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Metal Ion Binding by Humic Acid: Application of the NICA-Donnan Model

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A Donnan-type model for nonspecific binding of electrolyte ions has been combined with the non-ideal competitive adsorption (NICA) model for specific binding to produce a model for ion binding to humic substances. The model considers site heterogeneity, non-ideality, multicomponent competition, and electrostatic interactions. The NICA-Donnan model was fitted to data for H, Ca, Cd, Cu, and Pb binding by a purified peat humic acid. The model fits were good and covered a wide range of pH and free metal concentrations. The parameters from these single metal data sets were then used to predict the competitive effect of Ca on Cd and Cu binding at various pHs. These predictions agreed well with the experimental data although there were some small but systematic differences. The new NICA-Donnan model also predicted reasonably well the increase in Cd and Cu binding on changing from a 0.1 M KNO₃ background electrolyte to 0.01 M KNO₃. A shortcoming of the model is that in some cases it significantly underestimated the H⁺/M²⁺ exchange ratio, especially at high pH and for Cu binding.

Introduction

Humic substances (humics) are present in most natural waters at concentrations of 0.1–200 mg L⁻¹ dissolved

organic carbon (DOC). Solid organic matter is also found in soils and sediments at concentrations of 0.1–10% by weight. These humic substances bind a variety of metal ions and typically contain 2–10 equiv kg⁻¹ of ionizable groups. The binding of protons and metal ions to these substances is important for the speciation, transport, and toxicity of many trace metals, but it has proven difficult to find equations that describe this binding over a wide range of conditions.

Factors that need to be considered are as follows: (i) individual humics show intrinsic chemical heterogeneity on a molecular scale; (ii) the bound ions compete for binding sites; (iii) there are electrostatic interactions between the bound ions and the binding sites and among the bound ions; and (iv) humics from diverse sources have common properties and behavior but also show important differences that need to be characterized and specified. It is likely that the ability to describe competitive metal binding will prove to be a particularly important test of the various models (1–3).

A large number of models for ion binding by humics exist, but many of these have limited scope or are unduly sensitive to moderate extrapolation. In terms of scope, Model V of Tipping and Hurley (4) probably comes closest to being a comprehensive model that can describe ion binding by a range of humics. It allows for eight different types of sites, some of which are close enough together to behave as bidentate sites, and uses a simple electrostatic model to differentiate between generic Coulombic binding and specific binding. Model V has also been used to describe metal-metal competition (2). Model V assumes that the metal ion affinities are directly related to the proton affinities, i.e., the shapes of the implied affinity distributions for the metal ions are the same as for the proton except that they are "shifted" by an amount specified by each of the metal-binding parameters. We have recently demonstrated that this "fully coupled" assumption is not very successful when applied to calcium and cadmium binding over a wide range of concentrations (5). Model V also contains an inconsistency in the development of the electrostatic model. This is discussed later.

The non-ideal competitive adsorption (NICA) model (6, 7) attempts to separate those effects due to the generic heterogeneity experienced by all ionic species from those effects arising from effects specific to each particular ion. We have recently applied the NICA model to cation binding by a fulvic acid (6), to a purified peat humic acid (7), to soil organic matter (8), and to metal ion binding by soils and lake water (9). Our primary data are for a purified peat humic acid (PPHA) with the binding experiments carried out in a high and constant concentration of background electrolyte (0.1 M KNO₃). Our earlier analysis did not consider the effect that any change in ionic strength would have.

The effect of changes in background electrolyte can be described in terms of electrostatic models. Various approaches to the electrostatics have been adopted (Table 1). These range from numerical solutions of the Poisson-Boltzmann equation for spherical- and cylindrical-shaped particles (1, 10, 11) to Donnan models in which the humic material is treated as if it is a distinct, electrically neutral

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TABLE 1

Comparison of the Approaches Used in Some Models for Metal Ion Binding by Humic Substances

	NICA-Donnan [this paper]	fully coupled electrostatic [Milne <i>et al.</i> (5, 17)]	Model V [Tipping & Hurley (4); Tipping (14)]	oligoelectrolyte model [Bartschat <i>et al.</i> (7)]	polyelectrolyte model [Barak and Chen (38)]	polyelectrolyte model [Ephraim and Marinsky (39)]
type of binding	monodentate	monodentate	monodentate + bidentate	monodentate	monodentate	monodentate + bidentate (bidentate recognized but not formulated)
heterogeneity local isotherm	Henderson–Hasselbalch/Rudzinski	Langmuir	Langmuir	Langmuir	Langmuir	Langmuir
affinity distribution	continuous, bimodal quasi-Gaussian (Sips)	continuous, bimodal quasi-Gaussian (Sips)	bimodal, discretized	discrete: 3 sites for protons, 2 for Cu	more than a single type of group	three major sites + one minor site for H ⁺ binding
particle shape and size	not considered	cylindrical; single equivalent radius	not considered	two size classes of spheres	cylinders; radius varies with charge	not considered
electrostatics	Donnan	Poisson-Boltzmann eq for cylinders	Donnan	Poisson-Boltzmann eq for spheres	Poisson-Boltzmann eq for cylinders	Donnan (but obscure)
critical parameters	Donnan volume	equivalent radius of cylinder	empirical <i>P</i> factor relating proton charge to ionic strength	relationship between charge and the electrostatic (Boltzmann) factor	equivalent radius of cylinder	1 M curve

phase (12). All approaches are necessarily rather simplistic, but bearing in mind the other complexities, this is probably an advantage rather than a disadvantage. The Donnan approach is computationally simple since it does not involve the solution of the Poisson–Boltzmann equation. So far it appears to work well. In particular, it can account for the near-parallel nature of the proton titration curves at different ionic strengths, a feature often observed with humics (3, 4, 10–12).

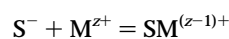
Our aims are therefore to (i) outline the NICA-Donnan model; (ii) fit the NICA-Donnan model to some of our earlier data for single metal binding at various pHs and in a 0.1 M KNO₃ background medium; (ii) use the parameters derived from this fitting plus the set of already published proton binding parameters for the same humic acid to predict the effect of Ca on Cd and Cu binding over a range of pHs; (iii) compare these predictions with some new experimental data showing the extent of this competition; and (iv) predict and measure Cd and Cu binding at a lower ionic strength (0.01 M KNO₃) to see how well the model can cope with changes of ionic strength.

The NICA-Donnan Model

General Approach. Cation binding to humics is assumed to occur through specific interactions between the cation and negatively charged surface functional groups and by nonspecific Coulombic binding to any residual negative charge. The specific binding is described by the NICA model, and the nonspecific binding is described by the Donnan model.

Non-Ideal Competitive Adsorption (NICA) Model. It is now widely accepted (3, 6, 13–15) that the specific binding can only be described over a wide range of conditions if a distribution of affinity constants is assumed. Some prefer a discrete distribution with from two to eight or more sites while others prefer a continuous distribution. The NICA model implicitly assumes a continuous distribution of site affinities. The NICA model makes a significant departure from earlier models in that it allows the affinity distributions for the proton and the various metal ions not only to have different median affinities for each ion, as reflected by shifts of the various distributions along the affinity axis, but also to have ion-specific nonideality or heterogeneity. A detailed discussion of the underlying foundations of the NICA model is given elsewhere (6). The electrostatic effects are incorporated into the NICA model by using the concentration of ions near the binding sites rather than concentrations in the bulk solution.

