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## Al(III) and Fe(III) binding by humic substances in freshwaters, and implications for trace metal speciation

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**Abstract**—Published experimental data for Al(III) and Fe(III) binding by fulvic and humic acids can be explained approximately by the Humic Ion-Binding Model VI. The model is based on conventional equilibrium reactions involving protons, metal aquo ions and their first hydrolysis products, and binding sites ranging from abundant ones of low affinity, to rare ones of high affinity, common to all metals. The model can also account for laboratory competition data involving Al(III), Fe(III) and trace elements, supporting the assumption of common binding sites. Field speciation data (116 examples) for Al in acid-to-neutral waters can be accounted for, assuming that 60–70 % (depending upon competition by iron, and the chosen fulvic acid : humic acid ratio) of the dissolved organic carbon (DOC) is due to humic substances, the rest being considered inert with respect to ion binding. After adjustment of the model parameter characterizing binding affinity within acceptable limits, and with the assumption of equilibrium with a relatively soluble form of Fe(OH)<sub>3</sub>, the model can simulate the results of studies of two freshwater samples, in which concentrations of organically complexed Fe were estimated by kinetic analysis.

The model was used to examine the pH dependence of Al and Fe binding by dissolved organic matter (DOM) in freshwaters, by simulating the titration with Ca(OH)<sub>2</sub> of an initially acid solution, in equilibrium with solid-phase Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub>. For the conditions considered, Al, which is present at higher free concentrations than Fe(III), competes significantly for the binding of Fe(III), whereas Fe(III) has little effect on Al binding. The principal form of Al simulated to be bound at low pH is Al<sup>3+</sup>, AlOH<sup>2+</sup> being dominant at pH >6; the principal bound form of Fe(III) is FeOH<sup>2+</sup> at all pH values in the range 4–9. Simulations suggest that, in freshwaters, both Al and Fe(III) compete significantly with trace metals (Cu, Zn) for binding by natural organic matter over a wide pH range (4–9). The competition effects are especially strong for a high-affinity trace metal such as Cu, present at low total concentrations (~1 nM). As a result of these competition effects, high-affinity sites in humic matter may be less important for trace metal binding in the field than they are in laboratory systems involving humic matter that has been treated to remove associated metals. Copyright © 2002 Elsevier Science Ltd

### 1. INTRODUCTION

Aluminium and iron are abundant and reactive elements, with a variety of geochemical and environmental chemical roles. In the dissolved and particulate phases of freshwaters, sediments and soils, they undergo significant interactions with natural organic matter (chiefly humic substances). In the case of Al, it has been shown that interactions with organic matter are central to the chemistry of the element in organic-rich soils (e.g., Tipping et al., 1995; Berggren and Mulder, 1995; Skylberg, 1999), and consequently to its transfer to surface waters. They also play a crucial role in determining Al toxicity (e.g., Driscoll et al., 1980). Dissolved iron–organic complexes and iron oxide–humic colloids are important in the transport and fate of the element in rivers and estuaries (Sholkovitz and Copland, 1981; Ross and Sherrell, 1999). Adsorption of humic matter alters the surface chemistry and colloid stability of iron oxides (Tipping, 1986). Photochemical processes involving Fe and natural organic matter lead to the decomposition of DOM,

the production of reactive species (superoxide anion, hydrogen peroxide, hydroxyl radical), and the generation of dissolved, bioavailable, ferrous iron (e.g., Collienne, 1983; Stumm and Morgan, 1996; Voelker et al., 1997). Iron and humic matter influence phosphorus speciation in lakes (Jones et al., 1993).

Whereas the presence in freshwaters of dissolved complexes of (monomeric) Al with natural organic matter is well established (Driscoll, 1984; LaZerte, 1984), the situation with regard to Fe(III) is less clear. According to Perdue et al. (1976) and Koenings (1976), soluble iron–humic complexes are significant components of surface freshwaters. Others (Shapiro, 1966; Cameron and Liss, 1984) attribute the high apparent solubility of Fe in freshwaters to the presence of small iron oxide particles stabilized by adsorbed humic matter. Estimates of the distribution of Fe(III) between the organically complexed and colloidal oxide forms have been made by kinetic analysis, i.e., by determining the rate of conversion of Fe(III) to a spectroscopically detectable complex, following the addition of an excess of a suitable ligand. The starting species are then identified and quantified by fitting the kinetic data to a model in which each species has a rate constant in a defined range. Tipping et al. (1982) found that ca. 30% of the Fe(III) in the supernatant of a centrifuged lake water sample was present as a fast-reacting component, possibly organically complexed Fe.

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Sojo and de Haan (1991) reported that ca. 60% of the Fe(III) in a filtered (0.2  $\mu\text{m}$ ) neutral lake water (DOC 9  $\text{mg L}^{-1}$ ) was present as organic complexes. In both studies, Fe(III) not complexed by organic matter was considered to be present as colloidal oxides.

The interactions of Al and Fe with humic substances affect not only the two metals, but also the organic matter itself. Their binding may alter the tendency of humic substances to aggregate and to adsorb to surfaces (Ong and Bisque, 1968; Tipping *et al.*, 1988b; Theng and Scharpenseel, 1975), and may affect the binding of other metals. Thus, Al has been shown to compete with Eu (Susetyo *et al.*, 1990; Bidoglio *et al.*, 1991), Pb (Mota *et al.*, 1996; Pinheiro *et al.*, 2000), and Cd (Pinheiro *et al.*, 2000), and competition by Fe(III) for Am and Cu has been proposed (Peters *et al.*, 2001). In view of the high concentrations of Al and Fe(III), compared to those of trace metals, such competition effects may be highly significant in natural systems. Clearly, therefore, a full understanding of metal chemistry in natural waters needs to take into account the competitive reactions of Al, Fe, and other metals with humic matter.

The aim of the present work was to bring together existing and new information about Al and Fe binding by humic matter in freshwaters, and to examine how that binding will affect interactions with trace metals. As a framework, we have used Humic Ion-Binding Model VI, a discrete-site, electrostatic, model of cation–humic interactions, which has been parametrized with a large number of data sets from experiments with isolated humic substances (Tipping, 1998). Model VI permits knowledge gained from laboratory studies to be applied to field situations. An important assumption of the model is that all binding sites are available to all metals.

In the following text, square brackets indicate concentrations. Fulvic acid, humic acid, and humic substances are abbreviated by FA, HA, and HS, respectively, dissolved organic carbon and dissolved organic matter by DOC and DOM. The variable  $\nu$  is moles of metal bound per gram of humic matter or DOM. For simplicity, oxide phases are represented by  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$ . The term “filterable” is used to indicate components that pass through a filter (typically with a pore size in the range 0.1–1  $\mu\text{m}$ ), and which might be classed as “dissolved” for some practical purposes. Such components will often include colloidal species, notably  $\text{Fe}(\text{OH})_3$  and also  $\text{Al}(\text{OH})_3$  and aluminosilicates.

## 2. SPECIATION MODELLING

### 2.1. Humic Ion-Binding Model VI

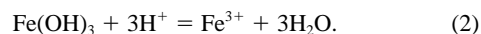
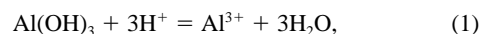
The model was described in detail by Tipping (1998). It uses a structured formulation of discrete, chemically plausible binding sites for protons, in order to allow the creation of regular arrays of bidentate and tridentate binding sites for metals. Metal aquo ions ( $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ , etc.) and their first hydrolysis products ( $\text{CaOH}^+$ ,  $\text{FeOH}^{2+}$ ,  $\text{CuOH}^+$ , etc.) compete with each other, and with protons, for binding. The same intrinsic equilibrium constant is assumed to apply to the aquo ion and its first hydrolysis product. 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 maximum number of parameters that can be optimized to describe metal binding is six:  $K_{\text{MA}}$ ,  $K_{\text{MB}}$ ,  $\Delta LK_{\text{A1}}$ ,  $\Delta LK_{\text{B1}}$ ,  $\Delta LK_2$ ,  $K_{\text{sel}}$  (see Table 1). In practice however, this number can be substantially reduced. Thus, Tipping (1998) described the setting of a single universal value for  $\Delta LK_{\text{A1}}$  and  $\Delta LK_{\text{B1}}$ , and the estimation of  $\Delta LK_2$  by correlation with the equilibrium constant for complex formation with  $\text{NH}_3$ . For dilute systems,  $K_{\text{sel}}$  can be set to unity. Finally,  $K_{\text{MA}}$  and  $K_{\text{MB}}$  are strongly correlated. Therefore, the fitting of a new data set can be achieved by adjusting only  $K_{\text{MA}}$ , which was the approach taken in the present work. Table 1 shows the values of the Model VI parameters used in the present work. It is important to note that the values of  $K_{\text{MA}}$  in Table 1, for all the metals except Fe(III), have been derived by fitting experimental data; the values for Fe(III) are estimated from linear free energy relationships (Tipping, 1998). High values of  $K_{\text{MA}}$  mean that the metal is strongly bound at the high-abundance “weak” sites. High values of  $\Delta LK_2$  mean that the metal is favored by the low-abundance “strong” sites, associated, according to the model, with nitrogen-containing groups. If  $\Delta LK_2$  is small, the strong sites are not favored, and binding is predominantly due to binding at oxygen-containing sites.

