific biological ligands are not generally invoked in the marine literature to explain the speciation of Pb.

General observations

For some datasets the model calculations show reasonable agreement with experimental measurements for both organically bound and free ion concentrations. This is the case for many data in the Cu dataset of Coale and Bruland^[34]; Fe datasets of Gerringa et al.,^[26] Boye et al.,^[24,25] plus agreement for some of the data in Boye et al.^[21]; and the majority of the data for Pb. Agreement for organic binding was observed for all data for Fe, Cu and Pb. For free ion data, Ni gives good agreement as does the Cd data of Bruland^[2] and Scarponi et al.^[39] Results for Fe, Cu and Pb support the idea that humic-type ligands can account for much of the observed results, i.e. humic-type ligands may exhibit the right type of affinity to get the observed free ion and organically bound concentrations. The weak correlation seen in some of the comparisons is not surprising given the generalised assumptions about the DOM and competing metal concentrations. Modelling results may be improved if site specific information was available for DOM and those trace metals that may exhibit competitive binding effects. The modelled fractions of inorganic metal present as free ion (Table 2, column 6) show only small variations, due to pH and salinity being relatively constant. Buffering of the samples in the experiments results in no or low pH variations between samples (i.e. low variation in the concentrations of ligands such as hydroxyl and carbonate groups). The larger variation in inorganic fractions for Cu is due to the lack of buffering in the experimental procedure and the resulting greater variations in inorganic speciation in the modelling.

Sensitivity to variations in metal concentrations and competition effects

Competition effects were examined using the model by altering estimates of other (un-measured) trace metals (see the methods section for the ranges used). Fig. 5 shows the results for Fe speciation in response to different scenarios for the concentrations of competing metals. To allow for easy comparison Fig. 5a repeats the results shown in Fig. 3. Where all competing metals are set at the upper estimates (Fig. 5b), the result is a large increase in competition for binding sites and a corresponding increase in the free ion concentrations of Fe. This occurs as a result of displacement from binding sites by competing ions. For the opposite scenario, where all trace metals are set at the lowest estimates (Fig. 5d) the result is a decrease in competition and thus greater binding of Fe resulting in decreased free ion concentrations. This scenario tends to give an improved model fit. Fig. 5c demonstrates that Cu is the most important competing metal controlling Fe free ion concentrations. In this scenario only Cu concentrations are lowered and the resulting predictions are only marginally different to those where all metals are considered. Given that the model gives a better fit under this scenario, model testing with data where dissolved Cu has been measured concurrently with Fe and Fe³⁺ would be beneficial.

Fig. 6 shows the effect that varying un-measured trace metals has on Cu speciation. Fig. 6a repeats the results shown in Fig. 4 to allow for easy comparison. An increase in the concentration of competing cations (Fig. 6b) results in only a small increase in the Cu free ion concentrations. Reducing the competing ion concentration to the lower estimates (Fig. 6d) or decreasing only the value for Fe (Fig. 6c) have similar effects, resulting in the Cu