In the following discussion, proton and metal ion binding to a negatively charged site of type S are assumed to follow the reactions:



where M^{z+} is a cation of charge z+; S[−], SH⁰, and SM^{(z−1)+} are surface species. These reactions imply monodentate binding to all of the sites, i.e., one cation per site. For simplicity at this stage, we do not consider bidentate binding. Under the assumptions of congruency of the distribution functions for H⁺ and M²⁺ and within the NICA

model, the total fractional surface coverage of component i , $\theta_{i,T}$, is then given by the following integral equation:

$$\theta_{i,T} = \int_{\Delta \log K_i} \theta_{i,L} f(\log K_i) d(\log K_i) \quad (2)$$

where $f(\log K_i)$ is the distribution function of the affinity constant, K_i , $\theta_{i,L}$ is the local adsorption isotherm, i.e., the isotherm for binding of ion i to a group of identical sites, and $\Delta \log K_i$ is the range of $\log K_i$ considered. This equation can be solved analytically for certain distributions in combination with certain local isotherms. It has also been extended to multicomponent systems (6, 16–18). By separating the non-ideality into an intrinsic heterogeneity part applicable to all ions and an ion-specific part applicable to each individual ion, Koopal *et al.* (6) have derived the monomodal form of the NICA equation:

$$\theta_{i,T} = \frac{Q_i}{Q_{\max}} = \frac{(\bar{K}_i c_{D,i})^{n_i}}{\sum_j (\bar{K}_j c_{D,j})^{n_j} 1 + \{\sum_j (\bar{K}_j c_{D,j})^{n_j}\}^p} \quad (3)$$

where Q_i is the total amount of component i bound to the humic acid in mol kg⁻¹, Q_{\max} is the number of sites in mol kg⁻¹, \bar{K}_j is the median affinity constant for component j , and $c_{D,j}$ is the local concentration of j near the binding sites in mol L⁻¹. The various summations are over all j components (including H^+). This includes the proton and all metal ions present. The relationship between the concentration of j in the aqueous phase (c_j and $c_{D,j}$) is determined by a Boltzmann factor, which depends on the local electrostatic potential in the humic phase. $c_{D,j}$ is calculated by using a Donnan-type model (see below).

The exponents n_i and n_j in eq 3 are ion-specific and account for any “non-ideal” behavior. For ion adsorption, n takes values $0 < n \leq 1$; the smaller the value of n , the greater the non-ideality. This ion-specific non-ideality can be most easily observed from the slope of a plot of log-bound metal ion vs log free metal ion concentration at trace concentrations (7). p represents the generic or intrinsic heterogeneity of the humic material and is common to all components. It also takes the value $0 < p \leq 1$. The smaller the value of p , the greater the heterogeneity. The value of p cannot be obtained from data for monocomponent binding alone since such data always reflect the combined effect of both the non-ideality and the generic heterogeneity and so can only give the product of $n_i \times p$. Therefore, a multicomponent set of binding data is needed to resolve n_i and p .

Where proton binding data are available over a wide range of pHs (pH 3.5–10.5), the data are consistent with a bimodal distribution of proton affinities for both humic acid and fulvic acid (11, 19). The bimodal distribution is composed of two independent distributions. These two distributions are considered to be due to phenolic- and carboxylic-type groups although other groups such as, for example, alcohols, ethers, and bidentate sites are also likely to be included in these distributions. The NICA model can

be easily extended to reflect this

$$Q_i = Q_{\max 1} \frac{(\bar{K}_{i,1} c_{D,i})^{n_{i,1}} \{\sum_j (\bar{K}_{j,1} c_{D,j})^{n_{j,1}}\}^{p_1}}{\sum_j (\bar{K}_{j,1} c_{D,j})^{n_{j,1}} 1 + \{\sum_j (\bar{K}_{j,1} c_{D,j})^{n_{j,1}}\}^{p_1}} + Q_{\max 2} \frac{(\bar{K}_{i,2} c_{D,i})^{n_{i,2}} \{\sum_j (\bar{K}_{j,2} c_{D,j})^{n_{j,2}}\}^{p_2}}{\sum_j (\bar{K}_{j,2} c_{D,j})^{n_{j,2}} 1 + \{\sum_j (\bar{K}_{j,2} c_{D,j})^{n_{j,2}}\}^{p_2}} \quad (4)$$

where the subscripts 1 and 2 refer to the carboxylic- and phenolic-type parts of the distribution, respectively. With a mixture of specifically-bound divalent cations, M^{2+} , the total number of sites is given by the sum of the concentration of all the surface species

$$Q_{\max 1} = Q_{\text{ref } 1} + Q_{H1} + \sum Q_{Mj,1} \quad (5)$$

$$Q_{\max 2} = Q_{\text{ref } 2} + Q_{H2} + \sum Q_{Mj,2}$$

where the subscripts 1 and 2 refer to the two-component distributions, Q_{ref} is the number of sites in the reference state, S^- (free of bound ions), Q_H is the number of protonated sites, and $\sum Q_{Mj}$ is the number of sites occupied by divalent cations. $Q_{\max 1}$, $Q_{\max 2}$, Q_{H1} , and Q_{H2} can be estimated from an acid–base titration over the range pH 3.5–pH 10.5 and $Q_{Mj,1}$ and $Q_{Mj,2}$ can be estimated from metal-binding isotherms over a broad range of concentrations. Once the site occupancies have been established, the net charge of the particle, q (in equiv kg⁻¹) is given by the charge contributions from the various surface species of the two distributions with

$$q_1 = -Q_{\max 1} + Q_{H1} + 2 \sum Q_{Mj,1} \quad (6)$$

$$q_2 = -Q_{\max 2} + Q_{H2} + 2 \sum Q_{Mj,2}$$

$$q = q_1 + q_2 \quad (7)$$

This net charge gives rise to a local electrostatic potential, which tends both to attract oppositely charged ions and to exclude coions.

The Donnan Model for Nonspecific (Coulombic) Binding. In the Donnan approach, the humic material is considered to behave as an electrically neutral phase having a particular volume throughout which there is a uniform, averaged electrostatic potential known as the Donnan potential, ψ_D . While such a concept is undoubtedly idealistic, it is not entirely unreasonable. Humic substances have a three-dimensional structure (20) and have many properties in common with polyelectrolyte gels for which the Donnan model has been widely applied (21). The volume of the Donnan phase can also be related to the swelling properties of humic suspensions (12).

The electroneutrality condition is given by

$$q/V_D + \sum z_j (c_{D,j} - c_j) = 0 \quad (8)$$

where q is the net charge of the humic substance (equiv kg⁻¹), eq 7, V_D is the volume of water in the Donnan phase (L kg⁻¹), $c_{D,j}$ are the molar concentrations of the various cations and anions present in the Donnan phase, and z_j refers to their charge, including sign. Note that the binding

in the Donnan phase has been written as an excess quantity, i.e., there is no net binding in the Donnan phase at zero charge. The $c_{D,j}$ can be related to their concentrations in the bulk solution, c_j , by a Boltzmann factor, χ :

$$c_{D,j} = \chi^z c_j \quad (9)$$

The Boltzmann factor is related to the Donnan potential by

$$\chi = \exp(-e\psi_D/kT) \quad (10)$$

where e is the charge on the electron, k is Boltzmann's constant, and T is the absolute temperature. Knowing (i) the Donnan volume; (ii) the bulk solution concentrations of all the ions present, and (iii) the appropriate NICA isotherm parameters, it is possible to solve eqs 4–10 simultaneously to give the Boltzmann factor, and thereby the amount of binding of each ion, and the Donnan potential. We have used Brent's method (22) for this.

The Donnan model described above has only a single unknown parameter, the Donnan volume, but a critical aspect of the model is how the Donnan volume varies, or does not vary, with changes in solution chemistry. Benedetti *et al.* (12) discussed this point in some detail and concluded that the Donnan volume is most sensitive to changes of ionic strength. It does not appear to vary greatly with changes of pH. Although there is not yet sufficient data to say how it varies with the concentration of specifically bound metals such as Cu^{2+} , we have assumed that it does not vary significantly. This is probably a reasonable assumption at trace concentrations where the surface coverage of the metal is low but not at high concentrations where significant charge reduction takes place and where macroscopic changes such as flocculation can be seen. Most of our data are for low metal concentrations where these effects are likely to be small. The variation of Donnan volume with ionic strength, I , for various humic substances is assumed to follow the following empirical relation (see Figure 4 of Benedetti *et al.* (12)):

$$\log V_D = b(1 - \log I) - 1 \quad (11)$$

where the coefficient b varies with the type of humic substance. For humic acids, $b \approx 0.43$, which gives the following V_D 's (in L kg^{-1}): 1.95 (0.01 M), 1.22 (0.03 M), and 0.72 (0.1 M).