The humic binding model is combined with an inorganic speciation model, the species list and constants for which were given in the description of the Windermere Humic Aqueous Model (WHAM; Tipping, 1994). The inorganic reactions in this database are restricted to monomeric complexes of metals. The possible effect of the formation of the dimeric species  $\text{Al}_2(\text{OH})_2^{4+}$ , considered important by Sutherland and Cabaniss (1997), was examined, for field samples, by using the formation constant given by these authors (Sect 4.4); it was assumed that the dimer did not bind to humic matter. 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, but in the absence of experimental information, reactions involving humic substances are assumed to be independent of temperature. The combined model used in the present work is referred to as WHAM / Model VI.

### 2.2. Solubilities of Aluminium and Iron (Hydr)oxides

For some simulations presented in this paper, it is assumed that solution activities of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  are controlled by the solubilities of  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$ , according to the reactions



From measurements on field samples (Johnson *et al.*, 1981; Tipping *et al.*, 1988a; LaZerte, 1989), the assumption of a simple solubility control of Al is reasonable for acidic waters low in [DOC], and neutral waters. Solubility products ( $a_{\text{Al}^{3+}} a_{\text{H}^+}^3$ ) at 25 °C ( $K_{\text{so},25}$ ) for such waters are in the range from  $10^8$  to  $10^9$ . However most acidic freshwaters high in [DOC] are undersaturated with respect to known forms of  $\text{Al}(\text{OH})_3$ , and therefore the use of a solubility control under these circumstances will lead to overestimation of dissolved inorganic Al concentrations, and thereby to overestimation of Al binding to

Table 1. Model VI parameters (Tipping, 1998).

Parameter	HA	FA	Comments
$M$	15000	1500	Molecular weight
$r$ (nm)	1.72	0.80	Radius
$n_A$ (mol g <sup>-1</sup> )	$3.3 \times 10^{-3}$	$4.8 \times 10^{-3}$	Number of type A groups
$n_B$ (mol g <sup>-1</sup> )	$1.65 \times 10^{-3}$	$2.4 \times 10^{-3}$	$=0.5 \times n_A$
$pK_A$	4.1	3.2	Median proton dissociation constant for type A groups
$pK_B$	8.8	9.4	Median proton dissociation constant for type B groups
$\Delta pK_A$	2.1	3.3	Range factor for $pK_A$
$\Delta pK_B$	3.6	4.9	Range factor for $pK_B$
$P$	-330	-115	Electrostatic parameter
$f_{prB}$	0.50	0.42	Proximity factor for bidentate sites
$f_{prT}$	0.065	0.03	Proximity factor for tridentate sites
$\Delta LK_1$	2.8	2.8	Range factor for metal binding
$\log K_{MA}$			
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: $\log K_{MB} = 3.39 \log K_{MA} - 1.15$ ( $r^2 = 0.80$ )
Al	2.6	2.5	
Ca	0.7	1.3	
Fe(III)	2.5	2.4	
Cu	2.0	2.1	
Zn	1.5	1.6	
Cd	1.3	1.6	
Pb	2.0	2.2	
$\Delta LK_2$			
Mg		0.12	Strong binding site term, obtained from the relation: $\Delta LK_2 = 0.55 \log K_{NH_3}$ ( $r^2 = 0.66$ ), where $K_{NH_3}$ is the equilibrium constant for complexation with $NH_3$
Al		0.46	
Ca		0.0	
Fe(III)		2.20	
Cu		2.34	
Zn		1.28	
Cd		1.48	
Pb		0.93	

humic matter (cf. Sections 4.6 and 4.7). Reported enthalpy changes for reaction (1) are in the range from  $-88$  to  $-125$  kJ mol<sup>-1</sup> (Couturier et al., 1984; Tipping et al., 1988a; Nordstrom et al., 1990), and a mid-range value of  $-107$  kJ mol<sup>-1</sup> is adopted here.

Reported solubility products ( $a_{Fe^{3+}}/a_{Fe^{3+}}$ ) at 25 °C for "amorphous iron oxide," "hydrous ferric oxide," ferrihydrite, etc., formed in the laboratory, are in the range from  $10^{2.5}$  to  $10^5$ . The lowest value was given by Baes and Mesmer (1976), whereas the range from  $10^3$  to  $10^5$  was proposed by Nordstrom et al. (1990). Lower values represent aged materials, whereas the higher ones are more typical for freshly precipitated material. It can be envisaged that natural waters and soils contain phases with a range of solubility products, depending for example on the intensity of redox cycling or photochemical effects. The enthalpy change for reaction (2) is taken to be  $-102$  kJ mol<sup>-1</sup>, based on data published by Liu and Millero (1999).

### 3. EXPERIMENT

#### 3.1. Isolation of Humic Acid

The procedure followed that of Swift (1996). One kilogram of peat was collected from a site in the Pennines (N. England), sieved, mixed with 1 liter of 0.1 M HCl and stirred overnight. The resulting suspension was centrifuged for 30 min at 4400 g, and the supernatant discarded. The pellet was mixed with 2 liters of 0.15 M NaOH and stirred overnight under an atmo-

sphere of N<sub>2</sub> in the dark. The basic soil suspension was centrifuged, the supernatant removed and acidified to pH  $\sim 1$  with 6 M HCl. The acid solution was stirred overnight, then centrifuged. The supernatant was discarded, and the pellet redissolved in 2.7 liters of 0.1 M KOH under N<sub>2</sub> in the dark. Then KCl was added to give a final K<sup>+</sup> concentration of approximately 0.3 M. The solution was centrifuged, the pellet discarded, and the humic acid reprecipitated with acid at pH 1. After centrifugation and removal of the supernatant, the solid was transferred to a 5 liter plastic beaker and stirred overnight with 2 liters of 0.1 M HCl / 0.3 M HF. The suspension was neutralized with 5% (w/v) H<sub>3</sub>BO<sub>3</sub> (AnalaR), and the resulting solution centrifuged. This process was repeated twice more. The humic acid product was slurried with water, placed in dialysis bags (Visking tubing size 9, MWCO 12 000–14 000, cleaned with hot NaHCO<sub>3</sub> and thoroughly rinsed with water), and dialyzed against 0.1 M HNO<sub>3</sub> in the dark at 10 °C, the outside solution being changed daily for 13 days. The final yield of humic acid was 34 g. Its ash content was 0.6%, and it contained 10.8  $\mu$ mol Fe g<sup>-1</sup>, as determined by microwave digestion with concentrated HNO<sub>3</sub> and measurement of iron with bathophenanthroline after reduction with NH<sub>2</sub>OH. This material is referred to as HA-1. The iron content of the humic acid was diminished by repeated washing with 3 M HCl (Hering and Morel, 1988), to give a sample (HA-2) containing 3.8  $\mu$ mol Fe g<sup>-1</sup>. The extractable Al contents of HA-1 and HA-2 were both very low (0.09  $\mu$ mol g<sup>-1</sup>).

### 3.2. Preparation of HA Samples with Different Fe Contents

Two 70 cm<sup>3</sup> portions of HA-1 suspension (~23 g L<sup>-1</sup>) in 0.1 M HNO<sub>3</sub> were taken and mixed, while stirring thoroughly, with different amounts of a solution of 0.01 M Fe(NO<sub>3</sub>)<sub>3</sub>/0.1 M HNO<sub>3</sub>. The mixtures were then placed in separate dialysis bags, and dialyzed against 4-liter volumes of 0.1 M NaNO<sub>3</sub>/10<sup>-4</sup> M HNO<sub>3</sub> (pH ~ 4) in the dark at 10 °C, with five changes of the outside-bag solution. Because the dialysis procedure brought about a gradual increase in pH from 1 to 4, the precipitation of ferric oxide colloids, which might have occurred if the iron salt was added immediately at pH 4, was assumed to have been avoided; the final ion activity products ( $a_{\text{Fe}^{3+}}/a_{\text{H}^+}^3$ ) were all appreciably lower than the solubility products of Fe(OH)<sub>3</sub> (see Sect 2.2). The final preparations are referred to as HA-3 (14.4 μmol Fe g<sup>-1</sup>) and HA-4 (35.9 μmol Fe g<sup>-1</sup>). We used HA in this work first because it could readily be obtained in the large quantities required for the Cu titration experiments (see below), and second because it is of sufficiently large molecular size to be retained by a dialysis membrane that could still allow relatively rapid passage of inorganic solutes, necessary to load the material with Fe.

