



Article (refereed) - postprint

Tipping, E.; Lofts, S.; Sonke, J.E.. 2011. **Humic Ion-Binding Model VII: a revised parameterisation of cation-binding by humic substances.** *Environmental Chemistry*, 8 (3). 225-235. [10.1071/EN11016](https://doi.org/10.1071/EN11016)

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Submitted to Environmental Chemistry Special Issue on Chemical Speciation, February 2011

Revised 16 March 2011

Humic Ion-Binding Model VII: a revised parameterisation of cation-binding by humic substances

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28 **Environmental context**

29 Natural organic matter exerts a powerful control on chemical conditions in waters and soils,
30 affecting pH and influencing the biological availability, transport and retention of metals. To
31 quantify the reactions, we collated a wealth of laboratory data covering 40 metals and acid-
32 base reactions, and used them to parameterise the latest in a series of Humic Ion-Binding
33 Models. Model VII is now available to interpret field data, and contribute to the prediction of
34 environmental chemistry.

35

Abstract

Humic Ion-Binding Model VII aims to predict the competitive reactions of protons and metals with natural organic matter in soils and waters, based on laboratory results with isolated humic and fulvic acids (HA and FA). Model VII is simpler in its postulated multidentate metal binding sites than the previous Model VI. Three model parameters were eliminated by using a formal relationship between monodentate binding to strong- and weak-acid oxygen-containing ligands, and removing factors that provide ranges of ligand binding strengths. Thus Model VII uses a single adjustable parameter, the equilibrium constant for monodentate binding to strong-acid (carboxylate) groups (K_{MA}), for each metallic cation. Proton-binding parameters, and mean values of $\log K_{MA}$ were derived by fitting 248 published datasets (28 for protons, 220 for cationic metals). Default values of $\log K_{MA}$ for FA were obtained by combining the fitted values for FA, results for HA, and the relationship for different metals between $\log K_{MA}$ and equilibrium constants for simple oxygen-containing ligands. The equivalent approach was used for HA. The parameterised model improves on Model VI by incorporating more metals (40), providing better descriptions of metal binding at higher pH, and through more internally-consistent parameter values.

Introduction

The Windermere Humic Aqueous Model (WHAM)^[1,2] incorporating Humic Ion-Binding Model V^[3] or VI^[4] permits the calculation of equilibrium chemical speciation for waters and soils in which natural organic matter plays a significant role. The ion-binding models are based on conventional chemical reactions involving O-containing weak acids, with empirical estimation of the influence of soft ligand atoms (N, S) and electrostatic corrections, and are parameterised from laboratory studies with isolated humic and fulvic acids. The NICA model^[5] is similarly parameterised and provides an alternative picture based on continuous binding-site distributions. Tipping^[2] identified both the Humic Ion-Binding Models and NICA as comprehensive models, meaning that they deal with competitive interactions involving all cations (including H⁺), and take account of ionic strength effects and metal-proton exchange ratios. They seek to represent cation-binding by the complex mixtures that comprise natural organic matter as efficiently as possible, with the minimum number of parameters, in order to be useful in addressing chemical processes in the environment. A different approach to these parameterised models, but also potentially comprehensive, is the “forward modelling” developed by Cabaniss^[6] in which binding is calculated *a priori* from the known or assumed distributed chemistry of humic substances.

WHAM has been applied in a variety of research and regulatory areas. Examples include the acidification of soils^[7-14] and surface waters^[15], trace metal behaviour in soils^[16-22], surface waters^[23-31] and groundwaters^[32], lake sediment diagenesis^[33,34], rare earth geochemistry^[35-37], iron and manganese geochemistry^[38-41], radionuclide geochemistry^[42-45], organic matter solubility in soils^[46,47], catchment modelling^[48,49], interactions of metals with biota^[50,51], ecotoxicology^[52-59] and Critical Loads^[60-62]. Given this evident utility, it is worthwhile to continue to improve the humic ion-binding model and incorporate new data into its parameterisation. Here we report on activities undertaken towards these goals, namely modification of assumptions about multidentate binding, the fitting of new data, and the introduction of a procedure to obtain more internally-consistent parameters.

Changes in binding site formulation were prompted by experience in applying Model VI to new data for the binding of lanthanides, Co and UO₂ by humic and fulvic acids^[63,64]. It became apparent that too strong a pH dependence was predicted by the model at higher pH values, which could be attributed to assumed multidentate sites involving more than one weak-acid ligand (e.g. phenolic oxygen). Therefore we modified the formulation of the array of assumed binding sites, to create Humic Ion-Binding Model VII.

Humic Ion-Binding Model VI is parameterised with data for the interactions of cationic metals with isolated humic substances that were available in the late 1990s. Since then, the number

of data sets suitable for parameterisation has approximately doubled, with new results notably available for protons, Al, Sc, Cr, Co, Ni, Cu, Zn, Y, Ag, Cd, Hg, MeHg, Pb, UO₂ and the lanthanides. All available data sets were fitted with Model VII to obtain binding parameters.

In past work^[2,4] linear free energy relationships (LFERs) were derived to relate model parameters for metal binding to conventional equilibrium constants for simple ligands, and the LFERs were used in some cases to estimate parameters in cases where measured data were not available. We extended this approach, making use of the study of Carbonaro & DiToro^[65] who showed how the Irving-Rossotti^[66] approach could be brought to bear to regularise equilibrium constants.

Modelling

WHAM

The original version of WHAM was simply a combination of a humic ion-binding model (see below) with an inorganic speciation model^[1]. The latter deals with reactions among the inorganic master species (protons, metal cations, hydroxyl ion, carbonate and phosphate species, sulphate, fluoride, chloride). Ionic strength effects on the inorganic reactions are taken into account using the extended Debye-Hückel equation. Temperature effects on reactions between inorganic species are taken into account using published or estimated enthalpy data; in the absence of experimental information, reactions involving humic substances are assumed to be independent of temperature. A given speciation problem is solved by finding the activities of all the master species at equilibrium, using a combination of algorithms. Inputs to the model are the total concentrations of reactants, as would be obtained by chemical analysis. The model can work with a specified pH, or calculate the pH if the necessary input data are available. The software package currently associated with the model is WHAM6.0 (http://windermere.ceh.ac.uk/Aquatic_Processes/wham/). It includes the Humic Ion-Binding Model VI and the inorganic model, together with further sub-models for the binding of cations to the oxides of Al, Si, Mn and Fe, and to a simple cation-exchanger.

Humic Ion-Binding Model VI

Humic Ion-Binding Model VI is the most important component of WHAM, describing the interactions of protons and metals with natural organic matter. The model was described in detail by Tipping^[4]. It 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.

Proton dissociation is represented by postulating 8 groups with different acid strengths, the reactions being characterised by intrinsic equilibrium constants, the negative logarithms of which are denoted by $pK_1 - pK_8$. The four most strongly-acid groups (groups 1-4) are referred to as type A groups, and consist mainly of carboxylic acid groups, while the remaining 4 groups (type B) represent weaker acids, such as phenolic acids. The 8 pK_i values are expressed in terms of 4 constants; pK_A and pK_B are the average pK values of the two types of group, and ΔpK_A and ΔpK_B are measures of the spread of the individual pK_i values around the means. Each type A group is assigned an abundance of $n_A/4$ mol g^{-1} humic matter, and each type B group an abundance of $n_A/8$ 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 bidentate and tridentate sites for metals (Table 1).

Metal binding at the type A and B sites is described with average intrinsic equilibrium constants (K_{MA} , K_{MB}) and associated “spread factors” ΔLK_{A1} and ΔLK_{B1} . Thus K_{MA} is the average equilibrium constant for the binding of a metal to a type A (carboxylate) group. The occurrence of bidentate and tridentate sites at the surface of the humic acid or fulvic acid molecule is calculated probabilistically. Additional binding site heterogeneity is generated by a parameter, ΔLK_2 , that characterises the tendency of the metal to interact with “softer” ligand atoms such as N and S. Thus, 9% of the bidentate sites have the logarithms of their binding constants increased by ΔLK_2 , while 0.9% have increases of $2\Delta LK_2$. For the tridentate sites, the respective increases are $1.5\Delta LK_2$ and $3\Delta LK_2$. In the standard model, all metal cations (e.g. Al^{3+} , Cu^{2+} , Hg^{2+}) and their first hydrolysis products ($AlOH^{2+}$, $CuOH^+$, $HgOH^+$) compete with each other, and with protons, for binding. The combination of multi-denticity and the increased binding strength of some sites, due to ΔLK_2 , generates many binding sites with a wide range of affinities. The most abundant (monodentate) sites are the weakest binders, while the least abundant (tridentate sites enhanced by $3\Delta LK_2$) are the strongest.

The intrinsic equilibrium constants are modified by empirical electrostatic terms, incorporating the electrostatic parameter P , that take into account the attractive or repulsive interactions between ions and the charged macromolecule. A Donnan sub-model is used to compute counterion accumulation in the diffuse zone around the molecule; each counterion can be assigned a selectivity coefficient (K_{sel}), so that accumulation can be made to depend on more than just the counterion charge; for example, Ca^{2+} can be favoured over Mg^{2+} . The selectivity coefficients are only used in soil applications where exchanges of major cations on solid-phase organic matter are important.