Total Amount of Metal Bound. The parameter most frequently measured experimentally is the total amount of metal ion i bound, $Q_{M,i,T}$ (in mol kg^{-1}), which is given by the sum of the specifically bound metal ion and the amount of metal ion bound in the Donnan phase. For a specifically-bound metal ion i :

$$Q_{M,i,T} = Q_{M,i} + V_D(c_{D,i} - c_i) \quad (12)$$

Data Acquisition

All of the data discussed below refer to the same purified peat humic acid (PPHA) (11). The measurements were made at 25.0 ± 0.1 °C in a N_2 atmosphere.

Existing Data. Data for the binding of Ca (pH 6, 8, and 10), Cd (pH 4, 6, and 8), and Cu (pH 4, 6, and 8) by PPHA in a 0.1 M KNO_3 medium were available from earlier studies (7, 11). The experiments were carried out at high solid/solution ratios, approximately 840 mg of PPHA L^{-1} , which enabled binding at very low free metal concentrations to

be measured. Proton binding data for PPHA over a range of ionic strengths were also available from Milne *et al.* (11) and have recently been re-analyzed according to the NICA-Donnan model by Benedetti *et al.* (12).

New Data. The following new data have been measured: (i) Cd binding by PPHA in 0.1 M KNO_3 at pH 10 using the same procedures as before. This extended the pH range covered and enabled us to see how well the NICA-Donnan model was able to extrapolate from the lower pHs; (ii) Pb binding by PPHA (0.03 M KNO_3 , pH 4.95) using a polarographic method to estimate free Pb concentrations (23); (iii) the effect of ionic strength on Cd (pH 4 and 6) and Cu (pH 4 and 8) binding in a 0.01 M KNO_3 background electrolyte; and (iv) metal–metal competition experiments (in 0.1 M KNO_3) carried out in two ways: (a) by titrating Ca into pH-statted systems containing 2.5×10^{-4} M Cd_T (pH 6 and 8) and monitoring the release of Cd as well as the binding of Ca (we will call these type 1 competition experiments); (b) by titrating Cd (pH 6, 8, and 10) or Cu (pH 4 and 6) into a pH-stated system containing 10^{-3} M Ca and monitoring the release of Ca as well as the binding of Cd or Cu (we will call these type 2 metal competition experiments). Type 1 experiments titrate a weakly bound ion into a system with a fixed total amount of a more strongly bound metal ion whereas type 2 experiments do the reverse.

All of the metal binding measurements except for Pb were made using ion-selective electrodes (ISEs) connected to an automatic titrator operating in pH stat mode (± 0.004 pH) (5, 11, 24). The metal standards for electrode calibration were made up in the appropriate background electrolyte, and the electrodes were calibrated directly in terms of free metal ion concentration. Proton and free metal ion concentrations, allowing for hydrolysis, were calculated using ECOSAT (25). In well-buffered systems, ISEs can be used down to very low free metal ion concentrations, e.g., with a humic concentration of 0.001 kg L^{-1} , at pH 8 and $\log [\text{Cu}_T] = -6$, $\log [\text{Cu}^{2+}] \approx -14$. Preliminary tests showed that with the free metal concentrations used in these metal–metal competition experiments, there was no interference between the added Ca and the readings on the Cd and Cu electrodes or from the much smaller concentrations of Cd and Cu on the Ca electrode.

Results and Data Analysis

Parameter Identification. The full NICA-Donnan model has a large number of parameters that need to be estimated. These were estimated using an unconstrained nonlinear least squares fitting program. The approach followed was:

(i) Convert all experimental data to log amount bound (in mol kg^{-1} PPHA) versus log free ion concentration (including H^+ concentration). In the case of the proton binding, the observed variable was the change in surface charge as a function of $[\text{H}^+]$. The initial charge was estimated by including it as an additional fitting parameter (11).

(ii) Estimate the proton binding parameters (K_{H1} , K_{H2} , m_{H1} , and m_{H2}) from the acid–base titrations in the absence of metal. m_{H1} and m_{H2} are the 'apparent heterogeneities' and are equal to $n_{H1} \times p_1$ and $n_{H2} \times p_2$, respectively (7). This is equivalent to fitting a bimodal Langmuir–Freundlich isotherm. It also fixes the number of binding sites in each of the two distributions ($Q_{\text{max}1}$, $Q_{\text{max}2}$). Since V_D varies with I , it was estimated for each point using eq 11.

(iii) Use the single metal data to resolve the apparent heterogeneity into their intrinsic heterogeneity (p_1 , p_2) and

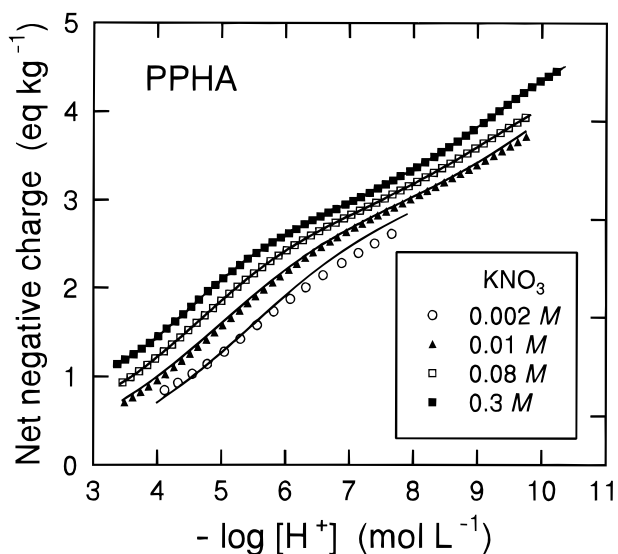


FIGURE 1. Proton binding for the purified peat humic acid (PPHA) at various ionic strengths. The solid lines and model fits are derived from the parameters in Table 3. The ionic strengths indicated are approximate since they varied somewhat between duplicate experiments, especially at high pH; the calculations used the exact ionic strength. Only every third data point is shown for clarity.

ion-specific, non-ideal (n_{H1} , n_{H2}) parts and to estimate the $\log \bar{K}$ s for each metal. Since each metal ion is likely to give a different estimate of p_1 and p_2 and only a single pair of values is needed, some judgement is required as to which set of values is best. Decide and then fix p_1 and p_2 at these values.

(iv) Re-analyze the single metal data given the adopted p values to estimate the optimal values for the remaining metal binding parameters.

(v) Test the fit of the above model and parameters to the new data without further adjustment of the parameters.

Parameter Estimates. Proton Data. The NICA-Donnan model provides a good fit to the acid-base titration data in KNO_3 (Figure 1). The greatest deviations were for the lowest ionic strength (about 0.002 M). This fit is maintained in the final set of parameters since the parameters derived from the acid-base data were not adjusted further during the fitting of the metal parameters. In order to fit the acid-base titration data well over the pH range 3.5–10.5, it was necessary to use a bimodal distribution with median proton binding constants of $\log \bar{K}_{H1} = 2.98$ and $\log \bar{K}_{H2} = 8.73$. These two distributions can probably be identified, at least in part, with carboxylic- and phenolic-type surface groups, respectively. However, these distributions are broad, and there is considerable overlap between them. Therefore, the attribution of sites with $5 < \log \bar{K}_H < 9$ to one or other of these two distributions becomes rather sensitive to the particular model used (electrostatic or non-electrostatic, assumed shape of the affinity distribution, etc). This sensitivity reflects a real difficulty, not just in model fitting, but in all experimental procedures that attempt to distinguish carboxylic- and phenolic-type sites merely on the basis of their acidity. The strong electrostatic binding of protons at high pHs and the high intrinsic proton affinity of humic substances mean that it is difficult to dissociate some of the phenolic protons experimentally. Therefore, the estimated number of such sites will always be highly model dependent.