### 3.3. Copper Titration Experiments

Measurements of pH were made with a Radiometer model GK2401C combination electrode connected to a Radiometer PHM. The electrode was calibrated with phthalate and phosphate BDH buffers, following procedures recommended by Davison (1990). Measurements of Cu<sup>2+</sup> were made with an Orion cupric half-cell model 9429 ion-selective electrode, and an Orion Ag/AgCl double-junction model 90-02 reference electrode, attached to an Orion Microprocessor Ionanalyzer 901. The Cu electrode was prepared according to Avdeef *et al.* (1983). Each day, before calibration and titration, the electrode was polished with Orion aluminium oxide (3 μ) polishing strip (moistened in MilliQ water), rinsed with MilliQ water, soaked in 0.025 M H<sub>2</sub>SO<sub>4</sub> for approximately 10 minutes, then rinsed with more MilliQ water. The outer solution of the reference electrode was replaced daily, and the inner solution weekly. Before each experiment, the electrode was calibrated at 20 °C over a range of 10<sup>-6</sup> to 10<sup>-3</sup> M in [Cu<sup>2+</sup>]. A calibration check was performed after each experiment. Calibration slopes were always within 1% of the Nernstian value. All titrations were performed with the apparatus covered to exclude light. According to the manufacturer (Orion), Fe(III) interferes when the concentration of Fe<sup>3+</sup> is greater than one-tenth of the Cu<sup>2+</sup> concentration; we calculate that in our experiments the maximum ratio of Fe<sup>3+</sup> to Cu<sup>2+</sup> was 0.003, which implies negligible interference.

To prepare the humic acid for titration, a dialyzed suspension (HA-2, HA-3 or HA-4) was diluted with 0.1 M NaNO<sub>3</sub>/10<sup>-4</sup> M HNO<sub>3</sub> to give [HA] = 1 g L<sup>-1</sup>. An aliquot of 100 cm<sup>3</sup> was taken, and bubbled at room temperature for approximately 1 h with wet air, enriched to 0.1% with CO<sub>2</sub>. (Note that for the experiments described here, the use of CO<sub>2</sub>-enriched air was not necessary, but the experiments followed the protocol of other experiments at higher pH, where control of pCO<sub>2</sub> was required.) It was then transferred to a thermostatted jacket at 20

°C, the electrodes were inserted, Cu(NO<sub>3</sub>)<sub>2</sub> was added to give an initial total Cu concentration of 10<sup>-6</sup> M, and the system was left to equilibrate for 1 h, still bubbled with air. The first EMF reading was then taken, and the titration was performed by adding further known amounts of Cu(NO<sub>3</sub>)<sub>2</sub>. At each addition, the EMF reading was accepted when the electrode drift became less than 0.1 mV min<sup>-1</sup>.

### 3.4. Analysis of Field Samples

Fifteen liters of each surface water sample were collected in acid-washed polyethylene containers taking care not to disturb any sediment. Powderless gloves were worn throughout the sampling procedure, and containers were rinsed with some sample water prior to collection. Samples were transported to the laboratory immediately after collection, and were filtered (Whatman, GF/F) before storage in the dark at 4 °C for up to one week (pH and Fe determinations were made within 3 days). Monomeric Al was determined by the method of Seip *et al.* (1984). The samples were analyzed for pH (glass electrode), DOC (Dohrmann analyzer; combustion to CO<sub>2</sub>) and alkalinity (Gran titration). A Perkin-Elmer 2380 atomic absorption spectrophotometer was used to analyze the filtered samples for major cations (Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>). Major anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) were determined by ion chromatography (Dionex 2000i / SP). The method for determining ferrous and ferric iron concentrations was based on the formation of a colored complex between ferrous iron and bathophenanthroline in acetate buffer (Smith *et al.*, 1952). Total filterable iron was determined following overnight reduction with hydroxylammonium chloride, and Fe(II) by measurement without reduction. Color was allowed to develop for 1–2 minutes following addition of the colorimetric reagent; this period is sufficiently short that little conversion of Fe(III) to Fe(II) would have taken place, in the absence of the reducing agent (Box, 1984). The Fe(III) concentration, required for modelling (Sect. 4.5), was calculated as the difference between the total iron (reduced solutions), and the ferrous iron (not reduced). In the samples studied, the Fe was mainly in the Fe(III) form, the average proportion being 70% (range 50–93 %). We assume that the filterable Fe(III) determined in this way comprises organically complexed metal, together with readily reducible (amorphous) iron hydroxide colloids.

## 4. RESULTS

### 4.1. Laboratory Data for Al(III)

The application of Model VI to some laboratory data for Al–humic interaction has been described already (Tipping, 1998). Additional data have subsequently been published by Kinniburgh *et al.* (1999) for “purified peat humic acid” (PPHA). Model VI was applied by fixing all the default values (Table 1), except that the value of  $K_{\text{MA}}$  for Al was optimized by least-squares minimization (Fig. 1). The fitting is successful in that the model provides the correct pH dependence, and the optimized log  $K_{\text{MA}}$  of 2.5 is close to the initial default of 2.6 (Table 1). However, the fit is not as precise as was achieved by the NICCA–Donnan model, using two adjustable parameters (Kinniburgh *et al.*, 1999).

Tipping (1998) and Lead *et al.* (1998) showed that Model VI

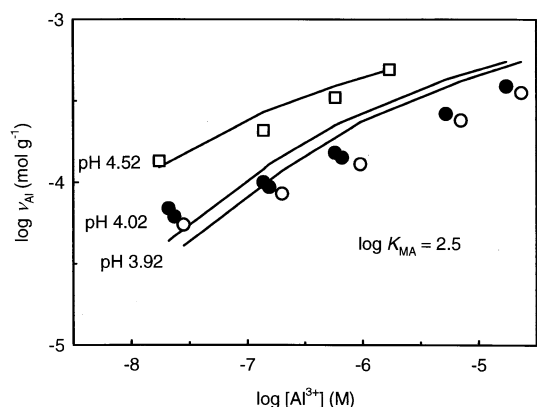


Fig. 1. Data of Kinniburgh et al. (1999) for Al binding by an isolated humic acid at  $I = 0.1$  M, fitted with Model VI.

can account for the competitive effects of Al on Eu binding to FA, and on Pb binding by HA. Additional data on the Al–Pb–PPHA and Al–Cd–PPHA systems have since been published by Pinheiro et al. (2000), as shown in Figure 2. WHAM/Model VI was applied by adjusting  $K_{MA}$  to fit the data obtained in the absence of Al. For Pb, the best value of  $\log K_{MA}$  for Pb was 2.1, close to the value of 2.15 obtained from earlier data for PPHA but at an ionic strength of 0.02 M (Pinheiro et al., 1994). For the Cd data, the best value of  $\log K_{MA}$  for Cd was 1.5, quite close to the value of 1.3 found for data for PPHA at higher ionic strengths (Pinheiro et al., 1994; Benedetti et al., 1995). Using these optimized values of  $K_{MA}$  for Pb and Cd, together with the  $K_{MA}$  for Al (see above), reasonable predictions of competition effects are obtained (Fig 2). The results provide further support for the model's basic assumption that the metals in question share common binding sites in humic substances. Independent evidence that metals share common sites also comes from fluorescence spectroscopic studies (Cabaniss, 1992), demonstrating competition by Al for Cu binding by fulvic acid.

#### 4.2. Laboratory Data for Fe(III)

There are few experimental data for Fe(III) binding by humic substances. Langford and Khan (1975) studied Fe(III) binding by FA in the pH range 1–2.5, using a stopped-flow kinetic method, and were able to derive equilibrium binding data. They obtained values of  $v$  in the range  $7 \times 10^{-5}$  to  $1.4 \times 10^{-3}$  mol  $g^{-1}$ ; at these relatively high values, the weaker, abundant, sites identified by the model would be dominant in the binding of Fe. The model was applied by fixing all the default values (Table 1), except for  $K_{MA}$ , which was adjusted to obtain the best fit. Only the data for pH 2.5 were used for fitting (Fig. 3), because at lower pH values the amount of binding was very small; even at pH 2.5 the maximum amount bound was only 20% of the total Fe(III), which probably explains the noise in the data. Some data at high total Fe concentrations were also rejected because the model calculations suggested that the solubility product of  $Fe(OH)_3$  might have been exceeded. The optimized value of  $\log K_{MA}$  was 2.8, which is somewhat greater than the default value of 2.4 shown in Table 1.