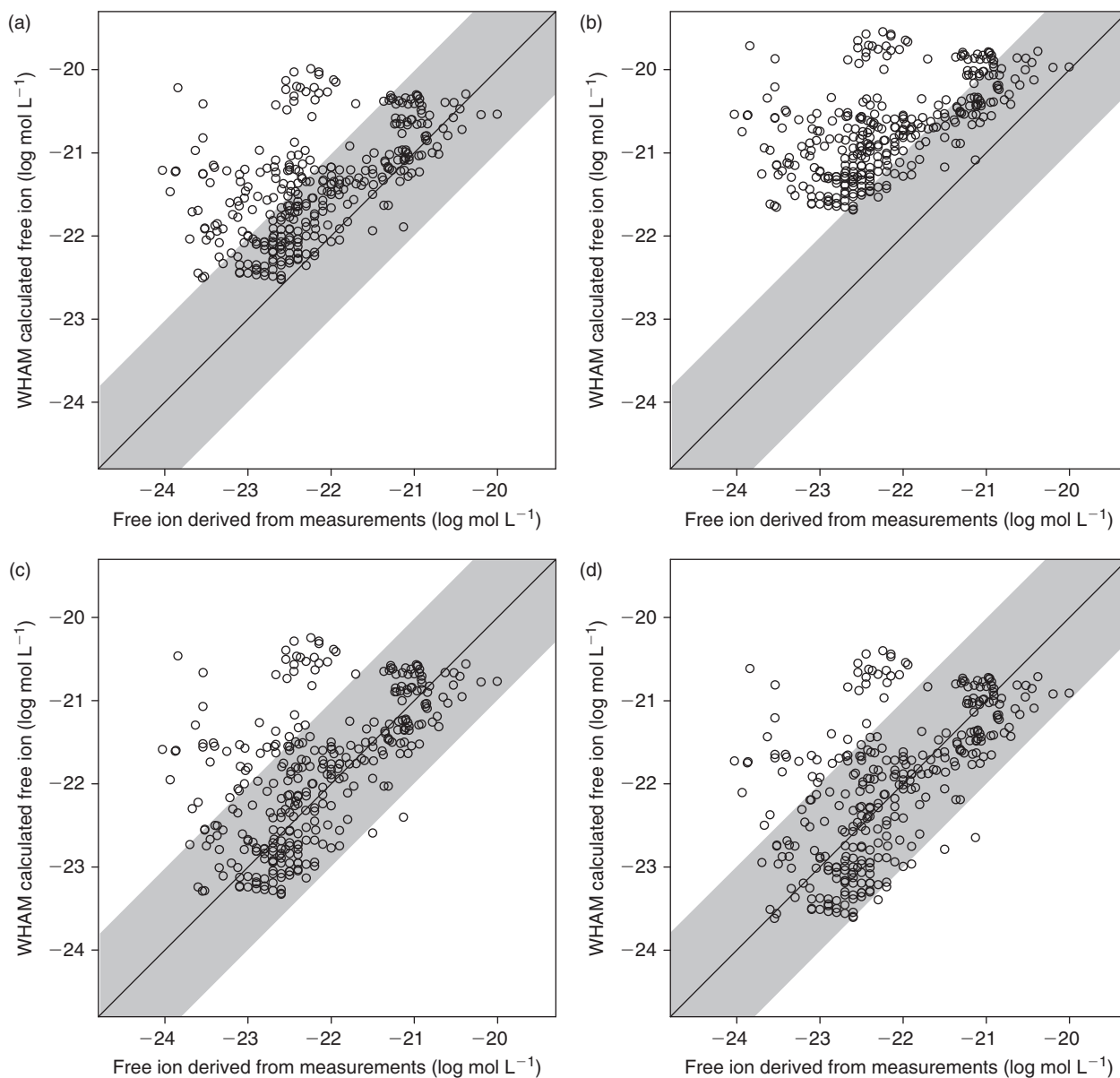


Fig. 5. Calculated competition effects exerted by trace metals affecting free ion concentrations of Fe^{III} . (a) Comparison of measured and modelled free ion concentrations using mid-range estimates for trace metal concentrations (the same data as Fig. 3). (b) Model results where upper estimates of trace metal concentration in the oceans are applied for all metals. (c) Model results where only Cu concentrations are lowered (from 2 to 0.5 nM). (d) Model results where all trace metals are lowered to the minimum estimates. See text for discussion. The solid line represents the 1 : 1 line and the shaded area represents one order of magnitude either side of the 1 : 1 line.

free ion concentrations decreasing slightly from the default scenario. This demonstrates that Cu speciation is most sensitive to competition effects exerted by Fe. However, given that Cu concentrations are typically greater than those of Fe (Table 2), the effect is not the same magnitude as the changes that are exerted by Cu on Fe speciation.

The response of Pb to varying competition is similar in magnitude to the variations observed for Fe. We have not included plots of competition effects on weakly binding metals, as there are no significant changes to the speciation (i.e. they are insignificantly bound under all scenarios).

These modelling results suggest that competition may be important in controlling the partitioning of strong-binding trace metals on organic matter in marine environments. This has

implications for our understanding on the limitations of trace elements for biological uptake. Furthermore, this highlights the importance of obtaining data for multiple analytes for the same location. The model has the capability to be used to design competition experiments to distinguish between specific and non-specific binding ligands, e.g. involving Cu and Fe or to eliminate the possibility of a Pb binding ligand. In terms of comparing modelled data with measurements the model could be used as a consistent benchmark for method testing.

Recently developed alternatives to CL-AdCSV, which have been deployed in marine systems, such as hollow fibre-permeable liquid membranes^[65] and Cu-electrodes^[66] need to be compared to determine the comparability of their respective detection windows.