Our analysis indicates that there are a total of 6.28 equiv kg^{-1} of sites with perhaps slightly more phenolic-type sites

TABLE 2

Values of Intrinsic Heterogeneity Parameters for Two Distributions Based on Calcium, Cadmium, and Copper Binding Data^a

metal	intrinsic heterogeneity parameter (p)	
	carboxylic-type sites (p_1)	phenolic-type sites (p_2)
Ca	0.72 ± 0.08	0.97 ± 0.5
Cu	0.51 ± 0.01	0.58 ± 0.02
Cd	0.57 ± 0.01	0.47 ± 0.12
accepted values	0.54	0.54

^a The standard errors of the estimates are given as well as the values used in all subsequent calculations.

than carboxylic-type sites. This differs from our earlier analysis using the basic NICA model, which indicated a total of just 4.41 equiv kg^{-1} sites with slightly more carboxylic than phenolic sites (7). However, this earlier analysis was based on the titration data in 0.1 M electrolyte and so was based only on conditional binding parameters that had not been corrected for electrostatic effects. The inclusion of an electrostatic correction will tend to increase the estimated number of sites since the correction removes some of the curvature in the binding curve observed at high negative charges (high pH). When the same set of proton titration data were analyzed according to a simple cylindrical electrostatic model, the total number of sites for the PPHA was estimated to be either 5.27 or 5.65 equiv kg^{-1} depending on whether the assumed underlying isotherm followed the Langmuir-Freundlich or Tóth models, respectively (11).

These estimated median proton binding constants are smaller than the conditional values derived from the non-electrostatic NICA approach (4.60 and 9.34, respectively) since in the electrostatic approach the \bar{K} 's refer to surface concentrations rather than bulk solution concentrations. This can be seen from the interdependence of \bar{K} and c in the $\bar{K}c$ term. For example, the $\bar{K}c$ term can be split in various ways depending on how the c term is defined, e.g., $\bar{K}[\text{H}^+_{\text{D}}] = \bar{K}'[\text{H}^+] = \bar{K}''[\text{H}^+]$ where $\bar{K}' = \bar{K}\chi$, χ is the Boltzmann factor and brackets refer to concentrations and parentheses refer to activities. Since χ is normally greater than 1, $\bar{K}' < \bar{K}$ as observed, although in the NICA model, the value of the non-ideality factor (n_H) also influences the fitted values of \bar{K} .

Single Metal Data. Metal ions inevitably have to compete for the binding sites with both protons and any other metal ions present. The presence of this competition enables the intrinsic heterogeneity factors, p_1 and p_2 , to be separated from the non-ideality factors, n_{H1} and n_{H2} , remembering that for the proton $m_{Hk} = n_{Hk} \times p_k$ ($k = 1$ or 2) is fixed by the acid-base titration in a metal-free environment. Values of p_1 and p_2 estimated from the Ca, Cd, and Cu data are shown in Table 2. The values based on Cd and Cu are fairly similar, but the Ca-based values are considerably higher and have relatively large standard errors, especially for the second distribution. This reflects the rather small range of Ca concentrations under which binding was measured and the fact that very little Ca is bound to the phenolic sites (see Surface Speciation). Therefore, the Ca estimates have been ignored when estimating the final p values. The value of p_1 was taken as the average of the Cu and Cd estimates ($=0.54$) since these two estimates have similar errors. The

TABLE 3

Parameters Derived for NICA-Donnan Model for Ion Binding to Purified Peat Humic Acid (PPHA) Based on Proton Titration Data and Data for Single Metal–H⁺–PPHA Interactions^a

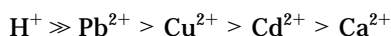
ion	H	Ca	Cd	Cu	Pb
Distribution 1: Low Proton Affinity or Carboxylic-Type Sites					
p_1			0.54		
$\log \bar{K}_1$	2.98	-2.12	0.10	0.40	0.73
n_1	0.86	0.64	0.81	0.52	0.6
$Q_{\max 1}$ (mol kg ⁻¹)			2.74		
Distribution 2: High Proton Affinity or Phenolic-Type Sites					
p_2			0.54		
$\log \bar{K}_2$	8.73	-3.32	2.03	6.42	4.90
n_2	0.57	0.33	0.48	0.32	0.9
$Q_{\max 2}$ (mol kg ⁻¹)			3.54		
R^2	0.998	0.975	0.993	0.995	0.978

^a Figures in boldface were estimated by a combination of fitting and user-defined constraints.

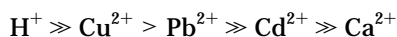
value of p_2 was also based on the Cu and Cd, but with slightly more weight being given to the Cu estimate because of its much smaller error estimate; this also gives a value of 0.54. The final set of parameter values derived from this analysis are summarized in Table 3; the coefficient of determination (R^2) was greater than 0.99 for the H⁺, Cd, and Cu binding and greater than 0.97 for the Ca and Pb binding. The H⁺ fitting was based on a constant absolute error in the protons bound whereas the metal ion binding data was fitted to the log of the amount of metal bound, which is equivalent to the assumption of a constant relative error (26). The goodness-of-fits were similar to those obtained for the basic NICA model (7).

Due to the lack of a wide range of Pb data (e.g., only one pH), it proved difficult to derive a unique set of Pb parameters. In particular, it was impossible to obtain a good fit without assigning a large value to n_2 . In the final stages of fitting, n_2 tended to drift toward a value greater than 1. However, there was little overall improvement in the fit as the value grew above 0.9, and so the value of n_2 was fixed at this value. The n_1 value was also fixed at 0.6 for similar reasons. For these reasons, the Pb data are regarded as provisional although the final fit was good (Figure 2). Judging from the $\log \bar{K}$ values, the strength of binding is in the sequence:

carboxylic-type sites:



phenolic-type sites:



The reversal of the Cu–Pb position may not be significant in view of the uncertainty in the Pb parameters. With the exception of Ca, the \bar{K} values for the metal ions are considerably greater for the phenolic-type sites than for the carboxylic-type sites.

Surface Speciation. The total metal binding is composed of contributions from the three bound components—the Donnan phase and the carboxylic- and phenolic-type sites. The relative importance of these various components varies between metals and with solution conditions (pH, free metal concentration, ionic strength, etc.). The estimated

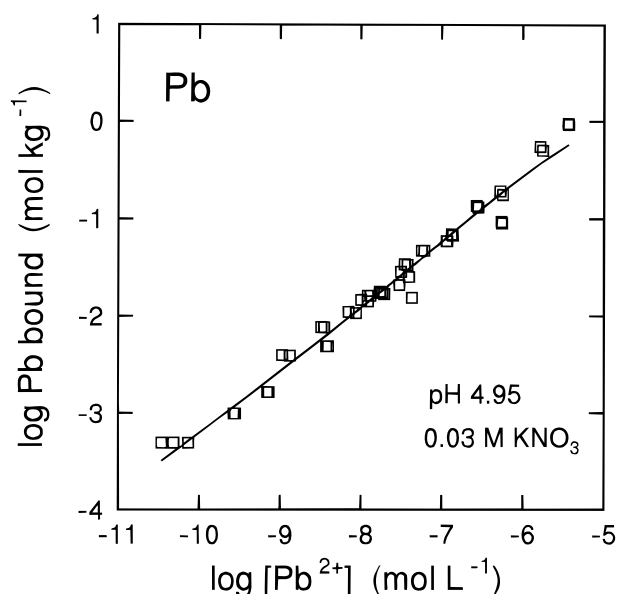


FIGURE 2. Lead binding to the PPHA in a 0.03 M KNO₃ background electrolyte.

surface speciation for Ca, Cd, Cu, and Pb (all in 0.1 M KNO₃) is shown for p[H] 4, 6, and 8 in Figure 3 (we use p[H] for $-\log [\text{H}^+]$ and pH for $-\log (\text{H}^+)$). The Ca speciation is dominated by the Donnan phase at the relatively high Ca concentrations typical of soil solutions and groundwaters, i.e., $10^{-3.5}$ to 10^{-2} M. This is especially true at pH 4 where binding is low. At higher pHs and lower Ca concentrations, the carboxylic-type groups become increasingly important. Within the concentration range considered, the phenolic-type sites never become significant for Ca binding although they do contribute some negative charge to the humic, which results indirectly in Ca being bound in the Donnan phase. Cd binding at trace concentrations ($[\text{Cd}^{2+}] < 10^{-8}$ M) is controlled by both carboxylic- and phenolic-type sites with the phenolic-type sites becoming relatively more important as the Cd^{2+} concentration decreases below 10^{-9} M. The Donnan phase is most important in percentage terms at low pH and high Cd concentrations and can account for up to 30% of the total Cd binding. Cu speciation is dominated by the phenolic sites at trace concentrations (less than 10^{-9} M Cu^{2+}). At higher concentrations and at pH 6 or less, the carboxylic groups become dominant. The Pb speciation is highly tentative in view of the paucity of data, but it would appear that at trace concentrations (less than 10^{-8} M Pb^{2+}) the speciation is dominated by the carboxylic groups. This contrasts with Cu.