The maximum number of parameters that can be optimised to describe metal binding is six (K_{MA} , K_{MB} , ΔLK_{A1} , ΔLK_{B1} , ΔLK_2 , K_{sel}). In practice however, this number can be substantially reduced. Thus, Tipping^[4] described the setting of a single universal value for ΔLK_{A1} and ΔLK_{B1} , and the estimation of ΔLK_2 by correlation with the logarithm of the equilibrium constant for complex formation with NH_3 ($\log K_{NH3}$) according to the equation;

$$\Delta LK_2 = 0.58 \log K_{NH3} \quad (1)$$

For dilute systems, as in laboratory experiments, K_{sel} can be set to unity. Finally, K_{MA} and K_{MB} are strongly correlated. Therefore, the fitting of a new data set can be achieved by adjusting only K_{MA} , which was the approach taken in the present work. High values of 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, according to the model, with N or S atoms. If ΔLK_2 is small, the strong sites are not favoured, and binding is predominantly due to binding at oxygen-containing sites.

During the course of developing Model VII from Model VI, we discovered a coding error in Model VI which means that the parameters ΔLK_{A1} and ΔLK_{B1} were not used as originally intended, and this means that Model VI was actually different from that described by Tipping^[4]. This error, which is described in full in the Accessory Material, did not invalidate Model VI as used with code written by ourselves, since fitting and model applications were performed consistently. As reported below, ΔLK_{A1} and ΔLK_{B1} are entirely absent from Model VII.

Humic Ion-Binding Model VII

Model VII is identical to VI with respect to its formulation of total monodentate binding sites, proton binding constants and electrostatic effects. It differs from Model VI with respect to metal cation binding, in that the arrangement of multidentate sites has been modified, and some parameters eliminated.

In Model VI there can be four parameters that describe monodentate metal binding, namely $\log K_{MA}$, $\log K_{MB}$, ΔLK_{A1} and ΔLK_{B1} . Tipping^[2] noted that the relationship between $\log K_{MB}$ and $\log K_{MA}$, i.e. mean equilibrium constants for binding to weaker and stronger acid sites, was roughly as expected on the basis of data for simple ligands, i.e. binding of a given metal (also the proton) to weak-acid groups such as phenolic OH groups is consistently stronger than to carboxylate groups. The work of Carbonaro & Di Toro^[65] showed this much more generally, and demonstrated that relative binding strengths of a given metal to different oxygen-containing ligands are interrelated. Therefore we defined $\log K_{MB}$ formally by the equation;

$$\log K_{MB} = \log K_{MA} \times (pK_B / pK_A) \quad (2)$$

In other words, the relative binding strengths for a given metal are the same as those for the proton. We attempted to apply this idea also to the spread factors ΔLK_{A1} and ΔLK_{B1} , i.e. to predict them from $\Delta pK_{H,A}$ and $\Delta pK_{H,B}$. However, when fitting the data for metal binding, we found that the spread factors could be entirely eliminated, i.e. it was preferable to fix $\log K_{MA}$ at the same value for each of the four type A sites, and $\log K_{MB}$ at the same value for each of the four type B sites.

Multi-dentate sites are formed in the model by combining mono-dentate (proton-binding) sites, but the choice of combinations has been found to be important. When fitting new data for Co, lanthanides and UO_2 with Model VI, we found overestimation of the pH dependence of binding at $pH > 7$. Examination of model outputs revealed that this was due to the assumed presence in humic matter of binding sites containing 2 or 3 weak-acid (type B) groups. Therefore multidentate sites containing more than one type B group are omitted from Model VII.

205 *Data sets*

206 The number of data sets available to calibrate Model VII was approximately twice as many
207 as for Model VI. For protons, we used 15 data sets for HA (4313 data points in all) and 13
208 for FA (4334 data); several of the sets previously used for Model VI were abandoned
209 because they were incomplete. A total of 107 data sets were available to quantify the
210 binding of 36 different cationic metals by HA (4420 data) and 108 data sets for the binding of
211 34 different metals by FA (4004 data). The grand total of data points was 17,116. Most of
212 the previous metal data sets used by Tipping^[4] were retained, and augmented with additional
213 data sets obtained from the collation of Milne and colleagues^[67,68], and by searching the
214 literature. The data sources are summarised in the Accessory Material.

215 *Data fitting*

216 The model was coded in BASIC, and the Nelder-Mead polytope method used for function
217 minimisation and parameter estimation. Since the previous fitting of proton binding data, a
218 significant number of new studies have been published. The availability of these extra data
219 made it possible to apply stronger acceptability criteria, with the objective of selecting data
220 best suited to provide robust estimates of the proton binding parameters. The criteria were
221 (a) the pH range of the data set had to extend above pH 10, in order to obtain good
222 estimates of the weak acid site binding parameters $pK_{H,B}$ and $\Delta pK_{H,B}$, and (b) each data set
223 had to refer to several ionic strengths, so that a value of the ionic strength dependency
224 parameter P could be calculated for each data set. Fitting involved the optimisation of six
225 parameters, namely the strong acid site density (n_A), the average strong and weak acid
226 binding site pK values ($pK_{H,A}$ and $pK_{H,B}$), the factors giving the spread of pK values around
227 the averages ($\Delta pK_{H,A}$ and $\Delta pK_{H,B}$), and the electrostatic factor P . We found that when fitting
228 individual data sets, adjustment of all the parameters simultaneously produced values that
229 were sometimes physically unreasonable. Therefore we adopted a two stage fitting process.
230 Firstly, $\Delta pK_{H,A}$ and $\Delta pK_{H,B}$ were fixed at the values derived by Tipping^[4], and all the data sets
231 were fitted individually to obtain values of the remaining four parameters, and an overall
232 goodness-of-fit parameter (sum of all squared deviations in HA or FA charge, Z), calculated
233 from all the data sets. Then the spread factors were adjusted and the process repeated
234 iteratively to minimise the goodness-of-fit parameter.

235 Metal binding data were fitted by optimising $\log K_{MA}$, using the default parameters obtained
236 from proton-binding data, and with ΔLK_2 obtained from equation (1). In the great majority of
237 cases, optimisation was done by minimising squared errors in $\log v$, where v is the moles of
238 metal bound per gram of humic matter. In a few cases, the effects of metal binding on
239 measured pH were modelled, and optimisation performed by minimising squared errors in

pH. To establish the new arrangement of multidentate sites, we forced a uniform representation of the monodentate sites, while keeping the system as simple as possible. All data sets were fitted with a number of trial multidentate arrangements and universal values of ΔLK_{A1} and ΔLK_{B1} (i.e. the same values for all data sets). The best arrangement of sites (Table 1) requires 50 different binding sites rather than the 80 sites of Model VI. Overall fitting was no worse if ΔLK_{A1} and ΔLK_{B1} were both set to zero, enabling these parameters to be eliminated. Thus, for dilute systems, Model VII has only two formal parameters for each cationic metal, namely $\log K_{MA}$ and ΔLK_2 , as opposed to the potential five in Model VI (although this number could be reduced to three in practice).

Results

Default parameter values for proton binding and ionic strength dependence were calculated as the means of the values obtained from each individual data set. New and previous parameter values are compared in Table 2, while Figure 1 compares calculated humic and fulvic net charge as a function of pH for the two parameter sets.

Mean values of $\log K_{MA}$ for the different metals are shown in the fourth and fifth columns of Table 3. The average root-mean-squared deviation in $\log v$ was 0.21 for HA and 0.23 for FA, and overall the fits with Model VII were marginally better than those with Model VI. Figure 2 shows how Model VII performs better than Model VI for lanthanum.

We applied the approach and findings of Carbonaro & Di Toro^[65] to analyse the Model VII results, by plotting $\log K_{MA}$ against α_O , the slope of the equation of Irving & Rossotti^[66] for ligands with oxygen donor atoms. Results for HA and FA (Figure 3) show reasonable correlations between $\log K_{MA}$ and α_O , indicating that HA and FA behave approximately as expected from simpler ligands with respect to binding at the major oxygen-containing ligand sites. A plot of $\log K_{MA,HA}$ against $\log K_{MA,FA}$ (Figure 4) falls close to the expected line, which has a slope of 1.11 on the basis of the pK_A values for HA and FA, which are 4.1 and 3.7 respectively. Thus $\log K_{MA,HA}$ for each metal is expected to be greater than $K_{MA,FA}$ by a factor of 1.11. The mean ratio ($\log K_{MA,HA} / \log K_{MA,FA}$) for the 33 metals with constants for both HA and FA was 1.09, supporting this expectation.

