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# Acid/Base, Copper Binding, and $\text{Cu}^{2+}/\text{H}^{+}$ Exchange Properties of a Soil Humic Acid, an Experimental and Modeling Study

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Acid/base, copper binding and proton exchange properties of a soil humic acid were studied over a range of pHs and ionic strengths. Results indicate that multiple classes of copper binding sites exist. A number of model formulations were used to simulate the data; none were able to reasonably match all aspects of the observed behavior. Model results and analyses suggest that successful replication of humic behavior over a wide range of conditions requires a model formulation which incorporates electrostatic effects for a variable geometry entity, multiple site classes, and probably both uni and multi dentate complexation. Additionally site heterogeneity estimates from acid/base titration data are not likely to reasonably assess the presence of low concentration, high (metal) affinity sites that can be relevant in the study of trace metal complexation.

## Introduction

Humic substances are believed to play an important role in the speciation, fate, and transport of metals in many aqueous environments. This belief arises from their ubiquity and their high concentration of functional groups known to interact with metals (total acidity is typically between 5 and 15 mol per kg of humic) (1–4). The complex, heterogeneous nature (molecular weight, composition, structure) of humic substances makes prediction of humic effects on metal behavior and the impact of solution conditions on these effects difficult, even for a single humic sample (5, 6). Models (3, 7–18) which attempt to replicate/simulate this behavior necessarily incorporate a simplified representation of the humic. Their effectiveness depends on their ability to reasonably account for humic properties (heterogeneity, electrostatic effects, etc.).

As part of a study of the effects of mineral/organic polymer interactions and their effect on metal behavior (19, 20) we have looked at the acid/base, copper binding, and  $\text{Cu}^{2+}/\text{H}^{+}$  exchange properties of a soil humic acid (Eliot Silt Loam, obtained from the International Humic Substance Society) dissolved in simple salt solutions. Portions or all of the data have been fit to a number of models; the results provide some insight into the applicability and limitations of various model formulations and some guidance regarding what humic properties should be considered in a model that can successfully describe humic ion binding over wide ranges of pH, ionic strength, and metal loading.

## Materials and Methods

All chemicals used were reagent grade or better. Experiments (potentiometric titrations, pH started Cu binding titrations and pH started  $\text{Cu}^{2+}/\text{H}^{+}$  exchange titrations) were conducted on 100 mL samples (sodium perchlorate electrolyte) at 25 °C using a computer controlled titration system. Solutions containing 100 (all); 200 (potentiometric); or 500 ( $\text{Cu}^{2+}/\text{H}^{+}$  exchange) mg/L humic acid were used. No concentration effects were observed. The Davies equation was used for activity corrections (21). Experimental solutions were allowed to equilibrate for at least 2 days at room temperature and overnight at 25 °C under an argon purge.

**Humic Acid Preparation.** The humic acid was extracted from a Joliet, IL Eliot Silt Loam, purchased from the International Humic Substance Society (IHSS). We extracted the humic acid using the same procedure the IHSS uses to extract its standard soil humic acid from this soil. After freeze-drying the humics were stored in a desiccator. A total (carboxyl plus phenolic) hydroxyl content of 7.2 mol per kg was determined using barium hydroxide ( $\text{Ba}(\text{OH})_2$ , (22)). An ultrafiltration analysis employing UV/vis spectroscopy showed a wide size distribution. Less than 15% of the humic passed a 10 000 molecular weight cutoff (MWCO) membrane; ~40% passed through a 100 000 MWCO membrane; and ~80% through a 300 000 MWCO membrane ((23), Supporting Information).

Stock solutions (pH 7–8,  $I = 0.001\text{--}0.002\text{ M}$ ) were prepared from the freeze-dried humic using measured volumes of calibrated, carbonate free sodium hydroxide, sodium perchlorate solutions, and boiled MilliQ water.

**Titant Solution Preparation.** Calibrated acid ( $\text{HClO}_4$ ), carbonate free base ( $\text{NaOH}$ ), and copper ( $\text{Cu}(\text{ClO}_4)_2$ ) solutions were used as titrants. Acid and base normalities were determined by titration against sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and potassium hydrogen phthalate ( $\text{KOOCC}_6\text{H}_4\text{COOH}$ ) (24), respectively. A standard copper solution was prepared by dissolving Supra Pur (99.999%) cupric oxide ( $\text{CuO}$ ) in concentrated ultrapure perchloric acid. Supernatant was collected and diluted to a nominal copper molarity of 0.1. The solution was standardized by titration against a standardized EDTA solution (Standard Methods, 1992). Titrant calibration precisions were ~0.3–0.5%.

**Electrode Calibration.** For potentiometric titrations the glass electrode/reference couple was calibrated with pH buffers (pH 4.00, 7.00 and 10.00) and by titrating 100.0 mL  $\text{NaClO}_4$  solutions ( $I_{\text{calib soln}} = I_{\text{exptl soln}}$ ) with calibrated  $\text{HClO}_4$  or  $\text{NaOH}$  solutions. Linear regressions were performed to determine a slope and intercept for each method. Typically slopes were essentially identical and near Nernstian. However electrolyte titration intercepts were generally 2–5 mV higher (av 4.0 mV) than buffer intercepts. pHs calculated from titration curves thus averaged 0.07 pH units higher than buffer curve pHs. The pH discrepancy becomes significant at low pHs where a significant fraction of added acid titrant remains in solution. Since pH titrant curve calibrations provided a direct measure of solution  $\text{H}^{+}$  concentration, they were used for pH determination in potentiometric titrations (23).