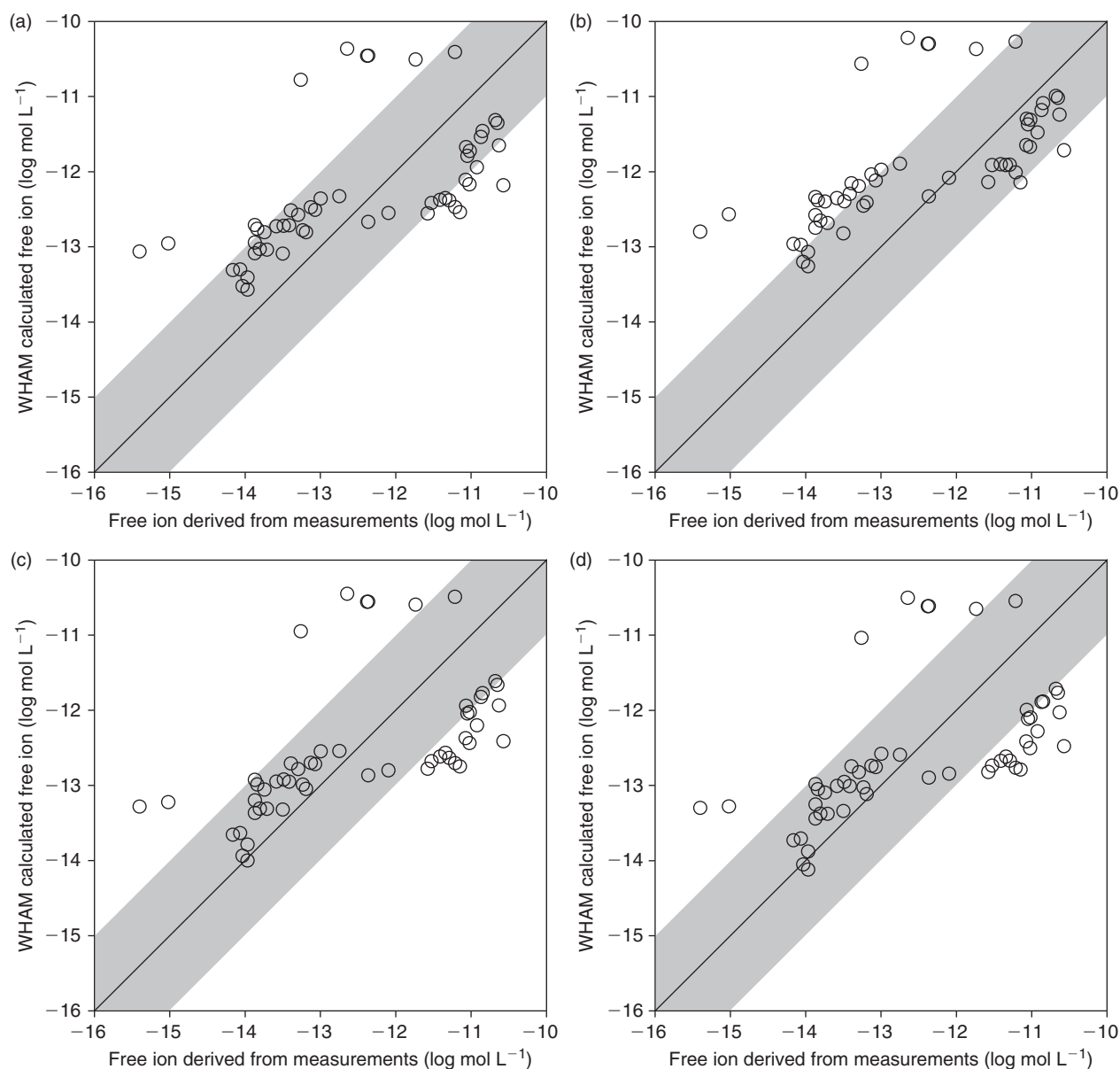


Fig. 6. Competition effects exerted by trace metals affecting free ion concentrations of copper. (a) Comparison of measured and modelled free ion concentrations using mid-range estimates for trace metal concentrations (the same data as the Cu panel in Fig. 2). (b) Model results where upper estimates of trace metal concentration in the oceans are applied for all metals. (c) Model results where only Fe concentrations are lowered (from 1 to 0.1 nM). (d) Model results where all trace metals are lowered to the minimum estimates. See text for discussion. The solid line represents the 1 : 1 line and the shaded area represents one order of magnitude either side of the 1 : 1 line.