We used these results to improve estimates of $\log K_{MA}$, and thereby reduce the possibility of excessive outliers. To derive the default constant for the binding of a given metal to FA we applied the equation;

$$\log K_{MA,FA,def} = \{n_{FA}\log K_{MA,FA,mean} + (n_{HA}\log K_{MA,HA,mean}/1.11) + (3.81\alpha_O+0.37)\} / (n_{FA}+n_{HA}+1) \quad (3)$$

where n_{FA} and n_{HA} are the numbers of datasets for FA and HA yielding estimates of the parameter $\log K_{MA}$, and $\log K_{MA,FA,mean}$ and $\log K_{MA,HA,mean}$ are the mean values obtained from fitting. Thus, we first weight the mean $\log K_{MA}$ value for FA. Second we weight the results for HA, taking into account that the average $\log K_{MA}$ for HA is 1.11 times the value for FA (Figure 4). Then we add a prediction of $\log K_{MA}$ using the equation from Figure 3. Finally the overall weighted mean is taken. For HA, the same approach leads to

$$\log K_{MA,HA,def} = \{n_{HA}\log K_{MA,HA,mean} + 1.11n_{FA}\log K_{MA,FA,mean} + (3.51\alpha_O+0.74)\} / (n_{HA}+n_{FA}+1) \quad (4)$$

Consequently the default parameters are more internally consistent. In a number of cases there is no available value of α_O , while for three cations (Be^{2+} , Fe^{2+} and Ba^{2+}) there is a value of α_O but there are no data for humic substances. The equations can still be applied under

either circumstance, but omitting the missing values. The seventh and eighth columns of Table 3 show the derived default $\log K_{MA}$ values for 40 metallic cations.

Comparisons of outputs from Models VI and VII

Differences between the models with respect to multidentate binding site arrangements and proton binding parameters generally lead to somewhat larger values of $\log K_{MA}$, especially for HA (Table 4). Differences will also have arisen from the use of additional data, and the new procedure for deriving default constants. The best-defined values of $\log K_{MA}$ are those of Cu, for which $\log K_{MA}$ for Model VII exceeds the Model VI value by 0.4 for HA but only 0.1 for FA; these differences can be used as references to compare metals between models (Table 4). Thus, for HA the differences in $\log K_{MA}$ between Models VII and VI are largest for Cr(III), Mn, Fe(III), Ba, Eu and Th, while for FA, those for Cr(III), Fe(III), Ba and Th are relatively large. Only for Ca binding by FA is the difference in $\log K_{MA}$ appreciably smaller than that for Cu.

Further comparisons can be made from calculated binding isotherms, examples of which are presented in Figure 5. For both HA and FA, Model VII predicts weaker binding of Al at high pH, because of the removal of binding sites containing two or three type B (weak acid) groups. A similar effect is seen for Eu, except that Model VII predicts stronger binding at low pH, but weaker at pH 8; Am and Cm also behaved like this. There is little change in the prediction of copper binding by either HA or FA. Zinc binding hardly differs between the models for HA, while Model VII predicts slightly stronger binding for FA, due to the new procedure for estimating default values of $\log K_{MA}$.

The new Model VII parameterisation leads to changes in predicted competition effects. Due to the complexity of competition reactions, and the large number of potential combinations of metals, generalised analysis of the results is not possible. However, some illustrative examples are given in Figure 6 of the effects on Cu and Zn binding of Mg, Al and Ca, three important competitors in typical soils and waters. The predictions of the two models do not differ very much for Al; only for Cu binding by HA is there a noticeable change, with weaker competition leading to lower concentrations of Cu^{2+} . In the case of HA, competition by both Mg and Ca for both Cu and Zn is calculated to be considerably stronger when Model VII is applied, reflecting higher $\log K_{MA}$ values for the alkaline earths. For FA, competition by Mg and Ca is weaker towards Zn, but stronger towards Cu.

Discussion

Because Models VI and VII are identical with respect to the six parameters (n_A , P , pK_A , pK_B , ΔpK_A and ΔpK_B) that together describe total binding site density, electrostatic effects and proton binding affinity, the new parameter values (Table 2) reflect the use of new more extensive data on proton dissociation from humic substances, especially for HA. The main differences are that, in comparison with Model VI, the Model VII HA and FA have slightly higher site densities, the FA type A groups are weaker acids, the HA type B groups are stronger acids, and the HA electrostatic factor is smaller. These led to the differences in calculated proton dissociation as a function of pH shown in Figure 1.

With regard to metal binding, Model VII is appreciably simpler than Model VI, having fewer combinations of monodentate sites to make multidentate sites (Table 1), a formalised relationship between $\log K_{MA}$ and $\log K_{MB}$ (equation 2), and with the spread factors (ΔLK_{A1} and ΔLK_{B1}) set to zero. There is an apparent inconsistency in that the model requires the equilibrium constants for metal-binding not to vary within the type A and B groups, but to differ between the type A and B groups. Full application of the model of Carbonaro & Di Toro^[65] would mean that ΔLK_{A1} and ΔLK_{B1} were non-zero, proportional to ΔpK_A and ΔpK_B respectively. However, we obtained appreciably better fits if such parallelism was not invoked. Inspection of the Carbonaro-Di Toro plots of $\log K_{ML}$ vs $\log \log K_{HL}$ shows that in several cases there is a lower local slope in the range of carboxylate groups ($3 < \log K_{HL} < 5$) indicating less relative variation in the $\log K_{ML}$ values than in $\log K_{HL}$, and so setting ΔLK_{A1} to zero is perhaps defensible. There are insufficient data to judge this for higher $\log K_{ML}$, $\log K_{HL}$, and ΔLK_{A2} . The values of $\log K_{MA}$ can be considered chemically reasonable in that they are similar to equilibrium constants for the equivalent reaction of metallic cations with simple carboxylate ligands such as lactic acid, as demonstrated for Model VI^[4]. But it is perhaps worth re-emphasising that $\log K_{MA}$ values *per se* do not describe binding to humic substances; rather, they predict binding to weak-acid groups (via equation 2), and are the basis for the appreciably greater constants that apply to multidentate sites, which can be further increased due to soft-ligand effects (equation 1).

Default Model VI parameters for different metallic cations were derived simply by taking the averages of the calibrated values of $\log K_{MA}$, a procedure which implies that samples of humic substances used in laboratory experiments have been taken from a range of different materials in the field, so that the average $\log K_{MA}$ is the best overall estimate, and the range of possible values can be characterised by the standard deviation of the $\log K_{MA}$ values. This is satisfactory when a reasonable number of different data sets can be analysed, but may produce an unrepresentative $\log K_{MA}$ if data for the metal in question come from only one or

two data sets. The new method of establishing default constants presented here (equations 3 and 4) makes greater use of relationships among the different metals, and between HA and FA, and draws directly upon relationships between WHAM parameters and equilibrium constants for well-defined ligands via the Irving-Rossotti slope α_O . This both improves the reliability of the parameters and makes the parameter set more internally consistent. In addition, the approach means that $\log K_{MA}$ can be estimated from constants for a wider range of simpler ligands.

In 19 cases for HA and 13 for FA there are at least two data sets per metal, and these can be used to compute standard deviations in $\log K_{MA}$. These range from 0.04 to 1.19, with means of 0.33 and 0.32 for HA and FA respectively. The standard deviations reflect differences in several factors, including the source of the humic substances, experimental methods and experimental conditions. The standard deviations for Cu are relatively low, 0.24 for HA and 0.21 for FA, and given that techniques for quantifying Cu binding are better than those for other metals, they probably reflect mostly humic variability. A standard deviation of 0.3 in $\log K_{MA}$ might reasonably be adopted as a standard when applying the model to estimate uncertainty in field predictions.

Although Model VII represents an improvement on Model VI, its predictions do not differ greatly (Figures 5 and 6). Therefore calculations that have already been run using Model VI are unlikely to be invalidated by the new model, except perhaps for metal binding at alkaline pH. There is probably merit in running both models, and also the NICA model^[5] for new problems, since any differences may provide insights or highlight uncertainty. It should also be borne in mind that “higher” models (such as the CHUM catchment model^[48,49], Critical Limit Functions^[62,70] and WHAM-F_{TOX}^[59]) that use predicted speciation, will have parameter values specific to the chosen Humic Ion Binding Model.

In summary, this work has produced a simpler Humic Ion-Binding Model, based on a considerably larger data set, with greater internal consistency, and parameterised for protons and 40 metallic cations. This should improve our ability to predict chemical speciation involving natural organic matter in field situations.

Acknowledgements

We are grateful to K. Delbeke, C.E. Schlegel, I. Schoeters, J. Meyer, R.L. Dwyer, D.S. Smith and R.C. Santore for their comments and suggestions on the report from which this paper was developed. The work was financed by the following organisations; International Copper Association (ICA), International Council on Mining and Minerals (ICMM), International Lead Zinc Research Organization (ILZRO), Nickel Producers Environmental Research Association (NiPERA), Cobalt Development Institute (CDI), Rio Tinto Minerals, International Chromium Development Association (ICDA), International Molybdenum Association (IMOA), European Aluminium Association (EAA), UK Natural Environment Research Council.