Liu and Millero (1999) carried out experiments in which iron oxide containing the radioactive isotope  $^{59}Fe$  was equilibrated

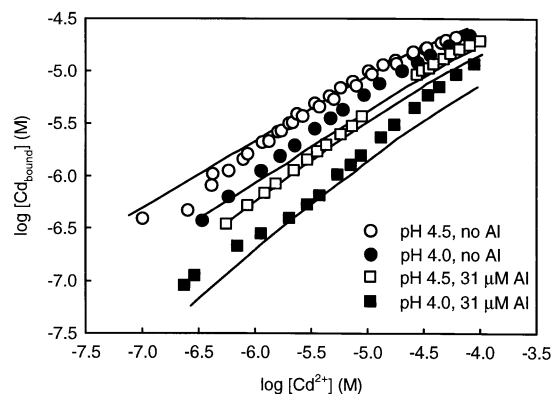
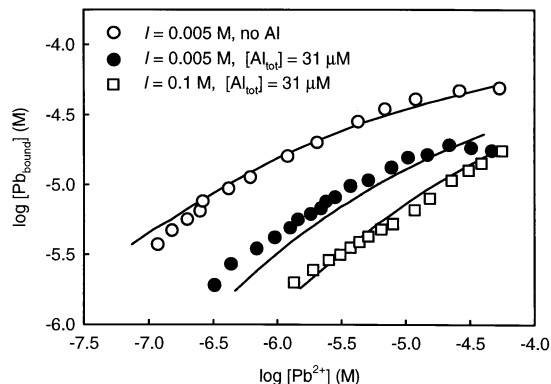


Fig. 2. Lead and cadmium binding by humic acid ( $65 \text{ mg L}^{-1}$ ), and the competitive effects of Al. The results for Pb refer to pH 4.5 throughout, those for Cd to  $I = 5$  mM throughout. Points are experimental data of Pinheiro et al. (2000); solid lines are Model VI fits (Al-free solutions) and predictions (solutions containing Al).

with solutions of different pH, with and without  $0.6 \text{ mg l}^{-1}$  HA, in  $0.7 \text{ M NaCl}$ . One set of data refers to constant  $[HA]$  and varied pH, the other to constant pH and varied  $[HA]$ . Concentrations of Fe(III) (either purely inorganic forms, or inorganic forms plus HA–Fe complexes) that would pass through a  $0.02 \text{ μm}$  filter were determined, by measurement of radioactivity. It was assumed by Liu and Millero, and is assumed here, that all such Fe(III) is actually truly dissolved, i.e., none is present as

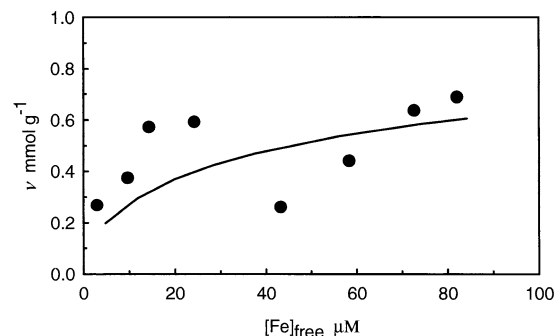


Fig. 3. Binding of Fe(III) by fulvic acid at pH 2.5,  $I = 0.1$  M. The data of Langford and Khan (1975) are shown by points, the Model VI fit by the line. The x axis refers to total inorganic Fe(III).

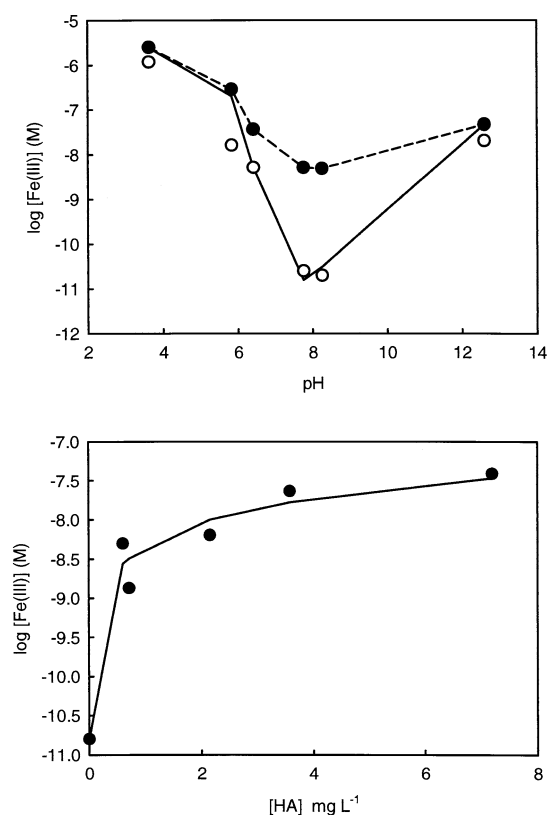


Fig. 4. The binding of Fe(III) by HA in 0.7 M NaCl. The points are data of Liu and Millero (1999). The upper panel shows the results of experiments at constant HA concentrations of zero (open points) or 0.6 mg L<sup>-1</sup> (closed points). The lower panel shows results at pH 8. The lines are fits with Model VI (see text).

small colloidal particles. The experimental results are shown in Figure 4, together with Model VI fits. The model was applied by calculating concentrations of inorganic Fe(III) species in the filtrates containing HA, i.e., by calculating the distribution of Fe between inorganic and organic forms. The calculated total inorganic Fe(III) concentrations were compared with the measured values from separate experiments in which HA was absent; these concentrations are assumed to be the same in the presence or absence of HA. The value of  $K_{MA}$  was adjusted to minimize the sum of squared differences between the observed and calculated inorganic Fe concentrations. The best fit for the data at constant HA concentration was obtained with  $\log K_{MA} = 2.4$ . For the constant pH set, the optimized value was 2.3. The model therefore provides a good description of the experimental data, with optimized  $\log K_{MA}$  values slightly lower than the default value of 2.5 (Table 1).

Figure 5 shows the effect of Fe(III) on the binding of Cu by humic acid at pH 4, determined in the present study. The ranges of  $\nu$  and  $[Cu^{2+}]$  cover substantial ranges, and especially the range of low-occupancy binding where the “strong” sites are dominant. A significant competitive effect by Fe(III) is observed. The model was applied by finding the values of  $K_{MA}$  for Cu and Fe(III) that gave the smallest sum of squared residuals in  $\log [Cu^{2+}]$ . The optimal  $\log K_{MA}$  for Cu was 1.82, which is close to the default of 2.0. The optimal  $\log K_{MA}$  for

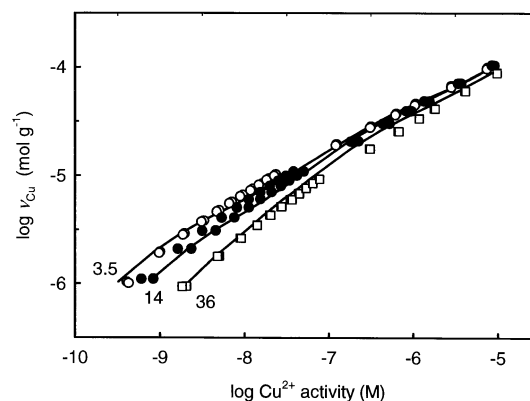


Fig. 5. Competition by Fe(III) for Cu binding by HA, pH 4,  $I = 0.1$  M. The figures next to the plots indicate the ratios of Fe(III) to HA in  $\mu\text{mol g}^{-1}$ . Points are experimental observations; lines are Model VI fits (see text).

Fe(III) was 2.6. The ion activity products ( $a_{Fe^{3+}}/a_{H^+}^3$ ) are calculated to be no greater than  $10^{1.7}$  for any of the solutions, so it can be assumed that there was no precipitation of  $Fe(OH)_3$ . The good simulation of the Fe–Cu competition experiments provides further support for the basic model assumption that the metals share sites in humic matter.

#### 4.3. Revised Default Values of $K_{MA}$ for Al and Fe(III)

The fitting exercises described above provide additional values of  $\log K_{MA}$  for both Al and Fe(III), and these can be used to revise the default values. For Al, combining previous and new estimates yields a  $\log K_{MA}$  for HA of 2.6 ( $n = 3$ , standard deviation = 0.2), while the value for FA is unchanged at 2.5 ( $n = 2$ , sd = 0.1). For Fe(III), we obtain values of 2.4 ( $n = 2$ , sd = 0.1) for HA and 2.6 ( $n = 2$ , sd = 0.2) for FA. The revised defaults are used in all subsequent calculations in this paper, except where  $K_{MA}$  is adjusted in order to perform data fitting.