Improving prediction of metal binding to humic-type ligands

Although model testing and applications will be most robust when complete input data are available, there is also a pressing need to investigate further the nature of marine DOM. Methods have been developed that allow discrimination of autochthonous and freshwater components of marine DOM.^[67] The chemical and metal-binding characteristics of marine organic matter are generally poorly defined. However, marine DOM has been reported as being approximately five times more enriched in nitrogen than their freshwater counterparts.^[20] As binding by amino functional groups has been statistically linked to the observed strong binding by humic substances,^[20] it would follow that metal-binding by DOM in the oceans may be

significantly greater than that predicted in the present study, i.e. with the default freshwater parameterisation.

Relating modelling results to the presence or absence of metal-specific ligands

In any marine system, humic-type DOM is present, and our predictions suggest that it is likely to be an important factor in metal complexation. If specific ligands were produced by marine organisms they would increase total complexation and reduce free ion concentrations further. The presence of specific ligands might explain cases where WHAM overestimates free ion concentrations, or underestimates bound metal. However, this cannot be concluded directly from the modelling results as WHAM is only an approximate model, and analytical data may

be subject to error. However, an outcome of this comparison is that the strongest evidence for possible specific ligands arises from the weak-binding metals, rather than the strong-binding ones. If WHAM underestimates free ion, then there is no evidence for specific ligands.

Conclusions

We have shown that in several cases speciation of trace metals in seawater environments may be reasonably predicted using the speciation model WHAM VI and the parameters provided in the default database. Any agreement with measurements is achieved without fitting any model parameters to the data. The results support the idea that humic-type ligands can account for observed organic binding in some cases and future marine metal speciation studies should consider the non-specific binding by bulk marine DOM when interpreting data. Although the model does not consistently provide agreement with the measured values it provides a useful benchmark to compare different datasets and to examine variation in speciation as a result of varying levels of competing metal ion and marine DOM concentration and the active fractions of marine DOM. Future work could employ the model to examine how changes in pH, temperature and dissolved carbonate concentrations induced by ocean acidification may affect the chemical speciation of essential cationic trace nutrients in marine systems.

The availability of data is important, there is an urgent need to measure DOM alongside multiple trace metals and to improve our understanding of marine DOM composition. The modelling presented here has also highlighted that of particular importance is the measurement of potentially competing metals such as Cu in the case of predicting Fe speciation.

Accessory publication

Tables of DOC estimates and a figure of side reaction coefficient comparisons, are available as Accessory Materials from the publishers website at http://www.publish.csiro.au/?act=view_file&file_id=EN11004_AC.pdf.

Acknowledgements

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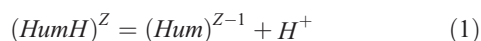
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Appendix

Description of Humic Ion Binding Model VI

Fulvic and humic acids are assumed to be rigid spheres of uniform size. From typical measured weight-average molecular weights (1500 for FA, 15 000 for HA), and assuming an effective density (humic matter plus included solvent) of 1.2 g cm^{-3} , the radii of the molecules are calculated to be 0.8 (FA) or 1.72 nm (HA). Ion-binding groups are positioned randomly on the molecular surfaces. Proton dissociation is represented by postulating 8 groups with different acid strengths. The dissociation reaction can be written generally as;



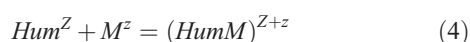
where *Hum* represents the humic molecule, and *Z* is the net charge. The reactions are characterised by intrinsic (i.e. separated from non-specific electrostatic effects: see below) equilibrium constants, the negative logarithms of which are denoted by $\text{p}K_1$ – $\text{p}K_8$. The four most strongly-acid groups (groups 1–4) are referred to as type A groups, and consist mainly of carboxylic acid groups, whereas the remaining 4 groups (type B) represent weaker acids, such as phenolic acids. The 8 $\text{p}K_i$ values are expressed in terms of 4 constants ($\text{p}K_A$, $\text{p}K_B$, $\Delta\text{p}K_A$ and $\Delta\text{p}K_B$) as follows:

$$\text{p}K_i = \text{p}K_A + \frac{(2i-5)}{6} \Delta\text{p}K_A \text{ for } i = 1-4 \quad (2)$$

$$\text{p}K_i = \text{p}K_B + \frac{(2i-13)}{6} \Delta\text{p}K_B \text{ for } i = 5-8 \quad (3)$$