389 **References**

- [1] E. Tipping, WHAM - A chemical equilibrium model and computer code for waters, sediments and soils incorporating a discrete-site / electrostatic model of ion-binding by humic substances. *Comp. Geosci.* **1994**, 20, 973. doi: 10.1023/A:1009627214459
- [2] E. Tipping, *Cation Binding by Humic Substances*, **2002** (Cambridge University Press; Cambridge).
- [3] E. Tipping & M.A. Hurley, A unifying model of cation binding by humic substances, *Geochim. Cosmochim. Acta* **1992**, 56, 3627. doi:10.1016/0016-7037(92)90158-F
- [4] E. Tipping, Humic Ion-Binding Model VI: an improved description of ion-binding by humic substances, *Aquat. Geochem.* **1998**, 4, 3. doi: 10.1023/A:1009627214459
- [5] D.G. Kinniburgh, W.H. van Riemsdijk, L.K. Koopal, M. Borkovec, M.F. Benedetti, M.J. Avena, Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency. *Coll. Surf. A: Physicochem. Eng. Aspects* **1999**, 151, 147. doi:10.1016/S0927-7757(98)00637-2
- [6] S.E. Cabaniss, Forward modeling of metal complexation by NOM: I. A priori prediction of conditional constants and speciation, *Environ. Sci. Technol.* **2009**, 43, 2838. doi: 10.1021/es8015793
- [7] E. Tipping, D. Berggren, J. Mulder, C. Woof, Modeling the solid-solution distributions of protons, aluminum, base cations and humic substances in acid soils, *Eur. J. Soil Sci.* **1995**, 46, 77. doi: 10.1111/j.1365-2389.1995.tb01814.x
- [8] H.A. de Wit, M. Kotowski, J. Mulder, Modeling aluminum and organic matter solubility in the forest floor using WHAM, *Soil Sci. Soc. Am. J.* **1999**, 63, 1141-1148. doi: 10.2136/sssaj1999.6351141x
- [9] H.A. de Wit, T. Groseth, J. Mulder, Predicting aluminum and soil organic matter solubility using the mechanistic equilibrium model WHAM, *Soil Sci. Soc. Am. J.* **2001**, 65, 1089. doi: 10.2136/sssaj2001.6541089x
- [10] S. Lofts, C. Woof, E. Tipping, N. Clarke, J. Mulder, Modelling pH buffering and aluminium solubility in European forest soils *Eur. J. Soil Sci.* **2001**, 52, 189. doi: 10.1046/j.1365-2389.2001.00358.x
- [11] B. Jansen, J. Mulder, J.M. Verstraten, Organic complexation of Al and Fe in acidic soil solutions - Comparison of diffusive gradients in thin films analyses with Models V and VI predictions, *Anal. Chim. Acta* **2003**, 498, 105. doi:10.1016/j.aca.2003.08.054
- [12] B. Jansen, J. Mulder, J.M. Verstraten, Modeling aluminum solubility in intrazonal podzols using WHAM-S/model, *J. Plant Nutr. Soil Sci.*, **2005**, 168, 325. doi: 10.1002/jpln.200421671
- [13] J.D. Cooke, J. Hamilton-Taylor, E. Tipping, On the acid-base properties of humic acid in soil. *Environ. Sci. Technol.* **2007**, 41, 465. doi: 10.1021/es061424h

- [14] J.D. Cooke, E. Tipping, J. Hamilton-Taylor, Proton interactions with soil organic matter; the importance of aggregation and the weak acids of humin. *Eur. J. Soil Sci.* **2008**, *59*, 1111. DOI: 10.1111/j.1365-2389.2008.01071.x
- [15] E. Tipping, H.T. Carter, Aluminium speciation in streams and lakes of the UK Acid Waters Monitoring Network, modelled with WHAM, *Sci. Tot. Environ.* **2011**, in press. doi:10.1016/j.scitotenv.2010.12.030
- [16] A.L. Nolan, M.J. McLaughlin, S.D. Mason, Chemical speciation of Zn, Cd, Cu, and Pb in pore waters of agricultural and contaminated soils using Donnan dialysis, *Environ. Sci. Technol.* **2003**, *37*, 90-98. doi: 10.1021/es025966k
- [17] E. Tipping, J. Rieuwerts, G. Pan, M.R. Ashmore, S. Lofts, M.T.R. Hill, M.E. Farago, I. Thornton, The solid-solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. *Environ. Pollut.* **2003**, *125*, 213. doi:10.1016/S0269-7491(03)00058-7
- [18] R. Vulkan, F.-J. Zhao, V. Barbosa-Jefferson, S. Preston, G.I. Paton, E. Tipping, S.P. McGrath, Copper speciation and impacts on bacterial biosensors in the pore water of copper-contaminated soils. *Environ. Sci. Technol.* **2000**, *34*, 5115. doi: 10.1021/es0000910
- [19] L.J. Evans, B. Sengdy, D.G. Lumsdon, D.A. Stanbury, Cadmium adsorption by an organic soil: a comparison of some humic - metal complexation models, *Chem. Spec. Bioavail.* **2003**, *15*, 93. doi: 10.3184/095422903782775172
- [20] A.M. Tye, S. Young, N.M.J. Crout, H. Zhang, S. Preston, F.J. Zhao, S.P. McGrath, Speciation and solubility of Cu, Ni and Pb in contaminated soils, *Eur. J. Soil Sci.*, **2004**, *55*, 579. doi: 10.1111/j.1365-2389.2004.00627.x
- [21] A.R. Almas, S. Lofts, J. Mulder, E. Tipping, Solubility of major cations and Cu, Zn and Cd in soil extracts of some contaminated agricultural soils near a zinc smelter in Norway: modelling with a multisurface extension of WHAM, *Eur. J. Soil Sci.* **2007**, *58*, 1074. doi: 10.1111/j.1365-2389.2007.00894.x
- [22] Z.Q. Shi, H.E. Allen, D.M. Di Toro, S.Z. Lee, D.M.F. Meza, S. Lofts, Predicting cadmium adsorption on soils using WHAM VI, *Chemosphere* **2007**, *69*, 605. doi: 10.1016/j.chemosphere.2007.03.001
- [23] J. Hamilton-Taylor, L. Giusti, W. Davison, W. Tych, C.N. Hewitt, Sorption of trace metals (Cu, Pb, Zn) by suspended lake particles in artificial (0.005 M NaNO₃) and natural (Esthwaite Water) freshwaters, *Coll. Surf. A - Physicochem. Eng. Aspects.* **1997**, *120*, 205. doi: 10.1016/S0927-7757(96)03722-3
- [24] J.R. Ferreira, A.J. Lawlor, J.M. Bates, K.J. Clarke, E. Tipping, Chemistry of riverine

- and estuarine suspended particles from the Ouse-Trent system, UK, *Coll. Surf. A-Physicochem. Eng. Aspects* **1997**, 120, 183. doi:10.1016/S0927-7757(96)03721-1
- [25] J. Hamilton-Taylor, A.S. Postill, E. Tipping, M.P. Harper, Laboratory measurements and modeling of metal-humic interactions under estuarine conditions, *Geochim. Cosmochim. Acta* **2002**, 66, 403. doi: 10.1016/S0016-7037(01)00777-3
- [26] D.M. Hill, A.C. Aplin, Role of colloids and fine particles in the transport of metals in rivers draining carbonate and silicate terrains, *Limnol. Oceanogr.* **2001**, 46, 331. doi: 10.4319/lo.2001.46.2.0331
- [27] S.E. Bryan, E. Tipping, J. Hamilton-Taylor, Comparison of measured and modelled copper binding by natural organic matter in freshwaters. *Comp. Biochem. Physiol. C* **2002**, 133, 37. doi: 10.1016/S1532-0456(02)00083-2
- [28] T. Cheng, K. De Schamphelaere, S. Lofts, C. Janssen, H.E. Allen, Measurement and computation of zinc binding to natural dissolved organic matter in European surface waters, *Analyt. Chim. Acta* **2005**, 542, 230. doi:10.1016/j.aca.2005.03.053
- [29] J.W. Guthrie, N.M. Hassan, M.S.A. Salam, I.I. Fasfous, C.A. Murimboh, J. Murimboh, C.L. Chakrabarti, D.C. Grégoire, Complexation of Ni, Cu, Zn, and Cd by DOC in some metal-impacted freshwater lakes: a comparison of approaches using electrochemical determination of free-metal-ion and labile complexes and a computer speciation model, WHAM V and VI. *Anal. Chim. Acta* **2005**, 528, 205. doi:10.1016/j.aca.2004.10.003
- [30] A. Turner, M. Martino, Modelling the equilibrium speciation of nickel in the Tweed Estuary, UK: Voltammetric determinations and simulations using WHAM. *Marine Chem.* **2006**, 102, 198. doi: 10.1016/j.marchem.2006.04.002
- [31] L.S. Balistrieri, R.G. Blank, Dissolved and labile concentrations of Cd, Cu, Pb, and Zn in the South Fork Coeur d'Alene River, Idaho: Comparisons among chemical equilibrium models and implications for biotic ligand models. *Appl. Geochem.* **2008**, 23, 3355. doi:10.1016/j.apgeochem.2008.06.031
- [32] J.B. Christensen, J.J. Botma, T.H. Christensen, Complexation of Cu and Pb by DOC in polluted groundwater: A comparison of experimental data and predictions by computer speciation models (WHAM and MINTEQA2), *Water Res.* **1999**, 33, 3231. doi:10.1016/S0043-1354(99)00020-2
- [33] A. Tessier, D. Fortin, N. Belzile, R.R. DeVitre, G.G. Leppard, Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: Narrowing the gap between field and laboratory measurements, *Geochim. Cosmochim. Acta* **1996**, 60, 387. doi:10.1016/0016-7037(95)00413-0
- [34] M.C. Alfaro-De la Torre, A. Tessier, Cadmium deposition and mobility in the sediments of an acidic oligotrophic lake, *Geochim. Cosmochim. Acta* **2002**, 66,