The principal difference between this speciation analysis and our earlier analysis using the NICA model (7) is the importance of the Donnan phase for Ca^{2+} binding. Although the Donnan phase is most important at low pH, it remains important at high pH and high Ca concentrations. The NICA model needs to invoke the phenolic sites to increase Ca binding above pH 8 since most of the carboxylic groups will be fully deprotonated above pH 8. The NICA-Donnan model accounts for this increase as binding in the Donnan phase. The Donnan potential responds to the negative charge arising from the dissociation of the weak acid surface groups and the binding of protons and metal ions. Its response is highly non-Nernstian. In the presence of Ca and Cd, the calculated Donnan potential in the p[H] range of 4–8 varies from -90 to -50 mV. These potentials

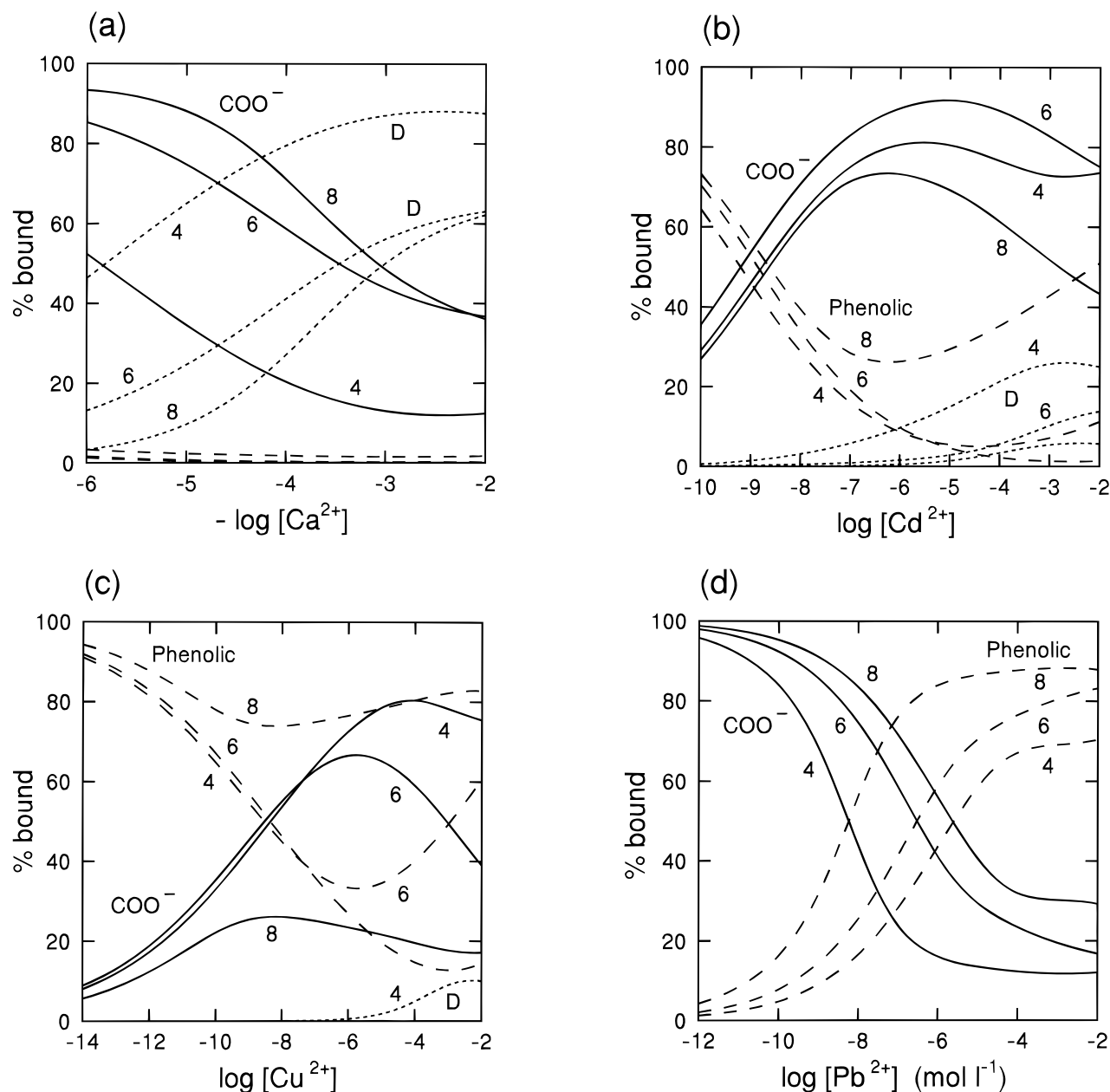


FIGURE 3. Calculated speciation of (a) calcium, (b) cadmium, (c) copper, and (d) lead bound to PPHA at the indicated pHs and free metal concentrations according to the NICA-Donnan model. The continuous line represents binding to the carboxylic-type sites (COO^-), the long dashed lines represent binding to the phenolic-type sites, and the short dashed line represent binding to the Donnan (D) phase. All calculations were for a 0.1 M KNO_3 background electrolyte. Minor contributions ($<5\%$) are not shown.

are about 30–40 mV more negative than the surface potentials previously calculated from the same data using a cylindrical electrical double-layer model, but the trends are broadly similar (5). At low free Cd^{2+} concentrations, typical of those found in the environment, the potential is governed by the pH and the free Ca^{2+} concentration with the Ca^{2+} concentration having a dominant effect especially at 10^{-2} M. As the Cd binding increases at free concentrations above 10^{-6} M Cd^{2+} , the Donnan potential tends to become dominated by the increased positive charge contributed by the bound Cd^{2+} ions and so becomes rather insensitive to the H^+ and Ca concentrations, especially at low Ca concentrations. High concentrations of Cu^{2+} can lead to a charge reversal, although $\text{Cu}(\text{OH})_2$ precipitation tends to mitigate against this.

Predictions of Metal Binding Based on the Single Metal Data in a 0.1 M KNO_3 Medium. Metal–Metal Competition.

The Ca–Cd type 1 competition experiments show that, as expected, Cd significantly reduces Ca binding (Figure 4). This observed reduction was up to 0.2–0.3 log unit, i.e., a reduction of Ca binding by a factor of up to two times for free Cd^{2+} concentrations ranging from pCd 5.6 to 4.0 (pCd = $-\log [\text{Cd}^{2+}]$). The predicted competition agreed well with the observations. The type 2 metal competition experiments showed these effects more clearly (Figure 5). The presence of pCa 3.5–3.1 significantly reduced Cd binding, especially at high pH, in line with the NICA-Donnan model predictions. The effect on Cu binding was much smaller, in agreement with the small effects predicted. However, the increasing concentrations of Cd did have a significant effect on Ca binding (Figure 6). A given concentration of Cu was more effective at displacing Ca than a similar concentration of Cd. At the highest Cd and Cu concentrations, the reduction in Ca binding was

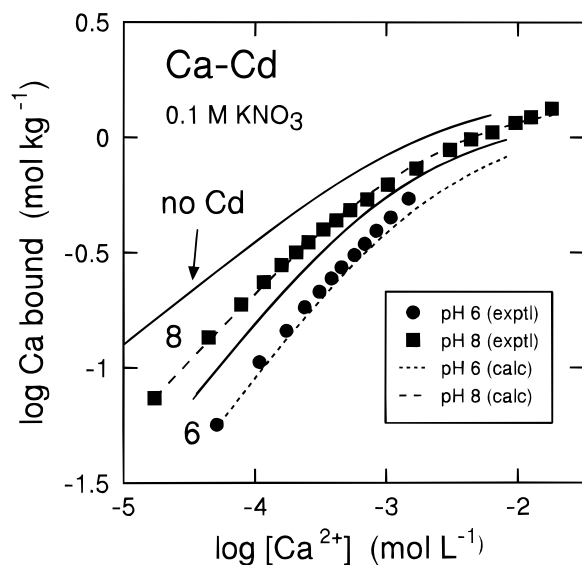


FIGURE 4. Effect of Cd on Ca binding by PPHA measured at pH 6 and 8 (type 1 metal competition experiments, $Cd_T = 2.5 \times 10^{-4}$ M). The solid lines are the calculated Ca binding in the absence of Cd and are based on earlier experiments in a pure Ca system. The dashed lines are the predicted Ca binding in the presence of added Cd.

equivalent to the effect that would be seen by a drop in pH by 1–2 pH units.