Thus the values of $\text{p}K_A$ and $\text{p}K_B$ are the average $\text{p}K$ values of the two types of group, whereas $\Delta\text{p}K_A$ and $\Delta\text{p}K_B$ are measures of the spread of the individual $\text{p}K_i$ values around the means. Positive values of $\Delta\text{p}K_A$ and $\Delta\text{p}K_B$ mean that the $\text{p}K_i$ values increase as *i* increases, i.e. the groups become progressively weaker acids. Each type A group is assigned an abundance of $n_A/4 \text{ mol g}^{-1}$ humic matter, and each type B group an abundance of $n_A/8 \text{ mol g}^{-1}$. Thus, within a type, each group is present in equal amounts, and there are half as many type B groups as type A groups. The imposed regularity of the groups facilitates the formulation of the multidentate binding sites for metals.

Metal ions, and their first hydrolysis products (e.g. FeOH^{2+} in the case of Fe^{3+}), compete with each other, and with protons, for the type A and type B groups. Monodentate binding takes place according to the general reaction:



The equilibrium constants sites are given by:

$$\log K(i) = \log K_{MA} + \frac{(2i-5)}{6} \Delta\text{LK}_{A1} \text{ for sites } 1-4 \quad (5)$$

$$\log K(i) = \log K_{MB} + \frac{(2i-13)}{6} \Delta\text{LK}_{B1} \text{ for sites } 5-8 \quad (6)$$

where ΔLK_{A1} and ΔLK_{B1} are constants estimated from data fitting. Thus the values of $\log K_{MA,i}$ are evenly spaced around the mean of $\log K_{MA}$ but the spacing is not necessarily the same

as that for protons, i.e. in general ΔLK_1 is not equal to $\Delta\text{p}K_A$. The same applies to the type B sites.

For a bidentate site comprising single sites *j* and *k*, the association constant $K(j, k)$ is given by:

$$\log K(j, k) = \log K(j) + \log K(k) + x\Delta\text{LK}_2 \quad (7)$$

where ΔLK_2 is an adjustable parameter. The value of *x* is 0 for 90.1% of the sites, 1 for 9%, and 2 for 0.9%. This generates heterogeneity, with a small number of strong sites, a larger number of moderately strong ones, and a majority of weak ones. Analogous rules are used for the tridentate sites, made up of single sites *l*, *m* and *n*:

$$\log K(l, m, n) = \log K(l) + \log K(m) + \log K(n) + y\Delta\text{LK}_2 \quad (8)$$

Here, *y* is 0, 1.5 or 3 for the 90.1, 9 and 0.9% abundances respectively. Each metal ion has a characteristic ΔLK_2 .

The fractions of single sites that contribute to the bidentate or tridentate sites are determined statistically based on geometry, by assuming the proton sites to be randomly positioned on the surfaces of the (spherical) molecules. Pairs of groups are considered to form bidentate sites, or triplets to form tridentate sites, if they are less than or equal to 0.45 nm apart. The fraction of sites forming bidentate sites is denoted by f_{prB} , that for tridentates is f_{prT} . For fulvic acid, $f_{prB} = 0.42$, $f_{prT} = 0.03$, whereas for humic acid, the corresponding values are 0.50 and 0.065. The bidentate and tridentate sites are fixed entities; with respect to metal binding, they are unable to revert to monodentate behaviour under any circumstances.

If all combinations of proton sites are allowed, 36 different bidentate sites and 120 different tridentate sites can form, for each of which there are three binding strengths, if ΔLK_2 is non-zero. Together with the eight monodentate sites therefore, there could be 476 different sites in all. The abundances of these sites depend on their composition, in terms of type A and type B sites, the latter being present at half the total abundance of the former. For example, tridentate sites comprising three type A proton sites are eight times more abundant than those comprising three type B sites. To avoid over-complication, and to speed computations, a sub-set of sites is used in the model, whereas maintaining the relative proportions of the contributing proton sites. To do this, bidentate or tridentate sites are allowed to consist only of different proton sites, and only 24 representative combinations are adopted. The 24 allowed combinations lead to 72 different sites, because of the heterogeneity terms (Eqns 7, 8). With the addition of the 8 monodentate sites, there are 80 different sites in all.