3549. doi: 10.1016/j.gca.2004.02.013
- [35] J.W. Tang, K.H. Johannesson, Speciation of rare earth elements in natural terrestrial waters: Assessing the role of dissolved organic matter from the modeling approach, *Geochim. Cosmochim. Acta* **2003**, 67, 2321. doi: 10.1016/S0016-7037(02)01413-8
- [36] J. Sonke, Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. *Environ. Sci. Technol.* **2006**, 40, 7481. doi: 10.1021/es060490g
- [37] O. Pourret, M. Davranche, G. Gruau, A. Dia, Organic complexation of rare earth elements in natural waters: Evaluating model calculations from ultrafiltration data. *Geochim. Cosmochim. Acta* **2007**, 71, 2718. doi: 10.1016/j.gca.2007.04.001
- [38] E. Tipping, E., C. Rey-Castro, S.E. Bryan, J. Hamilton-Taylor, Al(III) and Fe(III) binding by humic substances in freshwaters, and implications for trace metal speciation. *Geochim. Cosmochim. Acta* **2002**, 66, 3211. doi: 10.1016/S0016-7037(02)00930-4
- [39] J. Hamilton-Taylor, E.J. Smith, W. Davison, M. Sugiyama, Resolving and modeling the effects of Fe and Mn redox cycling on trace metal behavior in a seasonally anoxic lake, *Geochim. Cosmochim. Acta* **2005**, 69, 1947. doi: 10.1016/j.gca.2004.11.006
- [40] S. Lofts, E. Tipping, J. Hamilton-Taylor, The chemical speciation of Fe(III) in freshwaters. *Aquat. Geochem.* **2008**, 14, 227. doi: 10.1007/s10498-008-9040-5
- [41] C. Neal, S. Lofts, C.D. Evans, B. Reynolds, E. Tipping, M. Neal, Increasing iron concentrations in UK upland waters. *Aquat. Geochem.* **2008**, 14, 263. doi: 10.1007/s10498-008-9036-1
- [42] S. Lofts, E. Tipping, A.L. Sanchez, B.A. Dodd, Modelling the role of humic acid in radiocaesium distribution in a British upland peat soil. *J. Environ. Radioact.* **2002**, 61, 133. doi: 10.1016/S0265-931X(01)00118-7
- [43] A.J. Peters, J. Hamilton-Taylor, E. Tipping, Americium binding to humic acid. *Environ. Sci. Technol.* **2001**, 35, 3495. doi: 10.1021/es000295g
- [44] E.R. Unsworth, P. Jones, S.J. Hill, The effect of thermodynamic data on computer model predictions of uranium speciation in natural water systems. *J. Environ. Monitor.* **2002**, 4, 528. doi: 10.1039/B415287E
- [45] E. Tipping, C. Woof, M. Kelly, K. Bradshaw, J.E. Rowe, Solid-solution distributions of radionuclides in acid soils - application of the WHAM chemical speciation model, *Environ. Sci. Technol.* **1995**, 29, 1365. doi: 10.1021/es00005a032
- [46] E. Tipping, C. Woof, The distribution of humic substances between the solid and aqueous phases of acid organic soils - a description based on humic heterogeneity and charge-dependent sorption equilibria. *J. Soil Sci.* **1991**, 42, 437. doi:

- 10.1111/j.1365-2389.1991.tb00421.x
- [47] S. Lofts, B.M. Simon, E. Tipping, C. Woof, Modelling the solid-solution partitioning of organic matter in European forest soils, *Eur. J. Soil Sci.* **2001**, 52, 215. doi: 10.1046/j.1365-2389.2001.00367.x
- [48] E. Tipping, A.J. Lawlor, S. Lofts, Simulating the long-term chemistry of an upland UK catchment: major solutes and acidification, *Environ. Pollut.* **2006**, 141, 151. doi: 10.1016/j.envpol.2005.08.018
- [49] E. Tipping, A.J. Lawlor, S. Lofts, L. Shotbolt, Simulating the long-term chemistry of an upland UK catchment: heavy metals, *Environ. Pollut.* **2006**, 141, 139. doi: 10.1016/j.envpol.2005.08.019
- [50] C.D. Vincent, A.J. Lawlor, E. Tipping, Accumulation of Al, Mn, Fe, Cu, Zn, Cd and Pb by the bryophyte *Scapania undulata* in three upland waters of different pH, *Environ. Pollut.* **2001**, 114, 93. doi: 10.1016/S0269-7491(00)00201-3
- [51] E. Tipping, C.D. Vincent, A.J. Lawlor, S. Lofts, Metal accumulation by stream bryophytes, related to chemical speciation. *Environ. Poll.* **2008**, 156, 936. doi: 10.1016/j.envpol.2008.05.010
- [52] P.R. Paquin, J.W. Gorsuch, S. Apte, G.E. Batley, K.C. Bowles, P.G.C. Campbell, C.G. Delos, D.M. Di Toro, R.L. Dwyer, F. Galvez, R.W. Gensemer, G.G. Goss, C. Hogstrand, C.R. Janssen, J.C. McGeer, R.B. Naddy, R.C. Playle, R.C. Santore, U. Schneider, W.A. Stubblefield, C.M. Wood, K.B. Wu, The biotic ligand model: a historical overview. *Comp. Biochem. Physiol. C*, **2002**, 133, 3. doi: 10.1016/S1532-0456(02)00112-6
- [53] D.M. Di Toro, H.E. Allen, H.L. Bergman, J.S. Meyer, P.R. Paquin, R.C. Santore, Biotic ligand model of the acute toxicity of metals. 1. Technical basis. *Environ. Toxicol. Chem.* **2001**, 20, 2383. doi: 10.1002/etc.5620201034
- [54] C. Karlén, I.O. Wallinder, D. Heijerick, C. Leygraf, C.R. Janssen, Runoff rates and ecotoxicity of zinc induced by atmospheric corrosion. *Sci. Tot. Environ.* **2001**, 277, 169. doi: 10.1016/S0048-9697(00)00872-X
- [55] K.A.C. De Schamphelaere, C.R. Janssen, A biotic ligand model predicting acute copper toxicity for *Daphnia magna*: the effects of calcium, magnesium, sodium, potassium, and pH, *Environ. Sci. Technol.* **2002**, 36, 48. doi: 10.1021/es000253s
- [56] K.A.C. De Schamphelaere, F.M. Vasconcelos, D.G. Heijerick, F.M.G. Tack, K. Delbeke, H.E. Allen, C.R. Janssen, Development and field validation of a predictive copper toxicity model for the green alga *Pseudokirchneriella subcapitata*, *Environ. Toxicol. Chem.* **2003**, 22, 2454. doi: 10.1897/02-499
- [57] A.R. Almas, P. Lombnaes, T.A. Sogn, J. Mulder, Speciation of Cd and Zn in

- contaminated soils assessed by DGT-DIFS, and WHAM/Model VI in relation to uptake by spinach and ryegrass. *Chemosphere* **2006**, 62, 1647. doi: 10.1016/j.chemosphere.2005.06.020
- [58] B.E. Wesolek, E.K. Genrich, J.M. Gunn, K.M. Somers, Use of littoral benthic invertebrates to assess factors affecting biological recovery of acid- and metal-damaged lakes. *J. Nth. Am. Benthol. Soc.* **2010**, 29, 572. doi: 10.1899/09-123.1
- [59] A. Stockdale, E., S. Lofts, S.J. Ormerod, W.H. Clements, R. Blust, Toxicity of proton–metal mixtures in the field: Linking stream macroinvertebrate species diversity to chemical speciation and bioavailability *Aquat. Toxicol.* **2010**, 100, 112. doi:10.1016/j.aquatox.2010.07.018
- [60] J.R. Hall, M. Ashmore, J. Fawehinmi, C. Jordan, S. Lofts, L. Shotbolt, D.J. Spurgeon, C. Svendsen, E. Tipping, Developing a critical load approach for national risk assessments of atmospheric metal deposition, *Environ. Toxicol. Chem.* **2006**, 25, 883. doi: 10.1897/04-571R.1
- [61] W. de Vries, S. Lofts, E. Tipping, M. Meili, J.E. Groenenberg, G. Schutze, Impact of soil properties on critical concentrations of cadmium, lead, copper, zinc, and mercury in soil and soil solution in view of ecotoxicological effects. *Rev. Environ. Contam. Toxicol.* **2007**, 191, 47. doi: 10.1007/978-0-387-69163-3_3
- [62] E. Tipping, S. Lofts, H. Hooper, B. Frey, D. Spurgeon, C. Svendsen, Critical Limits for Hg(II) in soils, derived from chronic toxicity data. *Environ. Pollut.* **2010**, 158, 2465. doi: 10.1016/j.envpol.2010.03.027
- [63] J. Sonke, Lanthanide-humic substances complexation. II. Calibration of Humic Ion-Binding Model V, *Environ. Sci. Technol.* **2006**, 40, 7481. doi: 10.1021/es060490g
- [64] M.A. Glaus, W. Hummel, L.R. Van Loon, Experimental determination and modelling of trace metal-humate interactions: a pragmatic approach for applications in groundwater. *Paul Scherrer Institute Report 97-13*, **1997**, Villigen, Switzerland.
- [65] R.F. Carbonaro, D.M. Di Toro, Linear free energy relationships for metal-ligand complexation: monodentate binding to negatively-charged oxygen donor atoms. *Geochim. Cosmochim. Acta* **2007**, 71, 3958. doi:10.1016/j.gca.2007.06.005
- [66] H. Irving, H. Rossotti, Some relationships among the stabilities of metal complexes. *Acta Chem. Scand.* **1956**, 10, 72. doi: 10.1002/recl.19560750707
- [67] C.J. Milne, *Measurement and modelling of ion binding by humic substances*. PhD Dissertation, University of Reading, **2000**.
- [68] C.J. Milne, D.G. Kinniburgh, W.H. van Riemsdijk, E. Tipping, E. Generic NICA-Donnan model parameters for metal-ion binding by humic substances. *Environ. Sci. Technol.* **2003**, 37, 958. doi: 10.1021/es000123j