#### 4.4. Al Speciation in Freshwater Samples

Tipping *et al.* (1991) assembled field data on Al speciation from 12 locations in Europe and North America, a total of 108 samples. The data covered wide ranges of pH (3.9–7.3),  $[Al]_{total}$  (0.1–26  $\mu\text{M}$ ) and  $[DOC]$  (0.3–28 mg L<sup>-1</sup>). They were reanalyzed in the present work, together with eight additional data points taken from Sutheimer and Cabaniss (1997). The model was applied in three ways. First, it was assumed that all DOC in the samples had the ion-binding properties of isolated HS, with default parameters. Second, default parameters were used, and the fraction of DOM due to HS was adjusted to achieve the best agreement between measured and calculated concentrations of organically bound Al,  $[Al_{org}]$ , by minimizing the root mean squared difference. Third, all the DOC was ascribed to HS, and the  $K_{MA}$  value for Al was adjusted to achieve the best agreement, while maintaining all other model parameters at their default values. The calculations were performed assuming (a) all the HS to be FA and (b) the HS to be

Table 2. Aluminium speciation in 116 natural water samples, described with WHAM/Model VI. The root mean squared deviations (RMSD) refer to differences between observed and calculated organically bound monomeric Al. See Sec. 4.4 and Fig. 6. Optimized values are in bold; when  $K_{MA}$  values for both FA and HA were adjusted, the difference in  $\log K_{MA}$  was maintained at 0.1, as found for isolated humic matter (Sec. 4.3). Values marked with an asterisk were obtained assuming that the species  $Al_2(OH)_2^{4+}$  could form (cf. Sec. 2.1).

FA:HA	$\log K_{SO,25}$ Fe(OH) <sub>3</sub>	% DOC is HS	$\log K_{MA}$ for Al		RMSD $\mu M$
			FA	HA	
1:0	2.5	100	2.5		1.61
		<b>61</b>	2.5		1.06
		<b>63</b>	2.5		1.07
		100	<b>2.1</b>		0.92
1:0	4.0	100	2.5		1.35
		<b>69</b>	2.5		0.99
		<b>70*</b>	<b>2.5</b>		1.00
		100	<b>2.2</b>		0.93
0.8:0.2	2.5	100	2.5	2.6	1.56
		<b>63</b>	2.5	2.6	1.09
		100	<b>2.1</b>	<b>2.2</b>	0.94
0.8:0.2	4.0	100	2.5	2.6	1.34
		<b>70</b>	2.5	2.6	1.01
		100	2.2	2.3	0.94

80% FA and 20% HA, and two solubility products for Fe(OH)<sub>3</sub> were assumed. The results are shown in Table 2.

The fact that versions of the model, calibrated as described above, can explain a considerable amount ( $r^2 \sim 0.75$ ) of the variation in  $[Al_{org}]$  suggests that the DOM in the field samples behaves similarly to isolated humic matter in terms of ion binding. The optimizations improve the agreement between observed and calculated values, and this is achieved either by decreasing the amount of material available to bind the metal, or by weakening the binding affinity. The better agreements obtained without optimization when  $\log K_{SO,25}$  for Fe(OH)<sub>3</sub> is increased from 2.5 to 4.0 occur because this effectively decreases the affinity of the organic matter towards Al. The results in Table 2 also show that including the dimerization reaction, to form  $Al_2(OH)_2^{4+}$ , has relatively little effect on the calculation of organic complexation of Al.

The conclusion that natural water DOM as a whole binds metals either less extensively or less strongly than isolated humic matter has been drawn previously from Cu binding studies (Cabaniss and Shuman, 1988; Dwane and Tipping, 1998), and from application of a forerunner of WHAM/Model VI to the present Al data set and to ionic charge balance data (Tipping et al., 1991). Possible explanations are (1) the DOM consists partly of "active" humic matter and partly of material that is inert with respect to ion binding; (2) isolated HS are to some extent unrepresentative of natural DOM, perhaps because of alterations during isolation; (3) the model description of competition reactions is inadequate. It is not possible, on the basis of the present results, to make a definitive judgement. However, it can be noted that, with regard to goodness-of-fit, Tipping et al. (1991) showed that most, if not all, of the RMSDs could be due to analytical uncertainties in model input data, and in measured values of  $[Al_{org}]$ , which implies that model improvements would not lead to better fits. The adjustment of  $K_{MA}$  for Al, while maintaining all other parameters at their default values, is unsatisfactory, since it means abandoning the

interparameter relationships established from analysis of experimental data for isolated HS. Furthermore, it is known that DOC does not consist entirely of humic matter (Thurman, 1985). For these reasons, it seems preferable to calibrate the model by adjusting the fraction of DOC that consists of "active" HS. This approach leads to "active" HS fractions between 61% and 70% of DOC, depending upon assumptions about the FA:HA ratio and the value of  $\log K_{SO,25}$  for Fe(OH)<sub>3</sub>. These fractions easily represent the majority of the organic matter. Results for one of the cases are plotted in Figure 6.

#### 4.5. Fe(III) Binding by DOM in Freshwater Samples

Tipping et al. (1982) carried out kinetic analysis (see Introduction) on a centrifuged surface water sample from Esthwaite Water, a soft water lake of pH 7.1. They estimated that 30% of the Fe(III) (total concentration 0.40  $\mu M$ ) in a filtered sample was in a form that reacted at a rate compatible with that of Fe-organic complexes, while the other 70% was attributed to iron oxides. The concentration of dissolved HS was 2.0 mg l<sup>-1</sup>. Therefore  $v_{Fe} = 6.0 \times 10^{-5}$  mol g<sup>-1</sup>. Applications of WHAM / Model VI to this water sample, assuming all the HS to be FA, are summarized in Table 3. With default values of  $\log K_{MA}$  for Al and Fe, and  $\log K_{SO,25}$  set to 8.0 and 4.0 for Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub>, respectively, the calculated value of  $v_{Fe}$  is quite close to the observed value, and exact agreement can be obtained by slightly increasing  $\log K_{MA}$  for Fe to 2.62. If a higher solubility product is assumed for Al(OH)<sub>3</sub>, a correspondingly higher value of  $\log K_{MA}$  for Fe (2.72) is required to achieve the same degree of fit.

The same approach was applied to a filtered (0.2  $\mu m$ ) sample of Tjeukemeer, a hard water lake. Sojo and De Haan (1991) reported that 60% of the 2.1  $\mu M$  Fe(III) in a filtered sample of the lake water (pH 6.4) was complexed by organic matter. The computed value of  $v_{Fe}$  is  $1.1 \times 10^{-4}$  mol g<sup>-1</sup> if it is assumed that 65% of the DOC is due to FA (cf. Sect. 4.4). The model

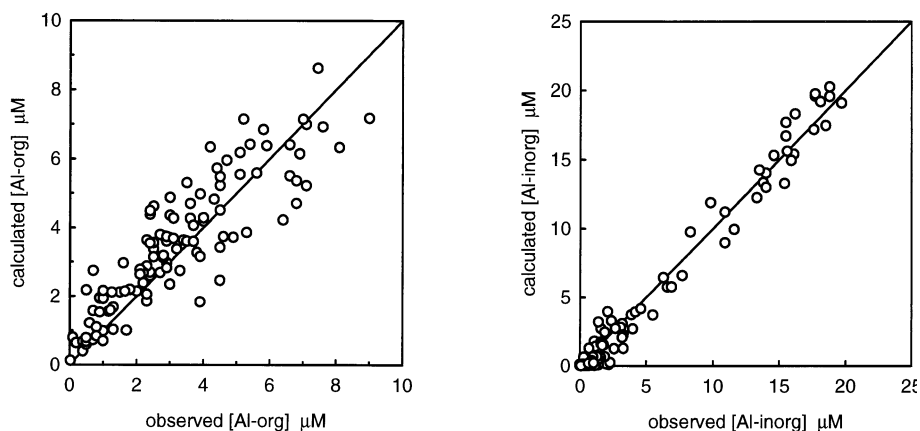


Fig. 6. Aluminium speciation in freshwaters (pH 3.9–7.3); comparisons of observed concentrations of organic (left hand panel) and inorganic (right hand panel) Al with values calculated using WHAM/Model VI. The results were obtained assuming  $\log K_{\text{so},25}$  for  $\text{Fe}(\text{OH})_3$  to equal 4.0, and 69% of the DOC to consist of FA (see Sect. 4.4).

constants required to match the Tjeukemeer observations are similar to those for Esthwaite Water (Table 3).

The results from the two samples studied provide similar model “fits.” The exercise illustrates the degree of uncertainty that exists with respect to modelling Fe(III) complexation by dissolved organic matter. However, the required parameter values are within the ranges that can be deemed allowable, based on available information. Very similar results were obtained if the humic matter was assumed to consist of 80% FA and 20% HA.