The pH started Cu binding and proton release experiments required calibration of both the glass/reference couple and the Cu ISE/reference couple. Buffers (pH 4.00 and 7.00) were used for the former titrations of 100 mL  $\text{NaClO}_4$  solutions ( $I_{\text{calib soln}} = I_{\text{exptl soln}}$ ) with  $\text{Cu}(\text{ClO}_4)_2$  ( $[\text{Cu}^{2+}]$  between  $1.00 \times 10^{-6}$  and  $1.00 \times 10^{-3}\text{ M}$ ) for the latter. To be consistent with the pH convention used for the potentiometric titrations,

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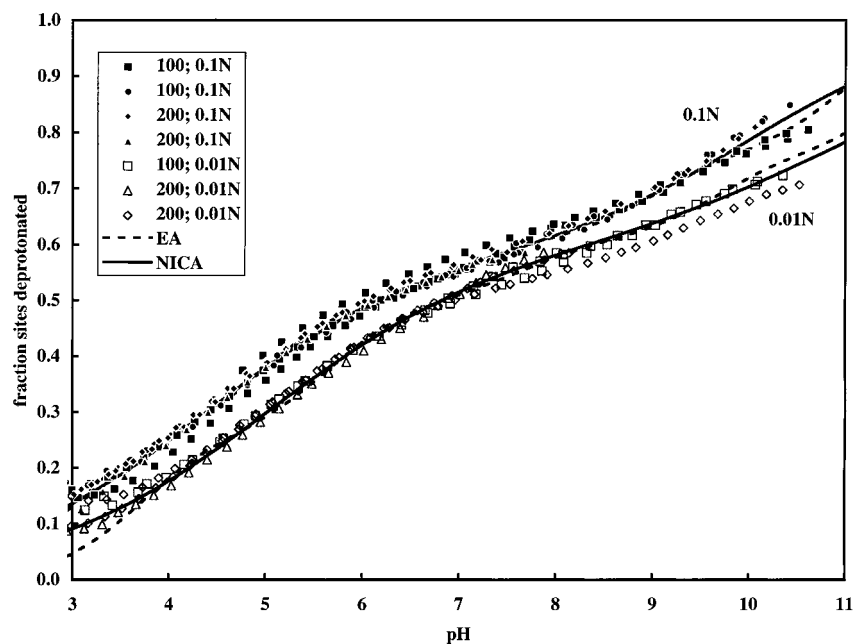


FIGURE 1. Humic charge versus pH as a function of ionic strength 0.01 N NaClO<sub>4</sub>; 100 or 200 mg/L humic acid. Lines represent model fits to data: EA, Electrolyte Association model (fit F, Table 2) and NICA, Non-Ideal Competitive Adsorption Model (fit C, Table 6).

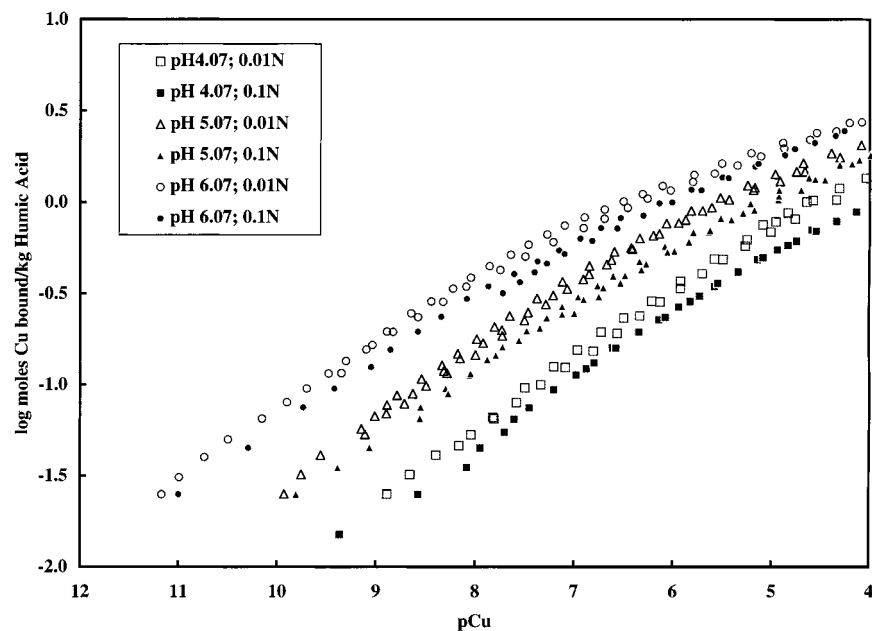


FIGURE 2. Humic copper binding behavior; pHs 4–6; ionic strength 0.01 N. Data includes two experiments for each pH and ionic strength.

the buffer calculated pH 4.00, 5.00, and 6.00 pH started experiments are considered to have been conducted at pH 4.07, 5.07, and 6.07. Cu ISE response was typically linear and near Nernstian over the complete calibration range. Tests of ISE response in solutions containing the copper complexant NTA showed a linear response to  $\sim pCu$  11 (23).

**Potentiometric Titrations.** Two or three legged titrations were conducted (acid leg first). Equilibrium was assumed when the periodic pH emf readings were sufficiently stable: slopes and standard deviations less than 0.005 mV/min and 0.04 mV, respectively. Initial pHs ranged between 7.5 and 8.2, and the titrations were conducted between pHs 2 or 3 and 11.

**pH Statted Copper Binding Experiments.** Copper ( $2 \times 10^{-7}$  mol) was added to the humic solution just before beginning the overnight 25 °C, argon purge equilibration. During the titration sodium hydroxide or perchloric acid was

added as necessary to maintain the desired pH within  $\pm 0.5$  mV ( $\sim 0.01$  pH units). Equilibrium was assumed when Cu ISE emf drift dropped below 0.005 mV/min. Titrations continued until the solution copper activity exceeded  $1 \times 10^{-4}$  M.