Earlier data for Cu–Ca(Mg) competition (27) showed only a very limited effect of Ca (or Mg) in reducing Cu binding. It was also shown that a discrete ligand site model strongly overpredicted the extent of this competition. More recent data of Town and Powell (28) have confirmed the small but measurable effect of Mg on Cu binding to a peat FA. Tipping (2) re-analyzed the Hering and Morel (27) data using his Model V and found that he could account ‘only approximately’ for the observed lack of Ca competition. This lack of extensive competition can be partly explained by the stronger preference of Cu compared to Ca for binding to the phenolic-type sites. It is also consistent with the NICA concept of ion-specific non-ideality since the competitive effect of an ion is related in part to the magnitude of the $(\bar{K}_Y^Z c)^n$ term for the competing ion both in relation to the target ion and the other ions present including H^+ . Models that assume ideality (all $n_i = 1$) will tend to overestimate the extent of competition. As can be seen above, major ions such as Ca affect metal binding not only through the \bar{K} and n_i terms but also through their effect on the electrostatics via the Boltzmann factor, χ .

It is interesting that data for Cu binding by Suwannee River fulvic acid (29) showed significant Ca competition even at quite low concentrations of Ca. This difference compared with our humic acid may be partly explained by the relatively small number of phenolic-type sites in fulvic acids compared with humic acids, especially peat humic acids (30). This will mean that more of the Cu is bound to the carboxylic-type sites where competition from Ca is greater. Ca competition is likely to be even greater at high Cu concentrations and low pH since this is where the Donnan phase Cu begins to become significant and competition in the Donnan phase is strictly related to charge and concentration. This is likely to become more important in the absence of a large concentration of background electrolyte.

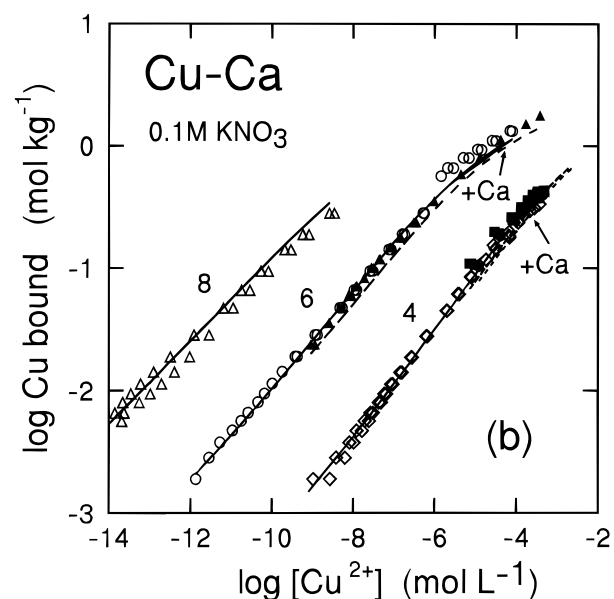
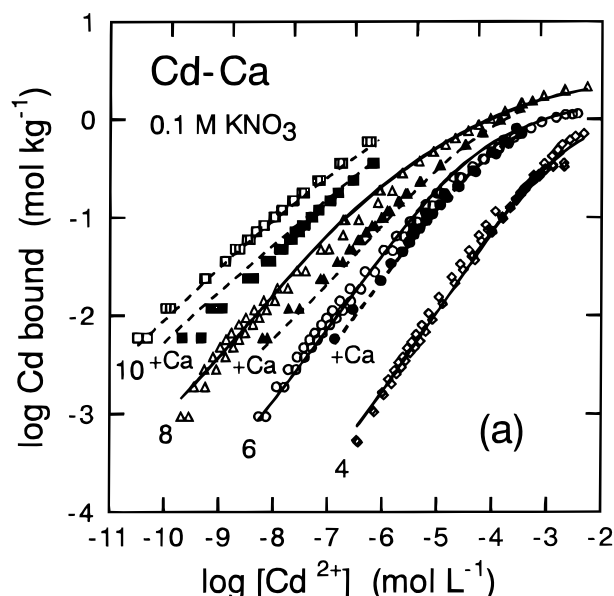


FIGURE 5. Effect of Ca competition on isotherms for (a) Cd and (b) Cu binding at pH 6, 8, and 10 (Cd) and pH 4 and 6 (Cu). The pH 4 Cd and pH 8 Cu data in the absence of Ca are also shown for reference. Open symbols are for data in the absence of Ca; solid symbols are for data in the presence of Ca (this ranged from $10^{-3.5}$ to $10^{-3.1}$ M Ca^{2+}). The dashed lines are predictions based on the single metal (Cd, Cu, and Ca) fits.

Effect of Ionic Strength. Reducing the ionic strength from 10^{-1} M to about 10^{-2} M leads to a significant increase in Cd binding at both pH 4 and pH 6 (Figure 7). The data show that this increase is about 0.5 log unit in both cases, i.e., binding is increased approximately 3-fold. Westall et al. (3) found a similar increase for Co binding by Leonardite humic acid (pH ≈ 6.7) on going from a 0.1 M $NaClO_4$ medium to a 0.01 M $NaClO_4$ medium. The NICA-Donnan model reflects this increase quite well although it consistently overestimated it. The description can be considerably improved by adjusting V_D . However, at this stage we prefer to keep to the assumption that the variation of V_D with ionic strength is independent of the type of ions present.

The ionic strength effect is much lower in the Cu systems. Cu binding at pH 4 is only slightly increased in the lower

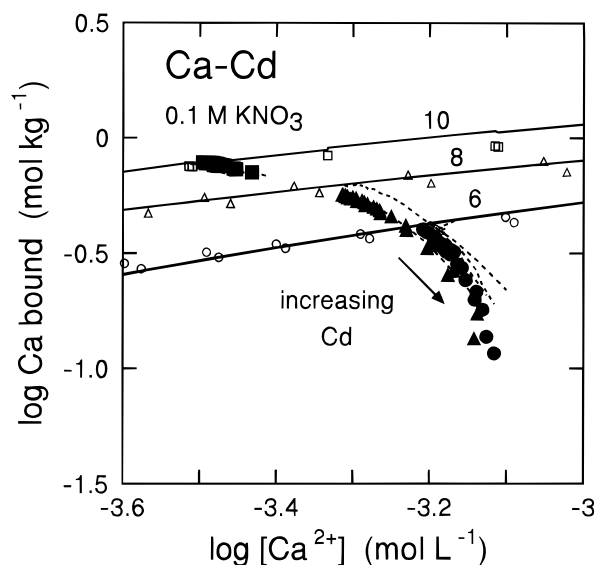


FIGURE 6. Effect of Cd on Ca binding by PPHA at pH 6, 8, and 10 (same experiment and symbols as shown in Figure 5). The solid lines were fitted; the dashed lines are predicted.