- [69] A.E. Martell, R.D. Hancock, *Metal Complexes in Aqueous Solutions*, **1996** (Kluwer, New York).
- [70] S. Lofts, D.J. Spurgeon, C. Svendsen, E. Tipping, Deriving soil critical limits for Cu, Zn, Cd, and pH: A method based on free ion concentrations. *Environ. Sci. Technol.* **2004**, 38, 3623. doi: 10.1021/es030155h

390

391

Table 1. Combinations of monodentate sites making bidentate and tridentate binding sites in Models VI and VII, expressed in terms of n_A the number of the most strongly-acid groups. Sites 1 to 4 are type A, present in equal amounts. Sites 5 to 8 are type B, and they total half of the type A sites. The factor f_{prB} specifies the fraction of the sites that are close enough to form bidentate sites, and f_{prT} does the same for tridentate sites. The values of f_{prB} and f_{prT} are 0.42 and 0.03 respectively for FA and 0.50 and 0.065 for HA. For each site combination there are three binding strengths governed by the parameter ΔLK_2 , their fractional abundances being 0.901, 0.09 and 0.009, so the model has three times as many multidentate sites as those shown here, 72 in Model VI and 42 in Model VII.

Model VI		Model VII	
sites	abundance	sites	abundance
<i>Bidentate sites</i>			
1-2	$f_{prB} \times n_A / 6$	1-2	$f_{prB} \times n_A / 8$
3-4	$f_{prB} \times n_A / 6$	3-4	$f_{prB} \times n_A / 8$
1-5	$f_{prB} \times n_A / 12$	1-5	$f_{prB} \times n_A / 8$
2-6	$f_{prB} \times n_A / 12$	2-6	$f_{prB} \times n_A / 8$
3-7	$f_{prB} \times n_A / 12$	3-7	$f_{prB} \times n_A / 8$
4-8	$f_{prB} \times n_A / 12$	4-8	$f_{prB} \times n_A / 8$
5-6	$f_{prB} \times n_A / 24$		
7-8	$f_{prB} \times n_A / 24$		
<i>Tridentate sites</i>			
1-2-3	$f_{prT} \times n_A / 27$	1-2-5	$f_{prT} \times n_A / 16$
1-2-4	$f_{prT} \times n_A / 27$	1-2-6	$f_{prT} \times n_A / 16$
1-3-4	$f_{prT} \times n_A / 27$	1-2-7	$f_{prT} \times n_A / 16$
2-3-4	$f_{prT} \times n_A / 27$	1-2-8	$f_{prT} \times n_A / 16$
5-6-7	$f_{prT} \times n_A / 216$	3-4-5	$f_{prT} \times n_A / 16$
5-6-8	$f_{prT} \times n_A / 216$	3-4-6	$f_{prT} \times n_A / 16$
5-7-8	$f_{prT} \times n_A / 216$	3-4-7	$f_{prT} \times n_A / 16$
6-7-8	$f_{prT} \times n_A / 216$	3-4-8	$f_{prT} \times n_A / 16$
1-2-5	$f_{prT} \times n_A / 18$		
3-4-6	$f_{prT} \times n_A / 18$		
1-3-7	$f_{prT} \times n_A / 18$		
2-4-8	$f_{prT} \times n_A / 18$		
1-5-6	$f_{prT} \times n_A / 36$		
2-7-8	$f_{prT} \times n_A / 36$		
3-5-7	$f_{prT} \times n_A / 36$		
4-6-8	$f_{prT} \times n_A / 36$		

403 Table 2. Default proton binding parameters for humic and fulvic acid.

Parameter	HA		FA	
	Model VI	Model VII	Model VI	Model VII
n_A^*	3.3	3.4	4.8	5.2
pK_A	4.1	4.1	3.2	3.7
pK_B	8.8	8.3	9.4	9.6
ΔpK_A	2.1	2.6	3.3	3.1
ΔpK_B	3.6	3.1	4.9	4.4
P	-330	-196	-115	-119

404 * mmol (gHS)⁻¹

405

Table 3. Default cationic metal parameters for Model VII. Values of $\log K_{\text{MA,HA,mean}}$ and $\log K_{\text{MA,FA,mean}}$ are averages from data-fitting (n_{HA} and n_{FA} are the numbers of data sets), while $\log K_{\text{MA,HA,def}}$ and $\log K_{\text{MA,FA,def}}$ are default values derived with equations (3) and (4), which involve the Irving-Rosotti parameter α_{O} . Values of ΔLK_2 were derived with equation (1) using the compilation of $\log K_{\text{NH}_3}$ values by Martell & Hancock^[69].

metal	n_{HA}	n_{FA}	$\log K_{\text{MA,HA,mean}}$	$\log K_{\text{MA,FA,mean}}$	α_{O}	$\log K_{\text{MA,HA,def}}$	$\log K_{\text{MA,FA,def}}$	ΔLK_2
Be	0	0	-	-	0.433	2.27	2.02	0.99
Mg	1	2	0.98	1.01	0.176	1.14	0.99	0.13
Al	4	4	2.67	2.69	0.607	2.82	2.57	0.46
Ca	8	11	1.19	1.17	0.194	1.26	1.13	0.00
Sc	1	0	3.61	-	-	3.61	3.28	0.39
VO	0	1	-	2.51	-	2.76	2.51	1.74
Cr	1	0	2.52	-	0.818	3.07	2.89	1.97
Mn	2	1	2.21	1.67	0.255	1.98	1.76	0.58
Fe(II)	0	0	-	-	0.287	1.76	1.46	0.81
Fe(III)	2	1	3.19	3.03	0.861	3.37	3.12	2.20
Co	2	8	1.51	1.32	0.306	1.50	1.35	1.22
Ni	2	5	1.6	1.41	0.301	1.60	1.43	1.57
Cu	13	16	2.54	2.07	0.466	2.38	2.16	2.34
Zn	2	4	1.87	1.71	0.304	1.87	1.68	1.28
Sr	1	1	1.49	1.01	0.171	1.32	1.13	0.00
Y	1	1	2.84	2.93	-	3.03	2.76	0.22
Ag	4	1	1.50	1.14	0.177	1.44	1.27	1.91
Cd	10	6	1.61	1.58	0.306	1.67	1.51	1.48
Ba	0	0	-	-	0.158	1.30	0.97	0.00
La	1	1	2.64	2.74	0.414	2.62	2.36	0.11
Ce	1	1	2.68	2.7	0.451	2.66	2.41	0.13
Pr	1	1	2.69	2.74	-	2.85	2.59	0.16
Nd	1	1	2.68	2.71	-	2.83	2.57	0.18
Sm	1	1	2.76	2.81	-	2.93	2.66	0.20
Eu	5	10	2.97	2.61	0.530	2.89	2.62	0.29
Gd	1	1	2.77	2.84	-	2.95	2.68	0.24
Tb	1	1	2.86	2.92	-	3.04	2.76	0.26
Dy	2	1	3.19	2.93	-	3.20	2.91	0.28
Ho	1	1	2.95	2.96	-	3.10	2.82	0.30
Er	1	1	3.03	3.09	-	3.21	2.92	0.32
Tm	1	1	3.09	3.07	-	3.23	2.94	0.35
Yb	1	1	3.12	3.05	-	3.24	2.94	0.37
Lu	1	1	3.17	3.1	-	3.29	2.99	0.39
Hg	3	5	4.1	3.4	0.796	3.84	3.51	5.10
MeHg	4	1	0.53	0.39	-	0.51	0.46	3.60
Pb	9	10	2.39	2.14	0.442	2.37	2.15	0.93
Th	2	0	3.41	-	0.902	3.58	3.34	0.23
UO ₂	4	4	2.64	2.28	0.621	2.61	2.38	1.16
Am	7	3	2.95	2.74	0.543	2.94	2.68	1.57
Cm	3	1	2.58	1.91	0.537	2.50	2.27	1.57

412 Table 4. Comparison of default $\log K_{MA}$ values for Models VI and VII. Values in bold indicate
 413 that the difference between the models is more than 0.2 log units greater or less than the
 414 difference for Cu.