**Proton Release Experiments.** Except that no copper was added before the overnight 25 °C, argon purge equilibration, solution preparation was identical to that for the copper binding experiments. To start the experiment the pH was brought to within 0.1 mV of the set point. When the pH was stable, copper ( $1.0 \times 10^{-6}$  mol) was added, the Cu ISE placed in the solution, and base added to return the pH to the set point. After 7–15 min the pH and Cu ISE emfs and titrant additions were recorded, more copper was added and the process repeated until the solution copper activity exceeded  $1 \times 10^{-4}$  M.

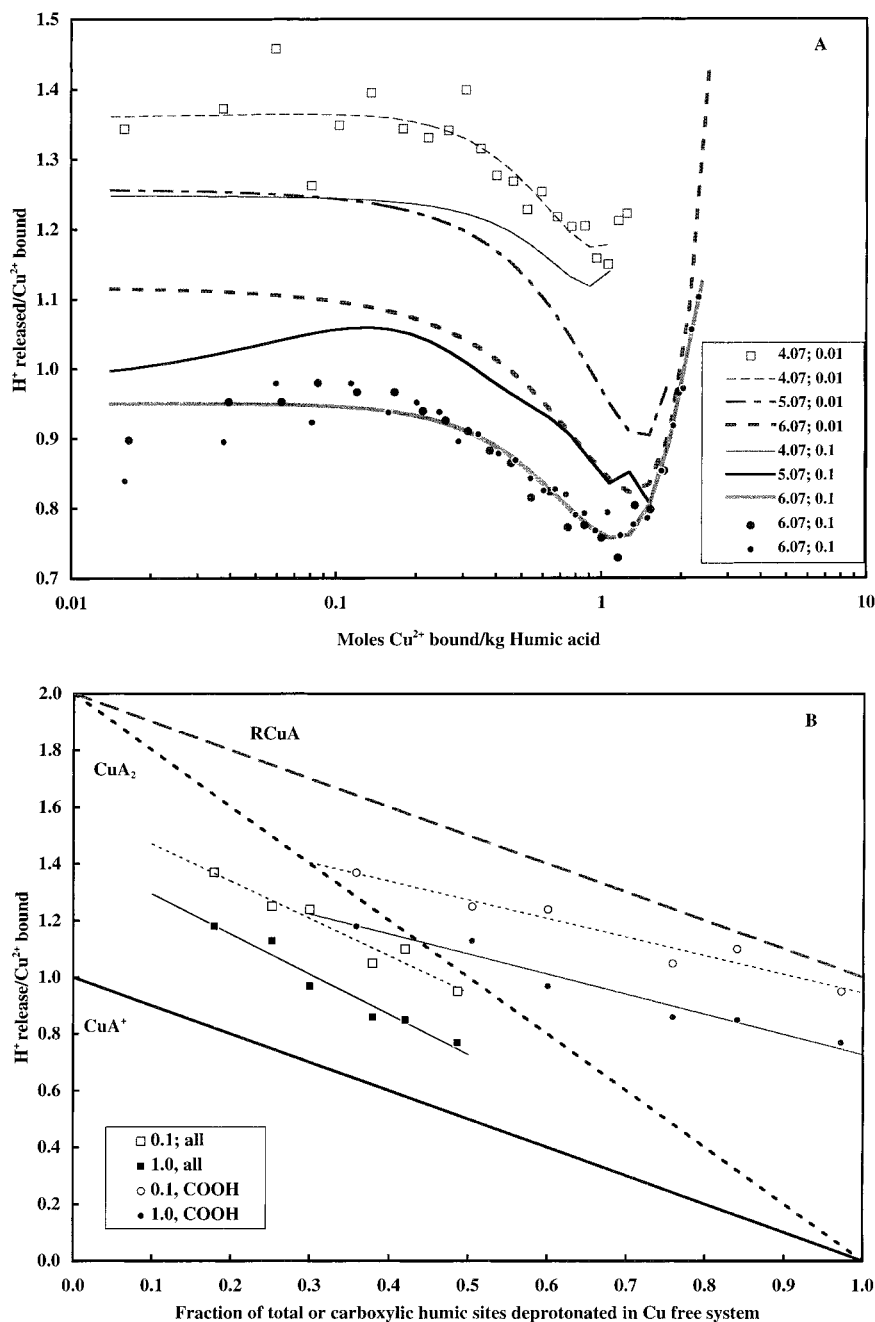


FIGURE 3. Incremental humic proton release versus pH, ionic strength, copper loading, and extent of humic dissociation. A. Data (symbols) and fourth order polynomial regressions (lines). Data for several conditions omitted for clarity. B. Release versus initial (copper free) extent of humic deprotonation. Thick lines represent proton release for reactions comparable to eq 2–4 of text. Open symbols show incremental releases when bound copper equals 0.1 mol per kg humic acid, filled symbols for 1.0 mol per kg. Thin lines through data are illustrative only. In the legend "All" refers to a deprotonatable site concentration equal to the total measured acidity—7.2 mol per kg humic acid. "COOH" assumes that only carboxylic sites deprotonate in the pH range considered (4–6), and they represent 50% of total sites.

## Results

**Potentiometric Titrations (Figure 1).** Initial acid legs show good reproducibility except below pH 3–3.5 ((23); Supporting Information). At low pHs only a small fraction of added base or acid goes to (de)protonate the humic, thus inherent uncertainty in pH measurements causes significant uncertainty in this region. The multilegged data show greater variability, some of which is due to experimental uncertainties in titrant volumes and normalities (23). Variability in high pH regions may occur because of changes in the chemical structure of the humic (15). Polynomial regressions of the data at each ionic strength show parallel curves separated,

by  $\sim 0.6$  pH units for equivalent  $\alpha$  (fraction sites deprotonated). There is a buffer capacity minimum at  $\alpha = 0.55$  to  $0.60$  ((23); Supporting Information). This is consistent with the view that roughly 50% of humic acidity is due to carboxylic moieties (3).