To gain further insight into Fe(III) speciation in natural waters, we applied WHAM/Model VI to field data collected for UK freshwaters, in which the concentration of filterable Fe(III) was determined (Sect. 3.4). This filterable Fe(III) is taken to comprise truly dissolved Fe(III), present almost entirely as organic complexes, together with colloidal  $\text{Fe}(\text{OH})_3$ . Monomeric Al was also determined, and taken to be a measure of the concentration of truly dissolved metal, making assumptions

about  $\text{Al}(\text{OH})_3$  solubility unnecessary. The activity of  $\text{Fe}^{3+}$  was assumed to be controlled by the equilibrium with  $\text{Fe}(\text{OH})_3$  ( $\log K_{\text{so},25} = 2.5$  or 4.0). The “active” organic binding component was assumed to be FA, concentrations of which were estimated from [DOC] using the percentages given in Sect. 4.4. The results of the calculations (Table 4) suggest that the fraction of organically complexed Fe(III) tends to decrease with pH, from values near to 1.0 at  $\text{pH} \approx 4$  to 0.1 or less at  $\text{pH} \sim 7$ . According to the solubility control model, values greater than 1.0 are impossible, since they mean that the calculated concentration of organically complexed Fe(III) exceeds the total measured concentration. In the few cases (one for  $\log K_{\text{so},25} = 2.5$ , three for  $\log K_{\text{so},25} = 4.0$ ) where the fraction is equal to or greater than 1.0, solubility control by  $\text{Fe}(\text{OH})_3$  may therefore not be operating. The calculated values of  $\nu_{\text{Fe}}$  in Table 4 are generally lower than those estimated by kinetic analysis (see above). This reflects the relatively high activities of  $\text{Al}^{3+}$ , corresponding to  $\log K_{\text{so},25}$

Table 3. Measured and modelled speciation of Fe(III) in surface lake waters. Concentrations of major ions required for the model calculations were taken from Sutcliffe *et al.* (1982) for Esthwaite Water, and from De Haan and Voerman (1988) and De Haan *et al.* (1990) for Tjeukemeer.

$\log K_{\text{so},25}$ $\text{Al}(\text{OH})_3$	$\log K_{\text{so},25}$ $\text{Fe}(\text{OH})_3$	$\log K_{\text{MA}}$ $\text{Fe}(\text{III})$	$\nu_{\text{Fe}}$ (calc) $\mu\text{mol g}^{-1}$	Fraction Fe-org (calc)
Esthwaite water (Tipping <i>et al.</i> , 1982) Observed $\nu_{\text{Fe}} = 60 \mu\text{mol g}^{-1}$ ; observed fraction of Fe(III) as organic complexes = 0.30				
8.0	2.5	2.6	11	0.05
	4.0	2.6	50	0.27
	4.0	2.62	58	0.31
9.0	2.5	2.6	5	0.03
	4.0	2.6	28	0.16
	4.0	2.72	61	0.32
Tjeukemeer (Sojo and De Haan, 1991) Observed $\nu_{\text{Fe}} = 110 \mu\text{mol g}^{-1}$ ; observed fraction of Fe(III) as organic complexes = 0.60				
8.0	2.5	2.6	12	0.07
	4.0	2.6	62	0.33
	4.0	2.69	110	0.59
9.0	2.5	2.6	6	0.03
	4.0	2.6	34	0.19
	4.0	2.79	110	0.59



Table 4. Fe(III) speciation in moderate-to-high [DOC] waters of northern England. The concentrations of Al and Fe are in  $\mu\text{M}$ , those of DOC in  $\text{mg L}^{-1}$ . Values of  $\nu$  are  $\mu\text{moles}$  of metal bound per g FA, and "frctn" is the fraction of Fe(III) calculated to be present as organic complexes (values  $> 1.0$  are in parentheses). Values of  $\log K_{\text{MA}}$  for Al and Fe were set to the defaults of 2.5 and 2.6, respectively (Sect. 4.3). The values of  $\log K_{\text{so},25}$  refer to  $\text{Fe}(\text{OH})_3$ . The temperature was assumed to be  $10^\circ\text{C}$  in all cases.

Site	NGR <sup>a</sup>	Fe(III)	pH	Al	DOC	$\log K_{\text{so},25} = 2.5$			$\log K_{\text{so},25} = 4.0$		
						$\nu_{\text{Al}}$	$\nu_{\text{Fe(III)}}$	frctn	$\nu_{\text{Al}}$	$\nu_{\text{Fe(III)}}$	frctn
Whitray Beck	SD 683 609	4.1	4.0	3.0	20.0	120	220	[1.3]	100	770	[6.6]
Pool X #1	NY 714 315	1.9	4.9	4.2	8.7	390	59	0.22	350	280	[1.3]
Pool X #2	NY 714 315	5.6	5.3	10.0	31.8	260	47	0.18	230	230	1.0
Pool Y #1	NY 714 315	2.1	6.3	4.3	23.7	150	18	0.09	130	89	0.50
Pool Y #2	NY 714 315	0.6	6.4	1.9	7.7	200	11	0.09	180	61	0.54
Coalburn	NY 694 777	1.1	6.9	5.9	11.5	390	3.2	0.04	360	25	0.35
Roudsea Wood	SD 330 828	4.2	7.2	32.0	26.7	520	0.6	0.005	500	6.1	0.05
River Tees at Whorlton Lido	NZ 106 145	3.1	7.6	1.0	9.3	76	4.9	0.02	67	27	0.11
River Tees at Stockton	NZ 459 191	3.0	7.7	0.7	11.5	38	3.6	0.02	34	20	0.11

<sup>a</sup> National Grid Reference.

$\sim 9$ , calculated for the samples of Table 4, and the use of the default  $\log K_{\text{MA}}$  for Fe, rather than the slightly higher values needed to obtain agreement with the field speciation results (Table 3). The overall conclusion from this analysis is that filterable Fe(III) in natural waters is due to both colloidal  $\text{Fe}(\text{OH})_3$  and truly dissolved complexes with humic matter, the dominant form depending upon solution conditions, notably pH and [DOC].

#### 4.6. Simulated Binding of Al and Fe by DOM in Natural Waters

In the preceding two sections, model calculations were compared with field observations. Here, the intention is to simulate Al and Fe binding by DOM over solution conditions representing a range of freshwaters. Calculations were performed to simulate the titration with  $\text{Ca}(\text{OH})_2$  of initially acid solutions,

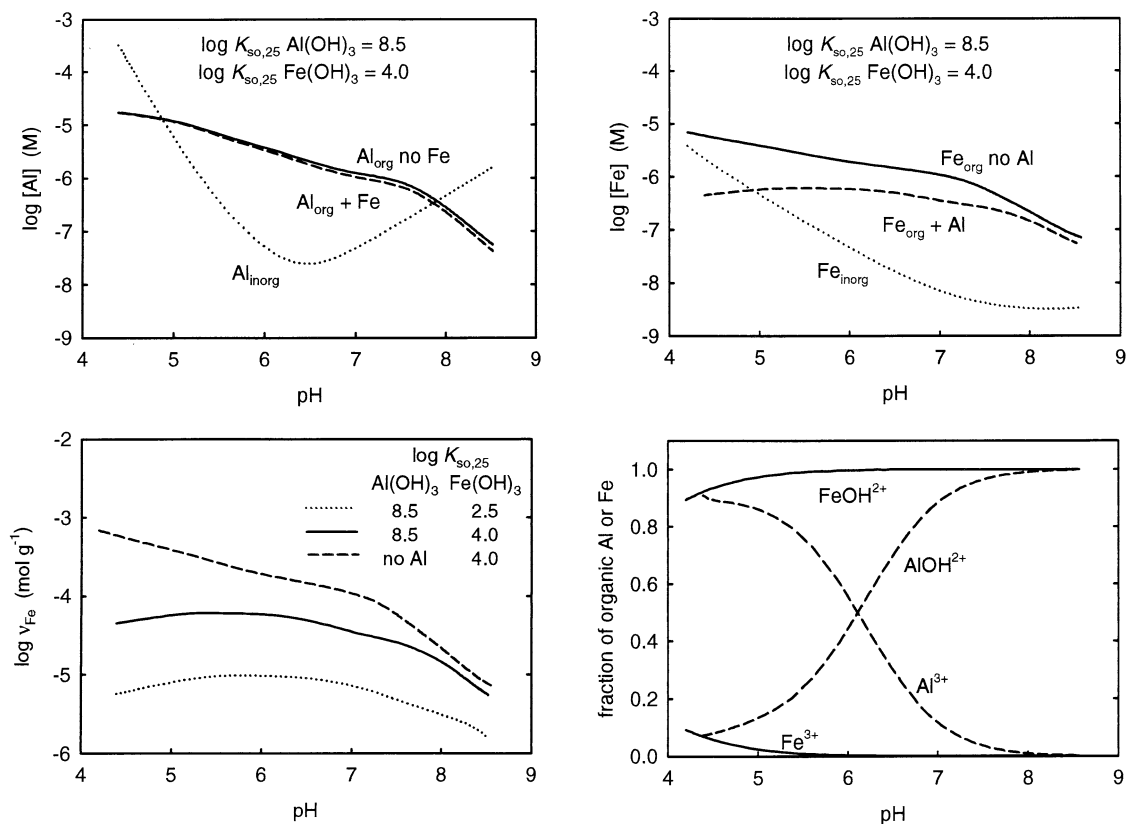


Fig. 7. Calculated binding of Al and Fe binding to FA, as function of pH. A temperature of  $10^\circ\text{C}$  was assumed. See Sect. 4.6 for explanation.