The intrinsic equilibrium constants are modified by empirical electrostatic terms, that take into account the attractive or repulsive interactions between ions and the charged macromolecule. The overall accumulation of counterions is described with a simple Donnan sub-model.

In Model VI, the maximum number of parameters that can be optimised to describe proton dissociation is six (K_{MA} , K_{MB} , ΔLK_{A1} , ΔLK_{B1} , ΔLK_2 and K_{sel} ; an adjustable selectivity coefficient). In practice however, this number can be substantially reduced. Thus, Tipping^[11] described the setting of a single universal value for ΔLK_{A1} and ΔLK_{B1} , and the estimation of ΔLK_2 by correlation with the equilibrium constant for complex formation with NH_3 . For dilute systems where non-specific

Table A1. Model VI parameters used in this work

Parameter	HA	FA	Comments	How derived		
M	15 000	1500	Molecular weight	Estimated from literature		
r (nm)	1.72	0.80	Radius	Estimated from literature		
n_A (mol g ⁻¹)	3.3×10^{-3}	4.8×10^{-3}	Abundance of type A groups	Fitted		
n_B (mol g ⁻¹)	1.65×10^{-3}	2.4×10^{-3}	Abundance of type B groups	Set to be equal to: $0.5 \times n_A$		
pK_A	4.1	3.2	Median proton dissociation constant for type A groups	Fitted		
pK_B	8.8	9.4	Median proton dissociation constant for type B groups	Fitted		
ΔpK_A	2.1	3.3	Range factor for pK_A	Fitted		
ΔpK_B	3.6	4.9	Range factor for pK_B	Fitted		
P	-330	-115	Electrostatic parameter	Fitted		
f_{prB}	0.50	0.42	Proximity factor for bidentate sites	Calculated from geometry		
f_{prT}	0.065	0.03	Proximity factor for tridentate sites	Calculated from geometry		
ΔLK_1	2.8	2.8	Range factor for metal binding	Fitted		
$\log K_{MA}$						
Mg	0.7	1.1	Intrinsic equilibrium constants for monodentate binding at type A sites. Values for type B sites are obtained from the relation: $\log K_{MB} = 3.39 \log K_{MA} - 1.15$ ($R^2 = 0.80$)	Fitted		
Al	2.6	2.5				
Ca	0.7	1.3				
Mn	0.6	1.7				
Fe ^{III}	2.5	2.4				
Co	1.1	1.4				
Ni	1.1	1.4				
Cu	2	2.1				
Zn	1.5	1.6				
Cd	1.3	1.6				
Hg	3.5	3.5				
Pb	2	2.2				
ΔLK_2						
Mg	0.12	0.12			Strong binding site term, obtained from the relation: $\Delta LK_2 = 0.58 \log K_{NH_3}$ ($R^2 = 0.66$), where K_{NH_3} is the equilibrium constant for complexation with NH_3	Based on thermodynamic data
Al	0.46	0.46				
Ca	0	0				
Mn	0.58	0.58				
Fe ^{III}	2.2	2.2				
Co	1.22	1.22				
Ni	1.57	1.57				
Cu	2.34	2.34				
Zn	1.28	1.28				
Cd	1.48	1.48				
Hg	5.1	5.1				
Pb	0.93	0.93				

cation exchange is not significant (i.e. non-soil systems), K_{sel} can be set to unity. Table A1 shows the values of the Model VI parameters used in the present work, these represent the default values for Model VI. The ‘how derived’ column details how each of the parameters was derived and is extracted from the cited literature. It is important to note that the values of $\log K_{MA}$ for all the metals except Fe^{III} have been derived by fitting

experimental data; the values for Fe^{III} are from linear free energy relationships.^[11] High values of $\log K_{MA}$ mean that the metal is strongly bound at the high-abundance ‘weak’ sites. High values of ΔLK_2 mean that the metal is favoured by the low-abundance ‘strong’ sites, associated with nitrogen groups; if ΔLK_2 is small, the strong sites are not favoured, and binding is predominantly due to binding at oxygen-containing sites.