**pH Statted Copper Binding (Figure 2).** Replicate experiments were conducted at each pH and ionic strength. Based on the measured total acidity ( $10^{0.86}$  mol per kg humic acid) observed copper binding ranged from  $\sim 0.4$ –40% of total acidity. The fraction of added copper bound to the humic ranged from  $\sim 25\%$  at pH 4.07, pCu 4.0, and 0.1 N ionic strength to  $\sim 99.9995\%$  at pH 6.0, pCu 11.0, and 0.01 N ionic strength.

Binding pH dependence ( $(\Delta pCu/\Delta pH)_{Cu \text{ sorbed},i}$ ) ranges from 1 to 1.3. At a constant  $pCu$  20–40% more copper is bound in 0.01 N  $NaClO_4$  than in 0.1 N. For equivalent humic bound copper, solution copper concentrations are roughly three times as high in 0.1 N solutions ( $\Delta pCu \sim 0.2-0.3$ ). Log Cu bound versus log  $\{Cu\}$  slopes range from 0.4 to 0.5 at the lowest copper loadings; they drop to  $\sim 0.1$  at the highest loadings. Similar behavior has been observed for other humics (8, 9, 25, 26).

**Proton Release Experiments (Figure 3).** Proton release decreases with increasing pH and ionic strength; it also depends on copper loading. The increasing releases at the highest loadings may reflect copper induced coagulation of the humic; such coagulation was visually apparent at the completion of release experiments. The apparent pH and ionic strength release dependencies are perhaps more properly considered a dependency on  $\alpha$ , the fraction of humic sites deprotonated (Figure 3b). Thick lines in Figure 3b represent proton releases for reactions of copper with the simple solution ligands HA and RH (eqs 1–4) as a function of the fraction of HA deprotonated (eq 1). RH ligands, which do not deprotonate over the pH region of interest, could include phenolic hydroxyls or water.

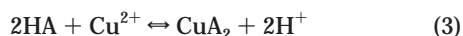
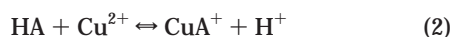


Figure 3b suggests that bidentate copper complexes may form. However electrostatic effects, not considered in the analysis can strongly influence observed proton releases (20, 27), consequently observed releases are not conclusive.

## Modeling

To model the humic's acid/base and copper binding behavior we first attempted to find a humic geometry consistent with the observed acid/base behavior. Three geometries were considered: solute impermeable spheres; solute impermeable cylinders; and solute permeable, fixed volume gels (10, 28–31). The (in)appropriateness of these geometries can be determined from analysis of multiple ionic strength acid/base titration data. For both the impermeable sphere and cylinder the following relationship holds (10, 31)

$$K_{ai} = \frac{\{H^+\}_s \{A_i^-\}_s}{\{HA_i\}_s} \quad \text{or} \quad \frac{K_{ai}}{\{H^+\}_s} = \frac{\{A_i^-\}_s}{\{HA_i\}_s} \quad (5)$$

$$pH_s = pH_b - \log(\exp(-F\psi_s/RT)) \quad (6)$$

where  $K_{ai}$  = equilibrium constant for acid class  $i$ ,  $HA_i$  = acid class  $i$ ,  $-_s$  = value at the humic surface,  $-_b$  = value in bulk solution,  $\psi_s$  = surface potential, volts,  $F$  = Faraday constant,  $R$  = gas constant, and  $T$  = temperature, K.

Equations 5 and 6 suggest that for a spherical or cylindrical polyelectrolyte, an appropriate choice of radius and site density will result in multiple ionic strength titration data ( $\alpha$  versus pH) collapsing to a single curve when  $pH_s$ , calculated from the measured, bulk solution pH (eq 6), is used (10, 31). We were unable to find a combination of radius, surface site density, and geometry that caused the data to collapse to a single curve ((23); Supporting Information)

Gel models (29, 30) assume a three-dimensional gel phase permeable to small ions and water with deprotonatable sites occurring uniformly throughout the gel phase. The charge resulting from deprotonation (eq 1) is completely compensated by mobile counterions located within the gel volume.

TABLE 1. Humic/Divalent Cation Electrolyte Association Model Reactions<sup>a,b</sup>

species	mass action relation	equilibrium constant
1. $HL_i$	$HL_i \rightleftharpoons L_i^- + H^+$	$K_{ai}$
2. $L_i^-$	$HL_i + M^+ \rightleftharpoons ML_i + H^+$	$K_{MLi}$
3. $ML_i$	$HL_i + Me^{2+} \rightleftharpoons MeL_i^+ + H^+$	$K_{MeLi}$
4. $CuL_i^+$	$HL_i + HL_j + Me^{2+} \rightleftharpoons MeL_iL_j + 2H^+$	$K_{MeLiLj}$
5. $CuL_iL_j$		

<sup>a</sup> Equilibrium constants of the form below: Pr, products; Re, reactants;  $n$ , stoichiometric coefficient; and  $\{ \}$  activity.  $K_- = [II_i(Pr_i)^n/II_j(Re_j)^n]$ .  
<sup>b</sup> Components— $H^+$ ,  $HL_i$  (humic ligand, class  $i$ );  $Me^{2+}$  (metal cation); and  $M^+$  and  $X^-$  (electrolyte ions).