	Model VI		Model VII	
	HA	FA	HA	FA
Mg	0.7	1.1	1.1	1.0
Al	2.6	2.5	2.8	2.6
Ca	0.7	1.3	1.3	1.1
VO	2.5	2.4	2.8	2.5
CrIII	2.2	2.2	3.1	2.9
Mn	0.6	1.7	2.0	1.8
FeII	1.3	1.6	1.8	1.5
FeIII	2.4	2.6	3.4	3.1
Co	1.1	1.4	1.5	1.4
Ni	1.1	1.4	1.6	1.4
Cu	2.0	2.1	2.4	2.2
Zn	1.5	1.6	1.9	1.7
Sr	1.1	1.2	1.3	1.1
Cd	1.3	1.6	1.7	1.5
Ba	-0.2	0.6	1.3	1.0
Eu	2.1	2.4	2.9	2.6
Dy	2.9	2.5	3.2	2.9
Hg	3.5	3.5	3.8	3.5
Pb	2.0	2.2	2.4	2.2
Th	2.8	2.7	3.6	3.3
UO ₂	2.2	2.1	2.6	2.4
Am	2.5	2.6	2.9	2.7
Cm	2.2	2.0	2.5	2.3

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Figure captions

- Figure 1 Proton dissociation calculated with Model VI and VII default parameters; Z is the charge per g of HA or FA. The upper of each pair of plots refers to an ionic strength of 0.1 M, the lower to 0.001M.
- Figure 2 Experimental data of Sonke (2006) for the binding of La(III) by humic acid (open circles) and fulvic acid (closed circles), expressed as $K_{app} = \nu / [La^{3+}]$, where ν is the amount of bound metal in mol g⁻¹. The lines are fits with Models VI (dashed lines) and VII (full lines).
- Figure 3 Fitted log K_{MA} for different metals (individual data sets) plotted against α_O , the Irving-Rossotti slope.
- Figure 4 Fitted log K_{MA} for HA (average value for each metal) plotted against the corresponding value for FA. The line has the expected slope of 1.11 (see Results). The triangles show data for lanthanides.
- Figure 5 Metal binding isotherms calculated with the default parameters of Models VI and VII. ν is moles bound per gram FA. Open symbols Model VI, closed symbols Model VII. Circles pH 4, squares pH 6, triangles pH 8.
- Figure 6 Competition by Mg, Al and Ca for Cu and Zn binding by HA and FA; comparison of results with default parameters for Models VI (broken lines) and VII (full lines). The calculations refer to pH 5 for Al and pH 7 for Mg and Ca, and an ionic strength of 0.01 M.