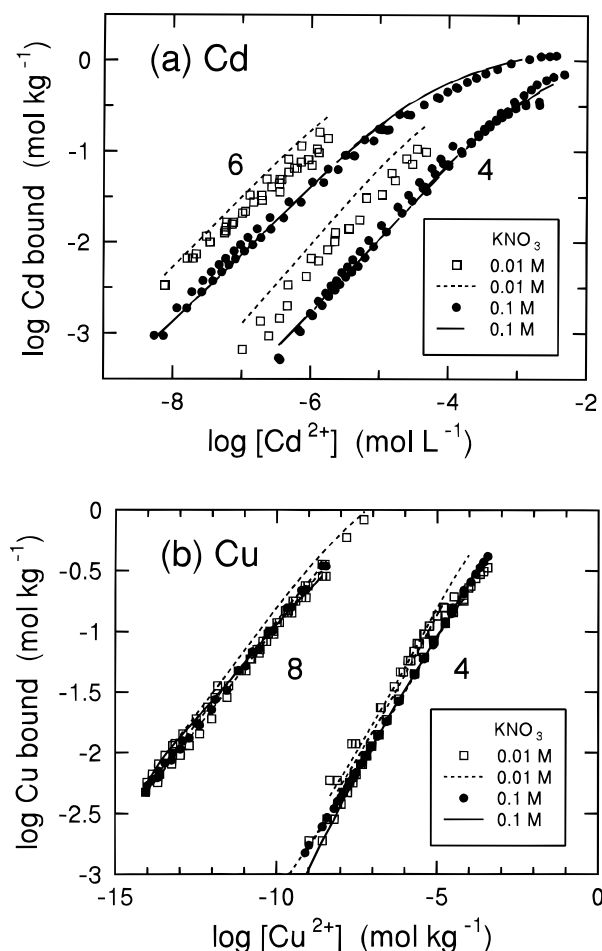


FIGURE 7. Change in (a) Cd and (b) Cu binding by PPHA when the background electrolyte was changed from 0.1 to 0.01 M KNO_3 . Dashed lines are predictions. The pHs are indicated.

ionic strength system, and the effect at pH 8 is even smaller (Figure 7). This is in good agreement with the predictions from the NICA-Donnan model. Literature data for the effects of a variation in ionic strength on Cu binding by fulvic acids are less clear: Cabaniss' data for Suwannee River fulvic acid [given in Bartschat *et al.* (1)] at ionic

strengths of 0.01 and 0.1 M show little ionic strength dependency at pH 5.14 but a strong dependency at pH 7.00 and pH 8.44. On the other hand, McKnight and Wershaw's (29) data for the same fulvic acid in 0.001 and 0.01 M KNO_3 show no significant ionic strength effect. Given our present set of parameters for PPHA, the NICA-Donnan model predicts only a weak ionic strength effect for Cu binding with little dependence on pH (Figure 7). It seems unlikely that this conclusion will be very different for other humic and fulvic acids. The smaller predicted ionic strength effect for Cu compared with Cd is due to the difference in magnitude of the non-ideality parameters, $n_{\text{Cu}} < n_{\text{Cd}}$ for both carboxylic- and phenolic-type sites. Therefore the non-ideality parameter not only determines the slope of the isotherm at trace concentrations but also controls the ionic strength dependency of binding.

Discussion

The intrinsic heterogeneity of humic substances inevitably means that the binding of protons and metals will be very complex. However, in order to test models for the competitive interactions that occur both between protons and metal ions and also between major ions and trace ions (e.g., Cd-Ca) and among strongly bound trace ions (e.g., Cd-Zn), a wide range of competition data are required. There remains a serious shortage of metal binding data for multi-metal systems. Data covering a very wide range of free metal concentrations are also useful since it is often the asymptotic behavior of the various models that serves to distinguish them. Most models have a sufficient, even an excessive, number of adjustable parameters and so may well be able to fit a narrow range of data very well, but may fail badly when extrapolated to a wider range of conditions. The ability of the NICA-Donnan model to make quite large extrapolations successfully is shown by the good fit of the pH 10 Cd PPHA data (Figure 5), which was estimated from data for pH 4, 6, and 8.

Scope of the NICA-Donnan Model. The scope and principal characteristics of the NICA model have been discussed earlier (7) and are inherited by the NICA-Donnan model. The inclusion of the Donnan model broadens the scope of the NICA model to include the effect of major ions of environmental importance such as Na^+ and Ca^{2+} . These ions may not be strongly bound but can impact the binding of other ions through competitive and electrostatic effects. Our re-analysis of the earlier single metal data has generally confirmed the earlier conclusions about the surface speciation of the bound metals, particularly the importance of the phenolic-type sites for trace Cu binding and the importance of both phenolic- and carboxylic-type sites for the Cd binding. The most important difference is that both the carboxylic-type groups and the Donnan phase are important for Ca binding. This surface speciation is important since competitive effects for each of these types of binding site may be different.

An important characteristic of the NICA-type models is that they can give highly nonlinear (Freundlich-like) behavior even at very low concentrations, i.e., when the non-ideality factors (n_i) are less than 1, they do not tend to the Henry's law limit. The nature of this limiting behavior is a critical feature of models that helps to distinguish them. Our experimental data support this feature, especially the pH 8 Cu data, which have a slope of about 0.3 on a log-log plot even at free metal concentrations well below $\text{pCu } 10$. Xue and Sigg (31) also demonstrated that Cu binding to

TABLE 4

Sources of Data Used for Copper Binding Data Plotted in Figure 8

ref no. in Figure 8	humic material/ method of measurement ^a	pH	background electrolyte	source
1	Suwannee River fulvic acid (SRFA)/ISE	7.00	0.1 M NaClO ₄	Cabaniss and Shuman (32), Figure 1
2	Suwannee River fulvic acid (SRFA)/ISE	6.0	0.01 M KNO ₃	McKnight and Wershaw (29), Figure 2
3	purified peat humic acid (PPHA)/ISE	6.0	0.1 M KNO ₃	Benedetti <i>et al.</i> (7), Figure 6
4	Suwannee Stream humic acid (SSHA)/ISE	8.2–8.3 (initially)	0.5 M NaCl/2 mM NaHCO ₃	Hering and Morel (27), Figure 3
5	soil (Sable) humic acid/ISE	4.0	0.005 M KClO ₄	Tipping <i>et al.</i> (36), Figure 2a
6	soil (Greifen) humic acid/ISE	5.0	0.005 M KClO ₄	Tipping <i>et al.</i> (36), Figure 2a
7	Lake (Greifen) DOC/DPCSV with catechol	8.0	natural composition	Xue and Sigg (31), Figure 4A
8	Shawsheen River fulvic acid (ShRFA)/ISE	6.25	0.001 M KNO ₃	McKnight <i>et al.</i> (40), Figure 1
9	Grassy Pond FA (GPFA)/ISE	6.0	0.001 M NaClO ₄	Fish <i>et al.</i> (41), Figure 1

^a ISE, ion-selective electrode; DPCSV, differential pulse cathodic stripping voltammetry.

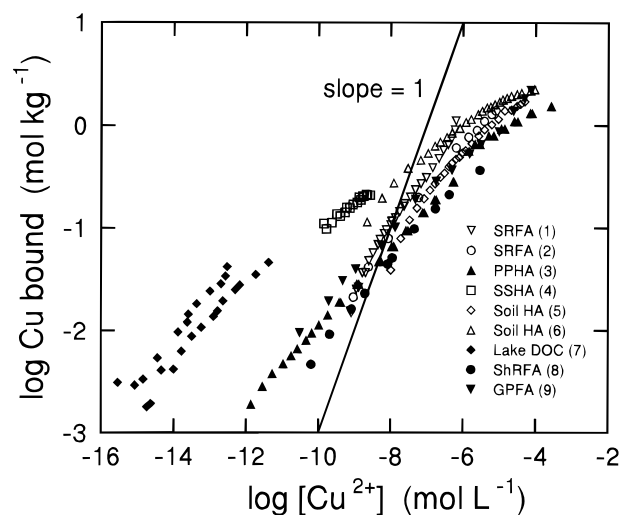


FIGURE 8. Literature data for Cu binding to various humic substances. A key to the data and their sources is given in Table 4.

lake water DOC remains highly nonlinear even at copper concentrations as low as pCu 14. Figure 8 presents experimental data for Cu binding to a wide variety of humic substances from soils and natural waters. Details of the sources of these data are given in Table 4. The data clearly show that, with the possible exception of the data of Cabaniss and Shuman (32) for Suwannee River FA, Cu binding remains consistently nonlinear even at very low free Cu²⁺ concentrations. The data of McKnight and Wershaw (29), also for Suwannee River FA, show no tendency to become linear even at the lowest concentrations, but these data differ from those of Cabaniss and Shuman since they cover a narrower range of free Cu concentrations and are for a slightly higher pH. Interestingly, recent data for the cellular Cu:C ratios in several marine phytoplankton at extremely low free Cu²⁺ concentrations (pCu²⁺ 15–10) also show a highly nonlinear response (33). The slope of the log Cu bound–log [Cu²⁺] plot is also about 0.3 (as for much of the data in Figure 8). Our Cd and Ca data also support the conclusion of nonlinearity at low free metal concentrations but show less nonlinearity than our Cu data (Cd and Ca behave more 'ideally' than Cu, Table 3). Our Cd (pH 8) data tend to show a slight curvature over the entire Cd²⁺ concentration range (e.g., Figure 5).