Thermodynamic arguments (29, 30) suggest the following relationship for an anionic gel in a simple 1,1 electrolyte

$$pH_g - pM_g = pH_b - pM_b \quad \text{or} \quad \frac{\{H^+\}_b}{\{M^+\}_b} = \frac{\{H^+\}_g}{\{M^+\}_g} \quad (7)$$

where  $b$  and  $g$  refer to bulk and gel phases, respectively, and  $M$  represents the electrolyte cation. For a gel whose volume does not depend on ionic strength eq 7 can be used to show

$$pH_b(\alpha_0, I_1) - pH_b(\alpha_0, I_2) = pM_b(I_1) - pM_b(I_2) = C_{12} \quad (8)$$

where  $\alpha_0$  = fraction of sites dissociated,  $I$  = ionic strength of solution, and  $C_{12}$  = constant.

For such gels, titration curve plots of site dissociation ( $\alpha$ ) versus pH will have congruent shapes, separated by a constant  $\Delta pH$  dependent upon the ionic strengths of the individual titrations. This humic's titration curves (Figure 1, Supporting Information) are roughly congruent; however, observed  $\Delta pH$ s are  $\sim 0.6$ , not 0.93 as required by eq 8 for experiments at 0.01 and 0.1 N.

Since the acid base data was not reasonably replicated using any of these three geometries, they were not used to analyze copper binding data.

Two models which do not require assumptions about humic geometry are the Electrolyte Association (EA) model of Westall et al. (18) and the Non-Ideal Competitive Adsorption (NICA) model (8). In the EA model the humic is treated as a suite of simple ligands which bind protons, electrolyte cations, and metals (Table 1). Heterogeneities and electrostatic (gel) effects are mimicked by assuming that the humic has a fixed number (say 3–5) of ligand classes with a known acidity and a single counterion association constant applicable to all classes. Potentiometric titration data can be analyzed using a chemical equilibrium program such as FITEQL (32) to solve for the concentration of each site class and the humic counterion association constant. Metal binding parameters are fitted from the metal sorption data incorporating acid/base equilibria determined from the potentiometric titration fits.

The NICA model is an isotherm approach which models binding affinities within a class of sites as a continuous distribution. For a system with multiple components that can bind to the humic partitioning of component  $i$  to site class  $y$  is described by

$$Q_{i,y} = Q_{\max,y} \left( \frac{(K_{mi,y}c_i)^{n_{i,y}}}{\sum_j (K_{mj,y}c_j)^{n_{j,y}}} \right) \left( \frac{(\sum_i (K_{mi,y}c_i)^{n_{i,y}})^{p_y}}{1 + (\sum_i (K_{mi,y}c_i)^{n_{i,y}})^{p_y}} \right) \quad (9)$$

where  $Q_{i,y}$  = total amount of component  $i$  bound to site class  $y$  of the humic,  $Q_{\max,y}$  = total class  $y$  site density,  $c_i$  = concentration or activity of component  $i$ ,  $K_{mi,y}$  = median



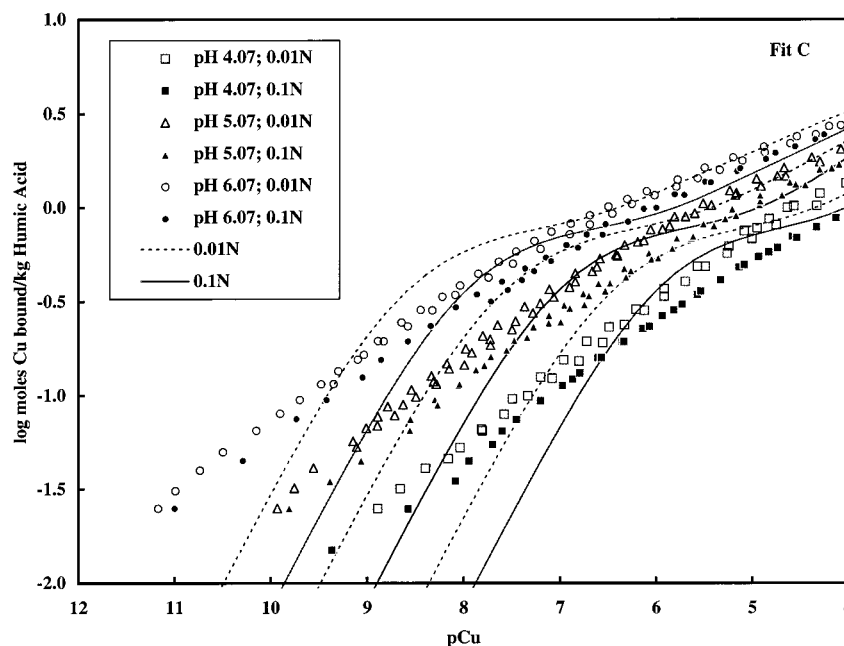


FIGURE 4. EA model fit (lines) to copper binding data (symbols), fit C of Table 3. Fits A and B included with Supporting Information.

affinity constant for component  $i$ ,  $n_{i,y}$  = sorbing component  $i$  nonideality factor, ideal if  $n_i = 1$ , and  $p_y$  = sorbent heterogeneity factor; sorbent is homogeneous if  $p = 1$ .

Heterogeneity parameters  $n_{i,y}$  and  $p_y$  determine the shape of the affinity spectrum. Where there is only one sorbing component eq 9 reduces to

$$Q_{i,y} = Q_{\max,y} \left( \frac{(K_{mi,y} c_i)^{m_y}}{1 + (K_{mi,y} c_i)^{m_y}} \right) \quad (9a)$$

where

$$m_y = n_{i,y} p_y \quad (9b)$$

For humics two classes of sites are generally considered important; carboxylic (median  $pK_a \sim 3-5$ ) and phenolic (median  $pK_a \sim 8-11$ ) (3, 8). The total of compound  $i$  that is bound by the humic is thus

$$Q_{i,\text{total}} = Q_{i,\text{carboxylic}} + Q_{i,\text{phenolic}} \quad \text{or} \quad Q_{i,1} + Q_{i,2} \quad (10)$$

Potentiometric titration data are fitted to eq 10 incorporating eq 9a. Metal binding data are fit using values from the potentiometric titration fits and incorporating eqs 9 and 9b into eq 10. NICA differs from other isotherm approaches (10, 33, 34) in that affinity distributions are allowed to vary from one sorbing component to the next.