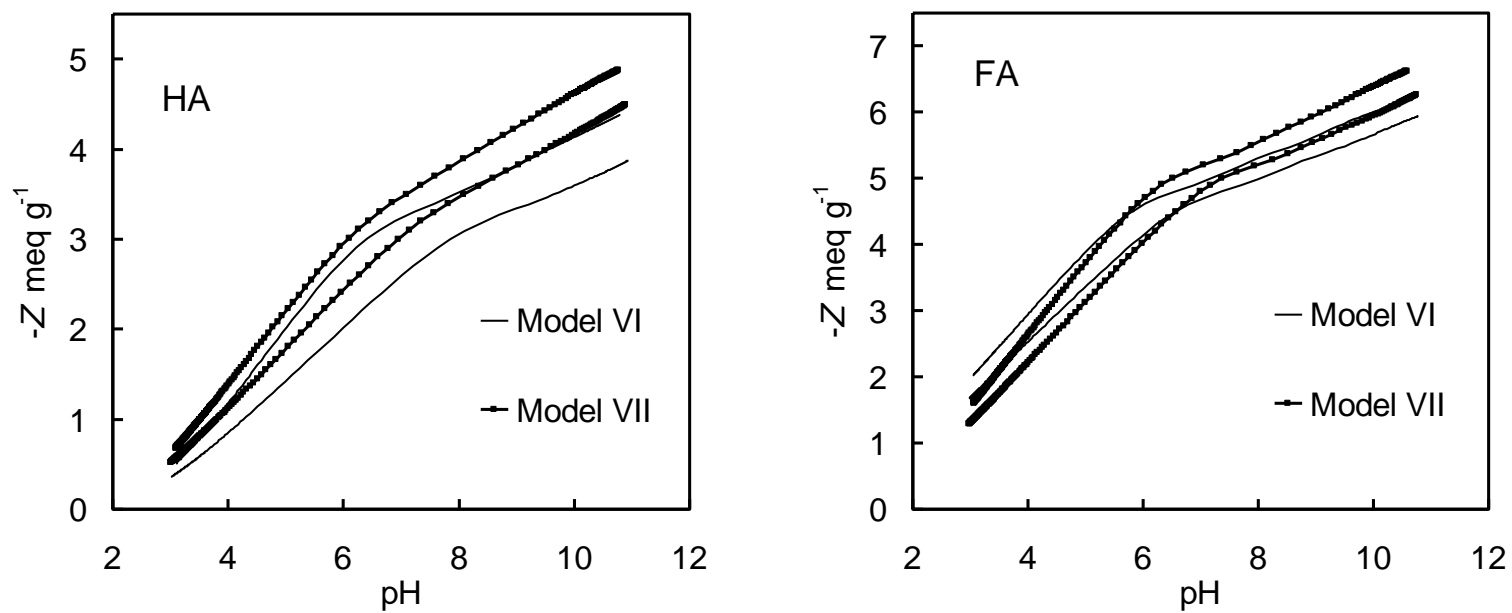


Figure 1

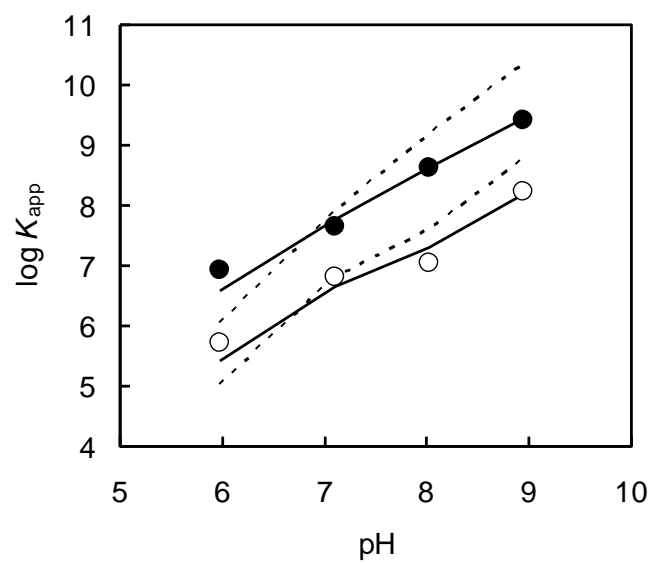


Figure 2

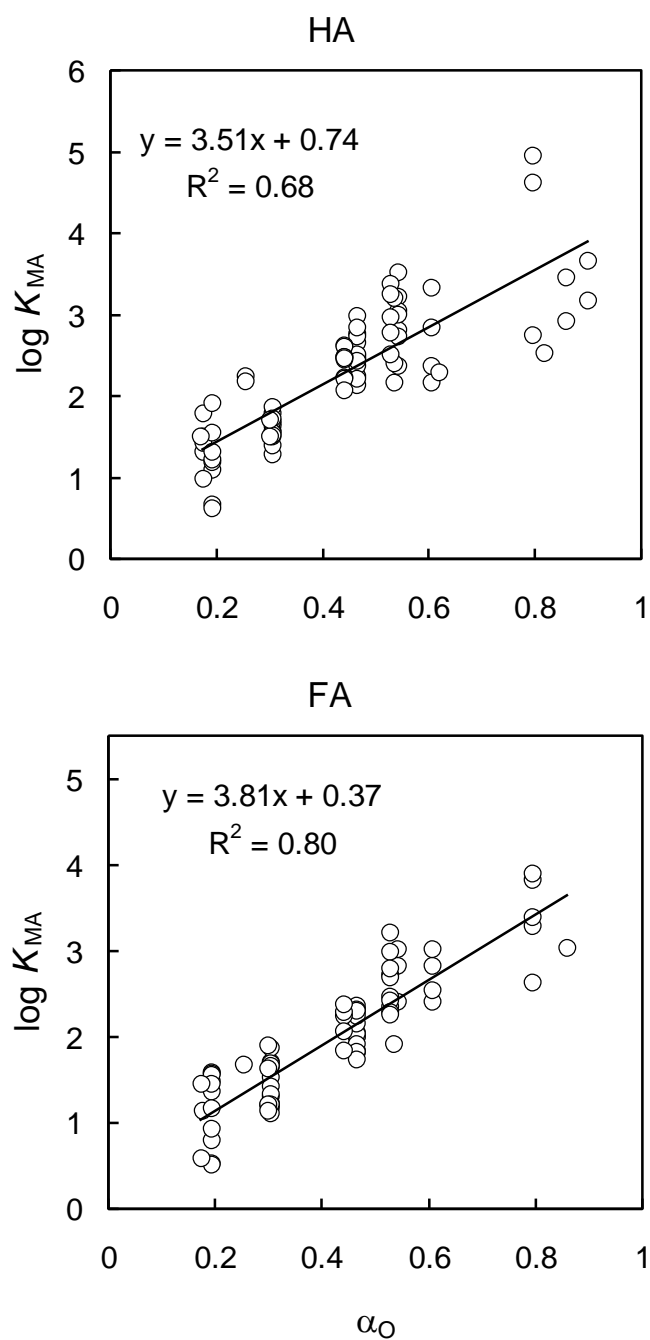


Figure 3

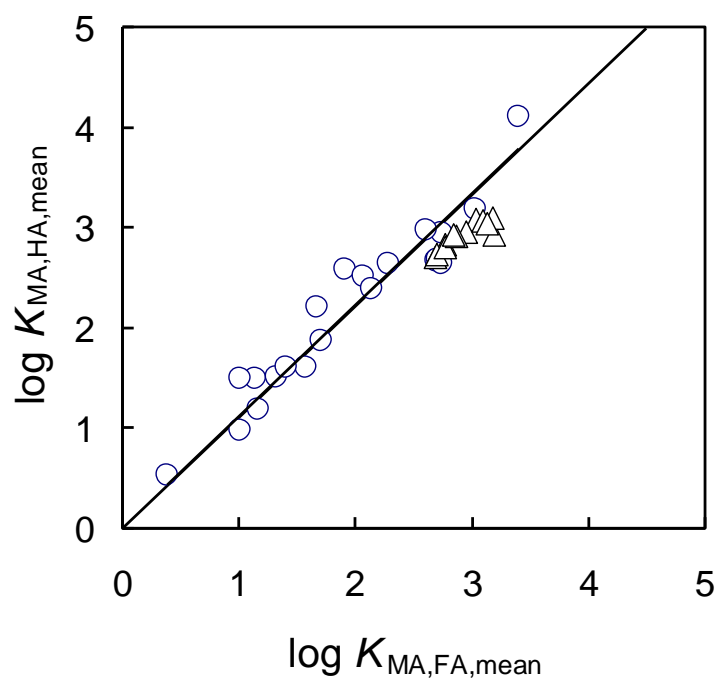


Figure 4

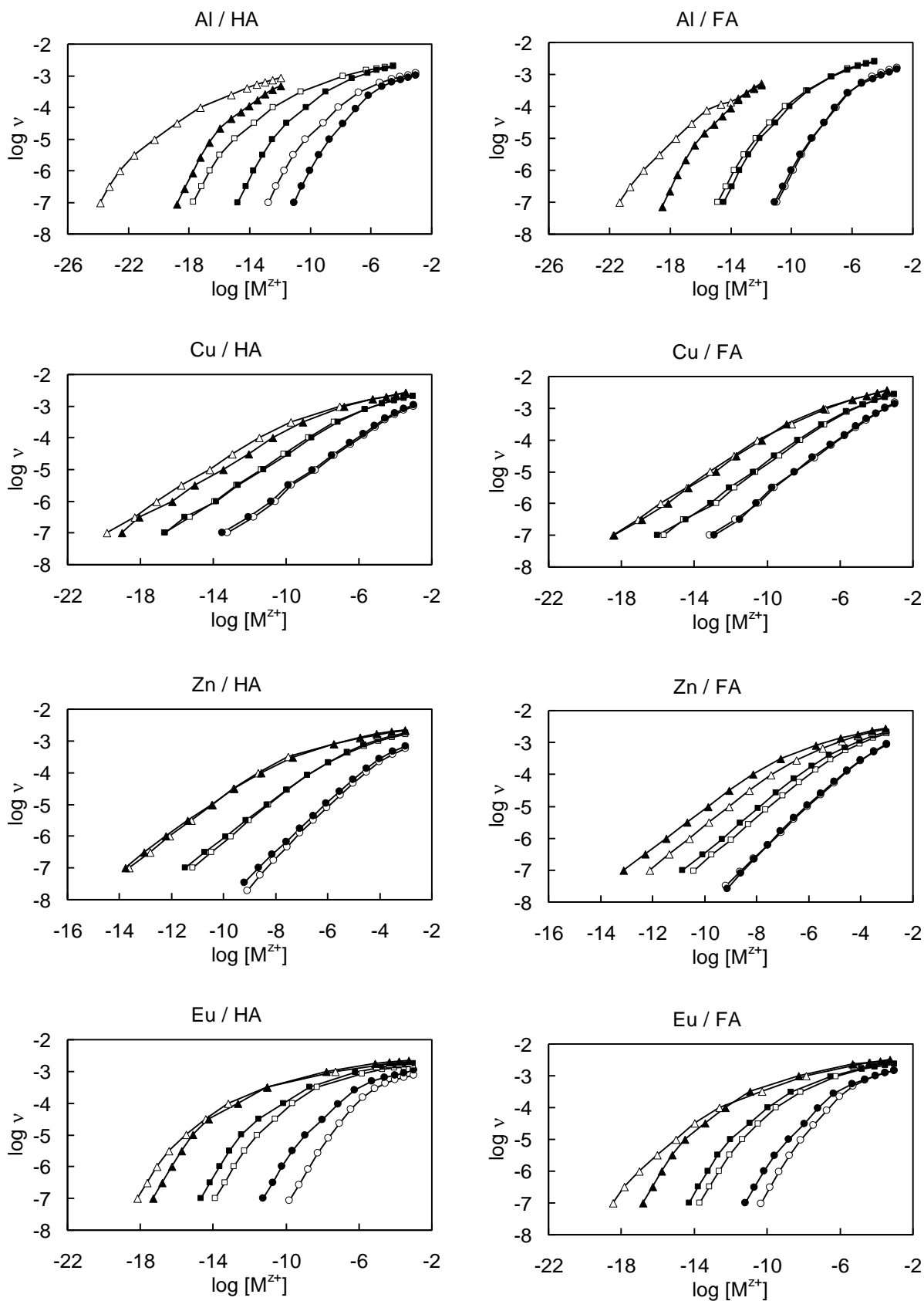


Figure 5

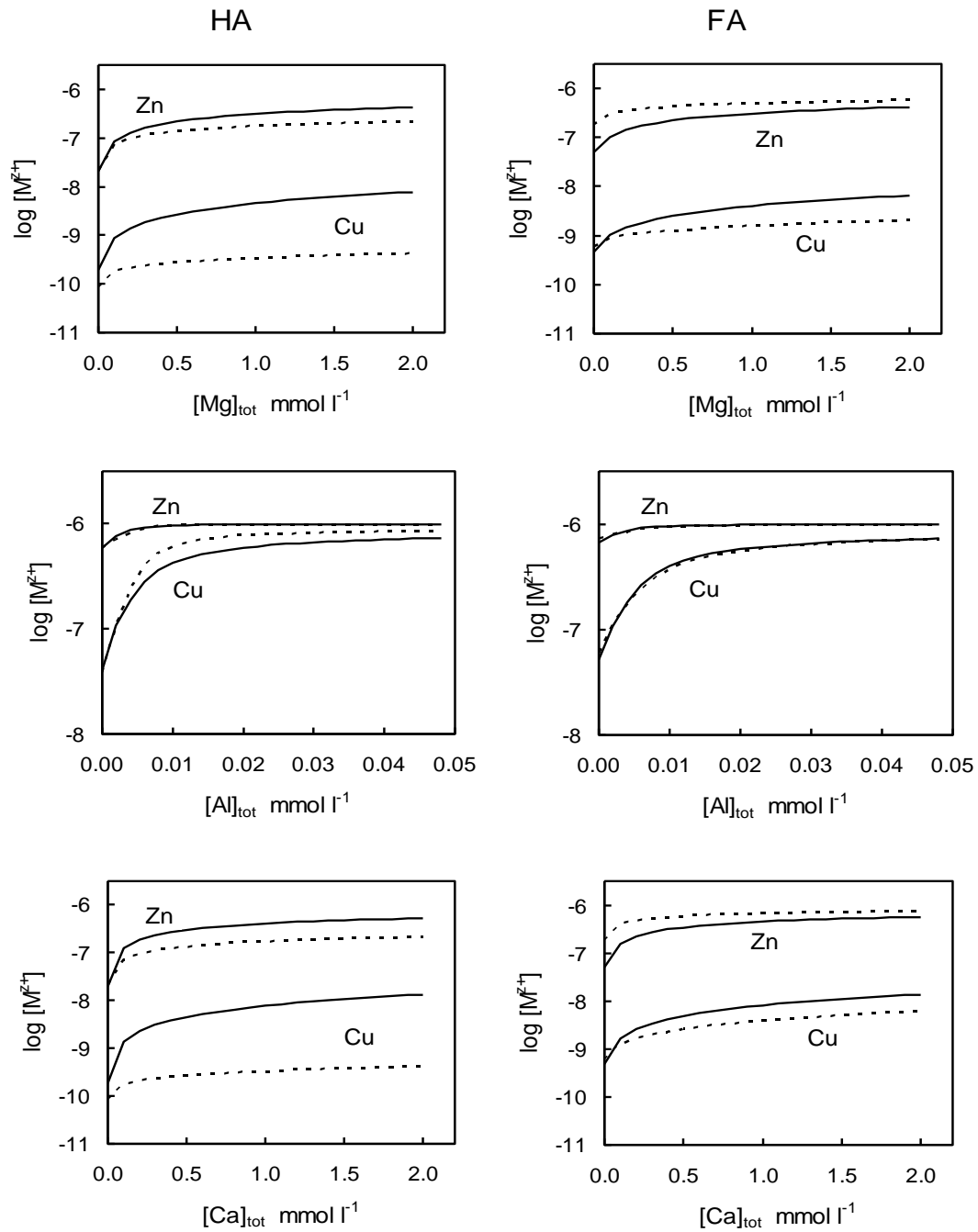


Figure 6