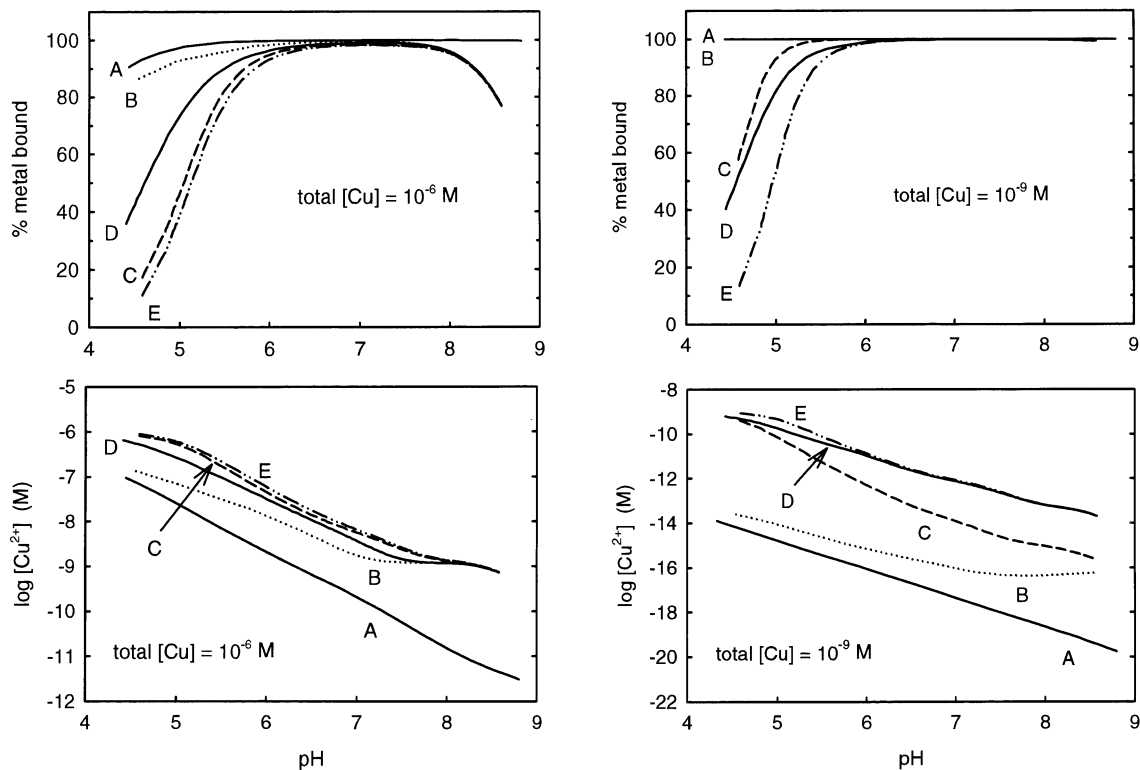


Fig. 8. Calculated binding of Cu by FA as a function of pH at 10 °C, in solutions of different composition with respect to Na, Ca, Al, and Fe. See Sect. 4.7 for explanation.

containing 10 mg L<sup>-1</sup> FA to represent freshwater dissolved organic matter, and in equilibrium with Al(OH)<sub>3</sub> and/or Fe(OH)<sub>3</sub>. All the solutions had  $p\text{CO}_2 = 0.0007$  atm. The additions of Ca(OH)<sub>2</sub> took the total Ca concentration to 0.003 M.

The upper panels in Figure 7 show the distributions of dissolved Al and Fe between inorganic and organic forms. For the chosen values of  $K_{\text{so},25}$ , organically bound Al in the absence of Fe is present at somewhat higher concentrations than organically bound Fe in the absence of Al. When both metals are present together, Fe has little effect on Al binding by organic matter, whereas Al substantially decreases the binding of Fe. Inorganic concentrations of Al exceed organic concentrations at low and high pH, whereas dissolved Fe is mainly in the organic form over the whole pH range considered. It should be noted that in many acid natural waters, Al is appreciably undersaturated with respect to Al(OH)<sub>3</sub> (see Sect. 2.2), so that the inorganic and organic concentrations of Al at low pH, shown in Figure 7, are likely to be too high. For the same reason, the competitive effect of Al towards Fe binding at low pH will tend to be overestimated. The bottom left-hand panel of Figure 7 shows how  $v_{\text{Fe}}$  depends upon the assumed  $K_{\text{so},25}$  value, on Al competition, and on pH. With  $\log K_{\text{so},25}$  values of 8.5 and 4.0 for Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub>, respectively, the total binding of Al and Fe(III) by FA is ca. 10<sup>-3</sup> mol g<sup>-1</sup> at pH 5, and 2 × 10<sup>-4</sup> mol g<sup>-1</sup> at pH 7. Thus, the two metals occupy ca. 30% and 5% of the total proton binding sites at the respective pH values.

Model VI assumes that humic matter can bind the free metal cations (Al<sup>3+</sup> and Fe<sup>3+</sup>) and also, with the same value of  $K_{\text{MA}}$ ,

their first hydrolysis products (AlOH<sup>2+</sup> and FeOH<sup>2+</sup>). The bottom right-hand panel of Figure 7 shows how binding of the two possible species of each metal varies with pH. For Al, the trivalent cation is the dominant form bound up to pH ~ 6, with AlOH<sup>2+</sup> becoming dominant at higher pH. For Fe, FeOH<sup>2+</sup> is the principal form of Fe bound under all pH values considered. The differences reflect the greater tendency of Fe(III) to hydrolyze.

Similar results to those shown here for solutions containing only FA as the humic component were found for solutions containing 80% FA and 20% HA.

#### 4.7. Simulated Effects of Al and Fe on the Binding of Trace Metals to Freshwater DOM

To explore the implications of Al and Fe binding for trace metal speciation in natural waters, WHAM/Model VI was used to simulate titrations with base at constant trace metal concentrations, and with metals at constant pH. Figures 8 and 9 show calculations for titrations of initially acid solutions containing 10 mg l<sup>-1</sup> FA, and either 1 μM or 1 nM Cu or Zn. All the solutions were at a partial pressure of CO<sub>2</sub> of 0.0007 atm. The titrations were as follows: A, additions of NaOH; B, additions of Ca(OH)<sub>2</sub>; C, additions of Ca(OH)<sub>2</sub>, solution in equilibrium with Al(OH)<sub>3</sub> ( $\log K_{\text{so},25} = 8.5$ ); D, additions of Ca(OH)<sub>2</sub>, solution in equilibrium with Fe(OH)<sub>3</sub> ( $\log K_{\text{so},25} = 4.0$ ); E, additions of Ca(OH)<sub>2</sub>, solution in equilibrium with Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub>. The point about the undersaturation of acid waters with respect to Al(OH)<sub>3</sub> (Sect. 4.6) applies here also; the

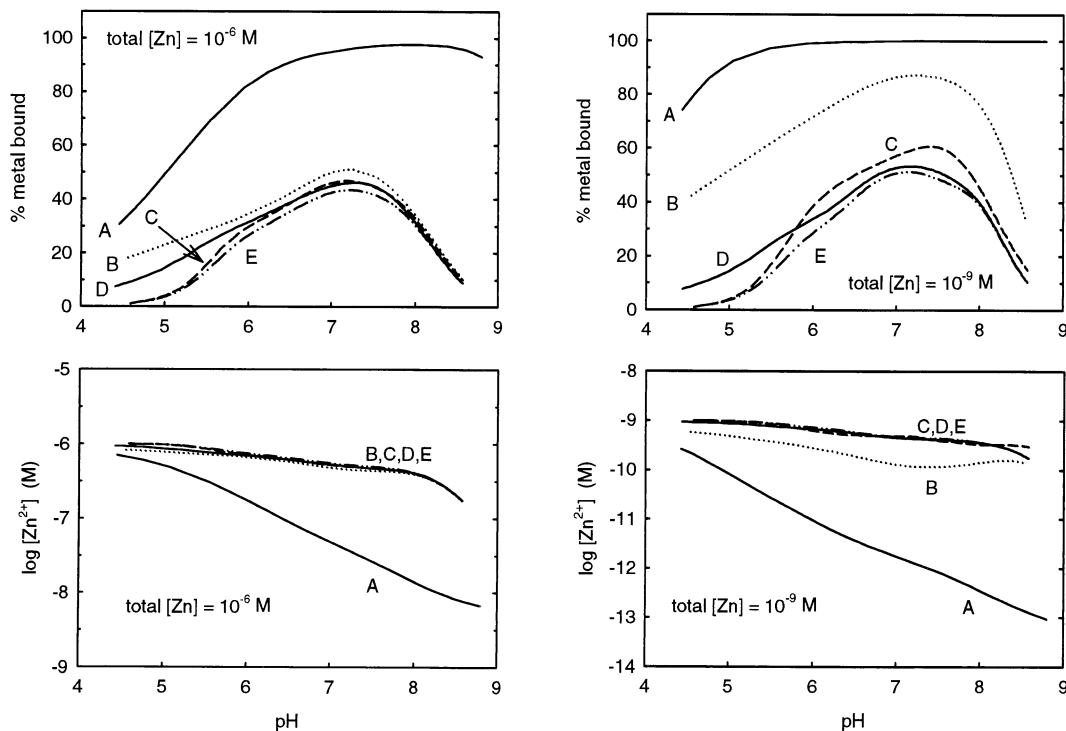


Fig. 9. Calculated binding of Zn by FA as a function of pH at 10 °C, in solutions of different composition with respect to Na, Ca, Al, and Fe. See Sect. 4.7 for explanation.

simulated competitive effects of Al at low pH should be regarded as maximal.