**EA Model Fits.** FITEQL v.3.1 (32) was used to determine site class concentrations and a counterion association constant ( $pK_{Na}$ ) from the potentiometric titration data. Table 2 and Figure 1 suggest that the model can fit the potentiometric titration data well using several parameter combinations. However close examination of the fits show differences between model and data curvature (23, Supporting Information).

Many combinations of both monodentate and bidentate copper humic complexes (Tables 1 and 3) were used in attempts to fit the copper data (pH 5 and 6, 0.01 N). Results for three combinations, representing the best goodness of fit, WSOS/DF, values for two, three, and four complex combinations are summarized in Table 3, Figure 4, and the Supporting Information. Below a total of  $10^{-0.5}$  mol Cu bound per kg humic acid fit values and curve shapes deviate sharply

TABLE 2. Electrolyte Association Model Fits of Humic Potentiometric Titration Data

mol sites/kg humic acid for site w/given $pK_a$								
fit	3	5	7	9	11	total	$\log K_{Na}$	WSOS/DF
A	1.02	1.94	1.13	1.05		5.14	1.784	3.806
B	0.98	1.89	1.26	0.69	1.97	6.80	1.914	1.537
C	1.00	1.89	1.26	0.63	<u>2.40<sup>a</sup></u>	7.19	1.883	1.608

mol sites/kg humic acid for site w/given $pK_a$								
fit	4	6	8	10	12	total	$\log K_{Na}$	WSOS/DF
D	1.89	1.74	0.75	1.24		5.62	2.012	1.278
E	1.87	1.74	0.79	1.04	2.77	8.21	2.046	1.138
F	1.87	1.74	0.78	1.12	<u>1.70<sup>a</sup></u>	7.21	2.041	1.147

<sup>a</sup> Value fixed so total site [ ] = 7.2 mol/kg. <sup>b</sup>  $\log K_{Na}$ , electrolyte binding constant; WSOS/DF, weighted sum of squares/degrees of freedom; values  $< \sim 20$  indicate reasonable fits (32).

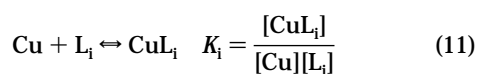
TABLE 3. Electrolyte Association Model Copper Binding Fits<sup>a</sup>

fit A		fit B		fit C	
complex	$\log K$	complex	$\log K$	complex	$\log K$
CuL5	-0.74	CuL4	-1.44	CuL2	-1.33
CuL1L3	2.65	CuL1L5	-0.46	CuL3	-1.14
		CuL2L3	1.00	CuL1L3	2.57
				CuL1L5	-0.15
WSOS/DF	254		250		259

<sup>a</sup> Fitted to pH 5 and 6; 0.01 and 0.1 N data; uses fit F of Table 2 for acid/base constants.

from the data. Replication improves at higher loadings, but even here curve shapes and pH and ionic strength dependencies differ from the observed behavior.

Table 4 and Figure 5 show why replication is poor at low copper loadings. They reflect FITEQL fits to the pH 5, 0.01 N copper binding data using the following reaction



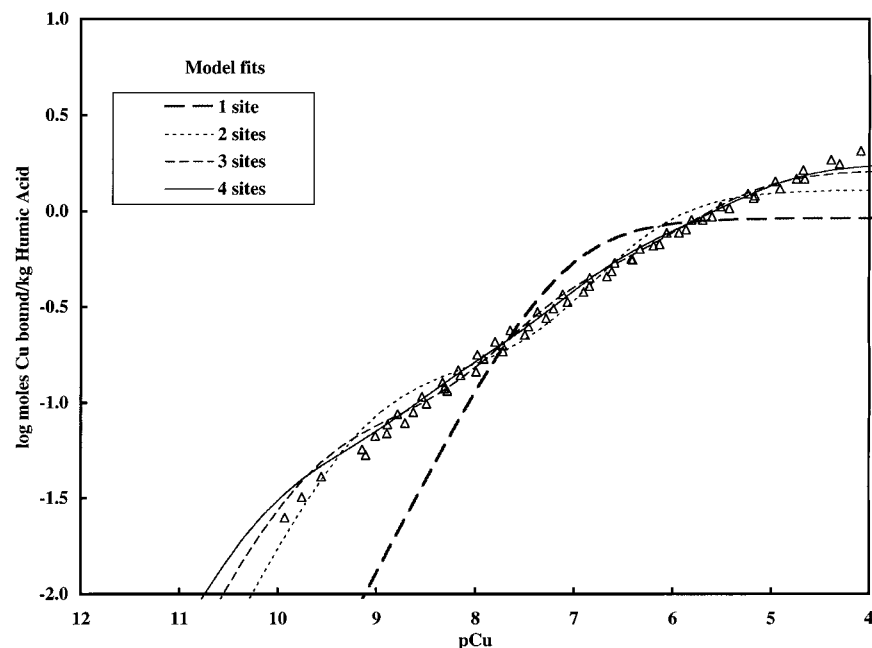


FIGURE 5. Multisite Langmuir fits (lines) to pH 5.07; 0.01 N data (open triangles). Refer to Table 4 for site concentrations and equilibrium constants employed.