Some literature data for other ions tend to suggest that there is an increase of slope toward 1 (i.e., toward a linear isotherm) at low concentrations, e.g., the Co²⁺–humic acid

data of Westall *et al.* (3). However, for most ions, the amount of data available at very low free metal concentrations is small and tends to be of rather poor quality. The limiting slope is often influenced strongly by just one or two points. In studies where ISEs have been used, the calibration at low concentrations becomes critical. ISEs tend to lose their near-Nernstian response at low concentrations, and if this is not fully taken into account, the derived isotherm will appear to become steeper at low concentrations. Where sufficient high quality data are available, the general conclusion appears to be that for humics nonlinearity is the rule rather than the exception even at the very low concentrations typical of environmental conditions (34, 35). A consequence of this is that if experimental data are fitted to a simple multiligand model, and then the model and fitted parameters are used to extrapolate to a significantly lower concentration, then the extent of binding will be underestimated.

Formulation of the Electrostatics in the Donnan-NICA Model and Model V. Since in conceptual approach and scope the NICA-Donnan model is similar to Model V of Tipping and Hurley (4), it is perhaps worthwhile to compare some of the similarities and differences in detail. Model V can be interpreted as a simple discretization of a bimodal distribution to which the possibility of bidentate binding has been added. In that respect, Model V can be compared to our use of the LF model (5), which gives a reasonable description of calcium and cadmium binding at different pHs but only when the strong link between proton binding and metal binding is relaxed. Subsequent calculations have shown that the LF model is unable to fit our copper data even after allowing this relaxation, and we expect that Model V will also experience a similar difficulty. An interesting aspect of the NICA model is that the LF model is a limiting case of the more general NICA model in which all of the non-ideality parameters are set to 1. In practice, the very different behavior of the different ions (H⁺, Ca²⁺, Cd²⁺, Cu²⁺, etc.) is a critical observation and led us to introduce the concept of ion-specific non-idealities.

While the treatments of the electrostatic interactions are broadly similar in the two models, there are also important differences. The NICA-Donnan model uses the Donnan model to calculate the concentration of counterions in the Donnan phase; the Donnan potential that is implicit in this is also used to account for the electrostatic part of the specific binding to the reactive groups. In Model V, an empirical correction term is used to account for the influence of the electrostatics on the specific binding, which

is equivalent to using a Boltzmann factor and a corresponding potential term. Then in addition, a type of Donnan model is used to estimate the composition of the double layer, which implies the use of a second potential term. In the NICA-Donnan model, there is only a single potential term involved. Minor differences are our inclusion of anion exclusion as a form of charge compensation in the Donnan phase and our definition of Donnan-bound components in terms of surface excess quantities.

H⁺/M²⁺ Exchange Ratio. Although an isotherm equation may be able to describe the pH dependence of metal ion binding well, this does not necessarily imply that the mass balance for the protons has been equally well described. An important aspect of general purpose multicomponent models is their ability to describe the binding of all components (including the proton) reasonably well. The change in proton binding can be derived directly from the experimental H⁺/M²⁺ exchange ratio measured at constant pH. An H⁺/M²⁺ exchange ratio is implicit in all multicomponent binding models and can be derived from the calculated change in proton and metal binding at constant pH. It can in principle vary with pH and metal ion concentration.

Experimental measurements of the exchange ratio for PPHA have shown that they generally follow the sequence Cu > Cd > Ca (7). There appears to be some systematic variation with free metal concentration and pH, although the trends are far from clear. In general, the NICA-Donnan model predictions of the exchange ratios (not shown) were similar to, or slightly better than, those found earlier (7). For example, the inclusion of the Donnan phase meant that the observed increase in the exchange ratio for Cd at high Cd concentrations and pH 8 was more faithfully followed. This increase largely reflects the indirect effect of the electrostatics on the specific binding (through the Boltzmann factor) rather than direct effects on the number of ions bound in the Donnan phase. The model tended to underestimate the exchange ratio, especially at low concentrations and high pH for all cations. This underestimation was greatest in the case of Cu where the experimental exchange ratios varied between about 1.3 and 1.9, and yet the model predicted values between 0.75 and 1.1. This is despite the fact that the NICA-Donnan model is able to describe the pH dependence of Cu binding well (e.g., Figure 5). Such an underestimate is not surprising since the NICA model is based on the assumption of monodentate binding, which imposes a maximum value for the exchange ratio of one (7). In theory, inclusion of the electrostatic interactions in the NICA-Donnan model enables exchange ratios of greater than 1 to be achieved, but in practice, predicted ratios only just exceed 1 for Cu binding at pH 4. Bidentate binding would also allow exchange ratios of up to 2 as does the binding of hydrolyzed species such as CuOH⁺. For Cu at least, some form of bidentate binding is to be expected. Tipping *et al.* (36) recently observed exchange ratios of 1.1–1.4 for Cu binding to a humic acid, which agreed reasonably well with their predictions using Model V. These ratios are slightly lower than those observed here.

Conclusions

Although several models account for some of the important factors involved in ion binding to humics, often very successfully, few attempt to account for them all. Our aim has been to develop a model that accounts for a sufficient number of the principal controlling factors to be able to

describe the change in metal ion binding over a broad range of solution conditions. We have attempted to retain a reasonable physical description of the key interactions in the belief that this would lead to a more compact description of the data.

Inevitably the simplifications that need to be made are great and, to some extent, arbitrary. For example, our approach has been criticized for ignoring the polydisperse nature of humic materials (37). While we accept that natural humic materials are indeed polydisperse and that this will be reflected in the electrostatic effects (*I*), we do not believe that at this stage it is essential to consider these effects explicitly. The radius of humic-type particles is fairly insensitive to molecular weight, and it appears that the NICA-Donnan model already has sufficient flexibility to reflect the consequences of any polydispersity.

The NICA-Donnan model gives a reasonable description of the competitive effects between different metal ions at various pH values. The model is unique in that the competitive effects of different ions are implicitly different, an attribute that accords with the available observations. It is important to be able to describe these competitive interactions reasonably well since natural waters normally contain a wide range of metal ions at various concentrations, ranging from major cations to the many trace cations that are often of interest. Binding of major ions such as Ca, although relatively weakly bound, is often of the same order as that of the more strongly bound minor ions because of their much larger concentration.

Although we believe that the predictions made in this paper are encouraging, we have not attempted to optimize the model further by adjusting the isotherm parameters using the pH 10 Cd data, the multi-metal competition data, or the new data for the 0.01 M ionic strength or by simultaneously optimizing the proton and metal binding data. At this stage, we believe that it is important to be able to make reasonable predictions given calibration data of limited scope, e.g., single metal data. In practice, it is likely that modeling of humic–metal interactions will often have to be undertaken without the benefit of large data sets. It remains to be seen to what extent the parameters determined here vary from one humic acid to another, but the indications so far are that the NICA-Donnan model can be successfully extended to real-world situations with a minimum amount of parameter adjustment (9). The NICA-Donnan model is included in the generalized chemical speciation and transport program, ECOSAT (25).

The inclusion of the Donnan model has extended the range of application of the original NICA model to conditions where the concentration of ions such as Na⁺ and K⁺ vary significantly and where weakly bound ions such as Ca²⁺ are also bound in significant quantities as nonspecifically bound counterions. The implicit addition of the electrostatic interactions in the Donnan model also provides a mechanism by which second-order effects can be included in the model, e.g., the binding of ions to one group of sites may affect the binding to another group of sites through the indirect effect of ion binding on the local electrostatic potential seen by all of the sites. The overall complexity of these various interactions often means that the results of changing solution chemistry can be difficult to predict and may even be counter-intuitive. In our implementation of the Donnan model, the critical additional parameter that is introduced is the Donnan volume. Although the evidence so far indicates that in rather simple systems the Donnan

volume depends primarily on the ionic strength, it remains to be seen how far this relationship changes in more complex systems and how sensitive the NICA-Donnan model is to such changes.

Acknowledgments

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