At a total Cu concentration of 1  $\mu\text{M}$  (Fig. 8, left-hand panels), binding by FA is maximal in titration A, and Ca exerts a competitive effect, in the absence of Al and Fe (titration B). Competition by Al further decreases Cu binding (titration C), to a greater extent than does Fe (titration D). When Al and Fe are both present (titration E), the binding curves are similar to the Al-only case. The effects of Al and Fe are reversed when the total Cu concentration is set to 1 nM (Fig. 8 right-hand panels). For titrations D and E at 1 nM Cu, the competitive effects are such that  $[\text{Cu}^{2+}]$  is ca. 5–6 orders of magnitude greater than in the NaOH titration.

Zinc binding by FA is much weaker than Cu binding, and at total Zn concentrations of both 1  $\mu\text{M}$  and 1 nM Ca is an effective competitor (Fig. 9). Aluminium and Fe decrease binding further, more so at 1 nM than 1  $\mu\text{M}$ . Because of the weak binding of Zn, competition effects are more evident in % metal bound, than the concentration of the free metal ion.

The results of calculations to simulate metal titrations at a constant pH of 7 are shown in Fig. 10. The binding isotherm for Cu is modestly affected by Ca, but strongly altered by Al and Fe, which drastically reduce the influence of the low-abundance high-affinity humic binding sites. As expected from the plots of Fig. 9, the isotherm for Zn (Fig. 10) is strongly affected by Ca, while Al and Fe add further modest competitive effects.

The above results refer to solutions in which the freshwater DOC that is active in metal binding is represented by isolated FA. Very similar patterns were obtained if the DOC was represented by a mixture of 80% FA and 20% HA.

## 5. DISCUSSION

Aluminium and iron have complex chemistries, and their binding reactions with humic substances have been subjected to relatively little experimental investigation. Humic substances themselves are complex and variable with respect to source. Consequently, our ability to predict equilibrium humic binding of Al and Fe in natural waters is imprecise. Nonetheless, the modelling results presented here, together with earlier findings, indicate a reasonably coherent picture of the interactions of the individual metals with humic matter, and of some competitive interactions involving trace metals (Cu, Cd, Eu, Pb). Thus, Model VI can account for the available information if some tolerance among examples is allowed in the values of the key parameter  $K_{MA}$ . The model can account approximately for field data on Al speciation, following calibration of the “activity” of DOM in terms of its HS content. The very limited field data for Fe(III) complexation by DOM do not permit a full calibration, but given reasonable assumptions, the model can be made to reproduce the observed values.

If it is accepted that the model has approximate validity, then the predictive calculations raise interesting issues in freshwater metal chemistry. First, it is evident that competition effects among metals can be highly significant in freshwaters. According to the calculations performed here, Al affects Fe(III) more than the reverse, but it would be premature to assume this always to be the case. Second, binding of Al and Fe by humic matter is expected to have strong effects on the binding of trace metals, exemplified in the present study by Cu and Zn. For the freshwater conditions considered here, the competition effects

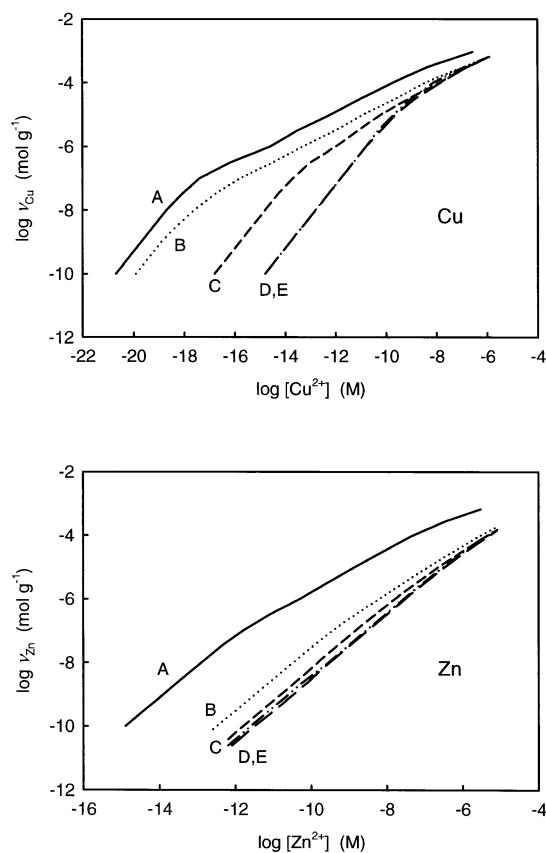


Fig. 10. Isotherms for the binding of Cu and Zn by FA at pH 7, 10 °C. See Sect. 4.7 for explanation.

are greater for the metal (Cu) with the higher affinity for humic matter (Figs. 8 and fig 10). Indeed, the isotherms of Figure 10 suggest that the low-abundance, high-affinity sites that have been demonstrated in isolated and purified humic matter (see, e.g., Benedetti *et al.*, 1995; Kinniburgh *et al.*, 1996) may be far less important under conditions prevailing in natural freshwaters. This being so, it is difficult to attribute the strong binding of metals such as Cu in some freshwaters (e.g., Xue and Sigg, 1993) to humic matter and related complexants, as Town and Filella (2000) recently have done. The alternative explanation, proposed by Xue and Sigg, is that the strong binding is by highly selective ligands, released by phytoplankton in order to control metal levels in their immediate environment. Similar conclusions have been drawn for the surface oceans (Bruland *et al.*, 1991). Our findings are compatible with the existence of the selective biogenic ligands.

This study has focused on solution interactions in systems assumed to be at equilibrium. In real natural waters, there are a number of additional factors. With regard to Fe(III) in particular, the equilibrium assumption can certainly be questioned, because of biologically or photochemically mediated redox cycling. In addition, the ageing of iron hydroxide colloids may lead to variations in their solubility product (cf. Sect. 2.2). Therefore, the equilibrium description of binding by humic substances and hydroxide precipitation is accurate only if these reactions take place rapidly compared to the redox and ageing

processes. With the same assumption, the present approach could deal with systems containing both Fe(II) and Fe(III). With regard to trace metal speciation, biogenic selective ligands have already been mentioned. In addition, binding by both colloidal and coarser particulate mineral surfaces may be significant in natural systems, and humic matter associated with colloids and particles may also be important. In principle, such interactions could be added to the present equilibrium analysis, using, for example, SCAMP (Lofts and Tipping, 1998) or CD-MUSIC (Weng *et al.*, 2001). These additional factors would need to be taken into account in order to obtain a full understanding of natural waters. Despite the simplifying approach, the work described here sets the role of humic binding in context, and contributes to a clarification of the theoretical basis of describing these complex systems.

A number of issues merit further investigation. Information about the binding of Al and, especially, Fe(III) by isolated humic substances—especially aquatic samples—remains sparse, and competition studies for solution conditions representative of natural waters are much needed. Future work should pay close attention to the Al and Fe(III) contents of the humic samples. With regard to measurements on natural waters, analytical capabilities for Al are reasonably good, since reliable speciation methods are available for dissolved forms of the metal (Driscoll, 1984; Seip *et al.*, 1984; Clarke and Danielsson, 1995; Sutherland and Cabaniss, 1995). There are several promising techniques for determining dissolved Fe(III) speciation, including complexation by humic substances. The kinetic approach was mentioned in Sec. 4.5. Other possibilities are the flow-injection technique of Pullin and Cabaniss (2001), the extraction method of Clarke and Danielsson (1995), and filtration methodology (e.g., Ross and Sherrell, 1999). An important next step is to apply some or all of these to natural waters, and to compare the results with model predictions, including competition effects.

Although the work described here has focused on metal binding to humic matter in freshwaters, the principles must apply to other environmental situations. Thus, competition by Al and Fe may be important for organic matter in seawater, soils and sediments, and also for interactions of metals with mineral surfaces. Understanding competition reactions in complex systems is essential if the large body of laboratory-based knowledge about complexation and adsorption reactions is to be applied to the natural environment.

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