TABLE 4. Langmuir Fits to pH 5<sup>b</sup>

site	site [ ] <sup>a</sup>	log K	site [ ] <sup>a</sup>	log K	site [ ] <sup>a</sup>	log K	site [ ] <sup>a</sup>	log K
1	0.92	1.95	1.14	1.12	1.12	0.32	0.95	-0.20
2			0.15	3.91	0.44	2.09	0.62	1.19
3					0.08	4.48	0.25	2.50
4							0.08	4.62
site [ ], total	0.92		1.29		1.64		1.82	
WSOS/DF		405		46		4.9		0.14

<sup>a</sup> Mol sites per kg humic acid. <sup>b</sup> 0.01 N copper binding data.

where *i* represents a class of copper binding ligands and [ ] indicates concentration.

One to four site classes were included. Isotherms for an individual site class are Langmuirian, i.e., slope of log Cu bound vs pCu  $\sim -1$  until [CuL] approaches the total concentration of the ligand, [L]<sub>T</sub>. The two complex fit of Table 4 replicates the single pH and ionic strength data better than any of Table 3's fits, while the three and four complex fits approximate the data reasonably well over the complete range. They do so because they contain a high affinity site class whose total concentration is 2% or less of total humic acidity, whereas the smallest site class used in the EA model fits (Table 2) represents 11% of the total acidity. Low concentration, high affinity classes are necessary to give the overall binding curve a slope between 0 and -1 ((20, 27); Supporting Information) when bound metal is far from saturating all available sites.

Table 5 highlights additional reasons for the poor fits. None of the 20 possible mono- or bidentate complexes (or obvious combinations of complexes) have pH or ionic strength dependencies that match those observed.

**NICA Model Fits.** FIT software (35) was used to fit the data to the NICA model. The basic NICA model cannot incorporate ionic strength effects; separate fits must be conducted for each ionic strength. Electrostatic or gel effects are not considered explicitly; to the extent they exist and vary with pH, they are accounted for in the log *K* values and the heterogeneity factors: *m*, *n*, and *p*. Table 6 summarizes acid/base fits; Figure 1 shows how fit C replicates the data. The

TABLE 5. Electrolyte Association Model pH and Ionic Strength Dependencies of Copper Complexes at Constant Copper Bound<sup>c</sup>

complex	pCu <sub>0.01N</sub> - pCu <sub>0.1N</sub> <sup>a</sup>			pCu <sub>pH5</sub> - pCu <sub>pH4</sub> <sup>b</sup>		pCu <sub>pH6</sub> - pCu <sub>pH5</sub> <sup>b</sup>	
	pH 4	pH 5	pH 6	0.01 N	0.1 N	0.01 N	0.1 N
CuL1	0.53	0.59	0.61	0.10	0.04	0.02	0.00
CuL2	-0.03	0.15	0.48	0.93	0.74	0.59	0.26
CuL3	-0.06	-0.06	-0.03	1.00	1.00	0.99	0.96
CuL4	-0.06	-0.06	-0.06	1.00	1.00	1.00	1.00
CuL5	-0.06	-0.06	-0.06	1.00	1.00	1.00	1.00
CuL1L1	1.19	1.31	1.34	0.21	0.08	0.04	0.01
CuL1L2	0.62	0.87	1.22	1.03	0.78	0.61	0.27
CuL1L3	0.59	0.66	0.70	1.10	1.04	1.01	0.97
CuL1L4	0.59	0.66	0.67	1.10	1.04	1.02	1.00
CuL1L5	0.59	0.66	0.67	1.10	1.04	1.02	1.00
CuL2L2	0.06	0.43	1.09	1.85	1.48	1.19	0.53
CuL2L3	0.03	0.22	0.58	1.92	1.74	1.59	1.23
CuL2L4	0.03	0.22	0.55	1.93	1.74	1.59	1.26
CuL2L5	0.03	0.22	0.55	1.93	1.74	1.59	1.26
CuL3L3	0.00	0.01	0.06	2.00	1.99	1.98	1.93
CuL3L4	0.00	0.00	0.03	2.00	2.00	1.99	1.96
CuL3L5	0.00	0.00	0.03	2.00	2.00	1.99	1.96
CuL4L4	0.00	0.00	0.00	2.00	2.00	2.00	2.00
CuL4L5	0.00	0.00	0.00	2.00	2.00	2.00	2.00
CuL5L5	0.00	0.00	0.00	2.00	2.00	2.00	2.00

<sup>a</sup> ( $\Delta pCu/\Delta p[II]_{Cu \text{ sorbed}, pH}$ ); experimental values were 0.2–0.3. <sup>b</sup> ( $\Delta pCu/\Delta pH$ )<sub>Cu sorbed, I</sub>; experimental values were 1.1–1.2. <sup>c</sup> Analysis holds when the fraction of the ligand bound to copper is  $\ll 1$ . Uses fit F of Table 2 for acid/base parameters.

*R*<sup>2</sup> values indicate fit quality; a value of 1 indicates that the model perfectly replicates the data (35).

In fit A the model was allowed to fit site densities. For fits B–D the site densities were fixed, with the total site density equal to 7.2 mol per kg humic acid (the Ba(OH)<sub>2</sub> calculated total acidity). For fit A, calculated class 2 site concentrations were much higher for the 0.1 N fit; however, for both ionic strengths the total, calculated site densities were significantly lower than the measured total acidity. Much of this discrepancy is probably due to the fact that pH titration endpoints were not high enough to dissociate all the functional groups, with more functional groups being dissociated in the 0.1 N titrations. The *R*<sup>2</sup> values show that fit

TABLE 6. NICA Model Potentiometric Titration Fits

parameter	A	B	C	D
		0.01 N		
log $K_1$	5.132 ± 0.03	4.914 ± 0.01	5.014 ± 0.01	5.146 ± 0.01
$m_1$	0.359 ± 0.005	0.387 ± 0.004	0.371 ± 0.004	0.351 ± 0.004
$Q_1^a$	4.505 ± 0.04	<b>4</b>	<b>4.25</b>	<b>4.5</b>
log $K_2$	9.459 ± 0.07	11.008 ± 0.05	11.113 ± 0.06	11.147 ± 0.08
$m_2$	0.880 ± 0.12	0.275 ± 0.009	0.338 ± 0.01	0.439 ± 0.03
$Q_2^a$	0.886 ± 0.09	<b>3.2</b>	<b>2.95</b>	<b>2.7</b>
$R^2$	0.9998	0.9996	0.9996	0.9994
		0.1 N		
log $K_1$	4.247 ± 0.06	4.232 ± 0.01	4.367 ± 0.01	4.518 ± 0.02
$m_1$	0.413 ± 0.01	0.413 ± 0.005	0.385 ± 0.005	0.356 ± 0.006
$Q_1^a$	4.054 ± 0.12	<b>4</b>	<b>4.25</b>	<b>4.5</b>
log $K_2$	9.539 ± 0.21	9.896 ± 0.02	10.051 ± 0.03	10.186 ± 0.04
$m_2$	0.423 ± 0.07	0.364 ± 0.008	0.423 ± 0.01	0.494 ± 0.03
$Q_2^a$	2.648 ± 0.42	<b>3.2</b>	<b>2.95</b>	<b>2.7</b>
$R^2$	0.9995	0.9995	0.9992	0.9985

<sup>a</sup> Mol sites/kg humic acid; bold, underlined values were fixed, not fit.

TABLE 7. NICA Copper Fits

parameter	site 1 only	site 2 only	site 1 dominates	site 2 dominates
		0.01 N		
log $K_{Cu1}$	5.099 ± 0.015		5.008 ± 0.029	2.983 ± 0.185
$p_1$	0.570 ± 0.017		0.593 ± 0.014	.555 ± 0.089
$n_{Cu1}$	0.392 ± 0.007		0.365 ± 0.007	0.895 ± 0.172
$n_{H1}^c$	0.651 ± 0.017		0.626 ± 0.015	0.668 ± 0.089
log $K_{Cu2}$		10.602 ± 0.180	9.473 ± 2.897	10.457 ± 0.144
$p_2$		0.891 ± 0.031	0.336 ± 0.173	0.992 ± 0.029
$n_{Cu2}$		0.398 ± 0.006	0.790 ± 0.166	0.357 ± 0.007
$n_{H2}^c$		0.380 ± 0.033	1.009 ± 0.173	0.668 ± 0.031
$R^2$	0.992	0.989	0.997	0.996
		0.1 N		
log $K_{Cu1}$	4.092 ± 0.050		3.644 ± 0.117	2.772 ± 0.107
$p_1$	0.445 ± 0.029		0.538 ± 0.022	0.545 ± 0.052
$n_{Cu1}$	0.463 ± 0.021		0.361 ± 0.014	<b>1.0<sup>a</sup></b>
$n_{H1}^c$	0.866 ± 0.029		0.626 ± 0.023	0.707 ± 0.052
log $K_{Cu2}$		9.586 ± 0.125	8.634 ± 0.593	9.992 ± 0.062
$p_2$		1.025 ± 0.029	0.679 ± 0.123	<b>1.0<sup>a</sup></b>
$n_{Cu2}$		0.397 ± 0.006	0.457 ± 0.059	0.364 ± 0.056
$n_{H2}^c$		0.413 ± 0.031	0.623 ± 0.123	0.423 ± 0.010
$R^2$	0.972	0.991	0.997	0.996

<sup>a</sup> Set to 1.0 because fitted value significantly greater than 1. Blank cells indicate that site class was assumed to not bind copper for that particular fit. <sup>b</sup> Fit C of of Table 6 used for acid/base parameters. <sup>c</sup> Calculated using eq 9b.

quality is not highly sensitive to the chosen site densities. Fit C (Table 6) was used in the copper binding analysis because a buffer capacity analysis of the acid/base titrations indicated a minimum at ~59% of total acidity (4.25 mol/kg; Supporting Information).

Figure 6 and Table 7 summarize results of fits to the pH 5 and 6 copper data. Comparison of pH 4 model predictions and data give a sense of a fit's ability to simulate partitioning outside the fitted data range. The 0.01 N data is fit reasonably well by all four combinations considered, though the site class 2 (nominally phenolic) dominant fit replicates pH 4 data poorly. For the 0.1 N data, fits employing both sites do the best job of matching the data and the fit employing only site class 1 (nominally carboxylic) poorly matches data below copper loadings of  $10^{-0.5}$  mol/kg for all three pHs.

**Model Predicted Proton Releases.** Proton releases predicted by EA model copper fits of Table 3 generally ranged between 0.9 and 1.3. Releases generally decreased with increasing pH and ionic strength (data not shown). Given the inability of the EA model to reasonably replicate the copper binding data this rough agreement between calculated and observed proton release may be merely serendipitous.

The isotherm approach of the NICA model permits formation of monodentate complexes only; calculated proton releases must be  $\leq 1$ . Class 2 sites (phenolic) are essentially completely protonated over the pH range 4–6, and calculated releases for copper bound to these sites were 0.98–1.00. The fraction of protonated class 1 sites varied, and calculated proton releases for copper bound to these sites ranged from ~0.8 at pH 4 to as little as 0.1 at the highest pH 6 copper loadings.

## Discussion

The experimental data are consistent with a heterogeneous, polymeric, and polyelectrolytic humic with a high capacity for copper (~3 mol Cu per kg humic acid). The pH, ionic strength, and proton exchange and copper loading properties of this soil humic acid are similar to observed properties of other humic substances (8, 9, 25, 26, 33).

This humic's properties are poorly replicated assuming a single, fixed sized, solute impermeable spherical or cylindrical entity with all acidic functional groups residing on the molecule's surface.

Ultrafiltration suggests a wide range of molecular weights with most of the acidity located on entities containing over



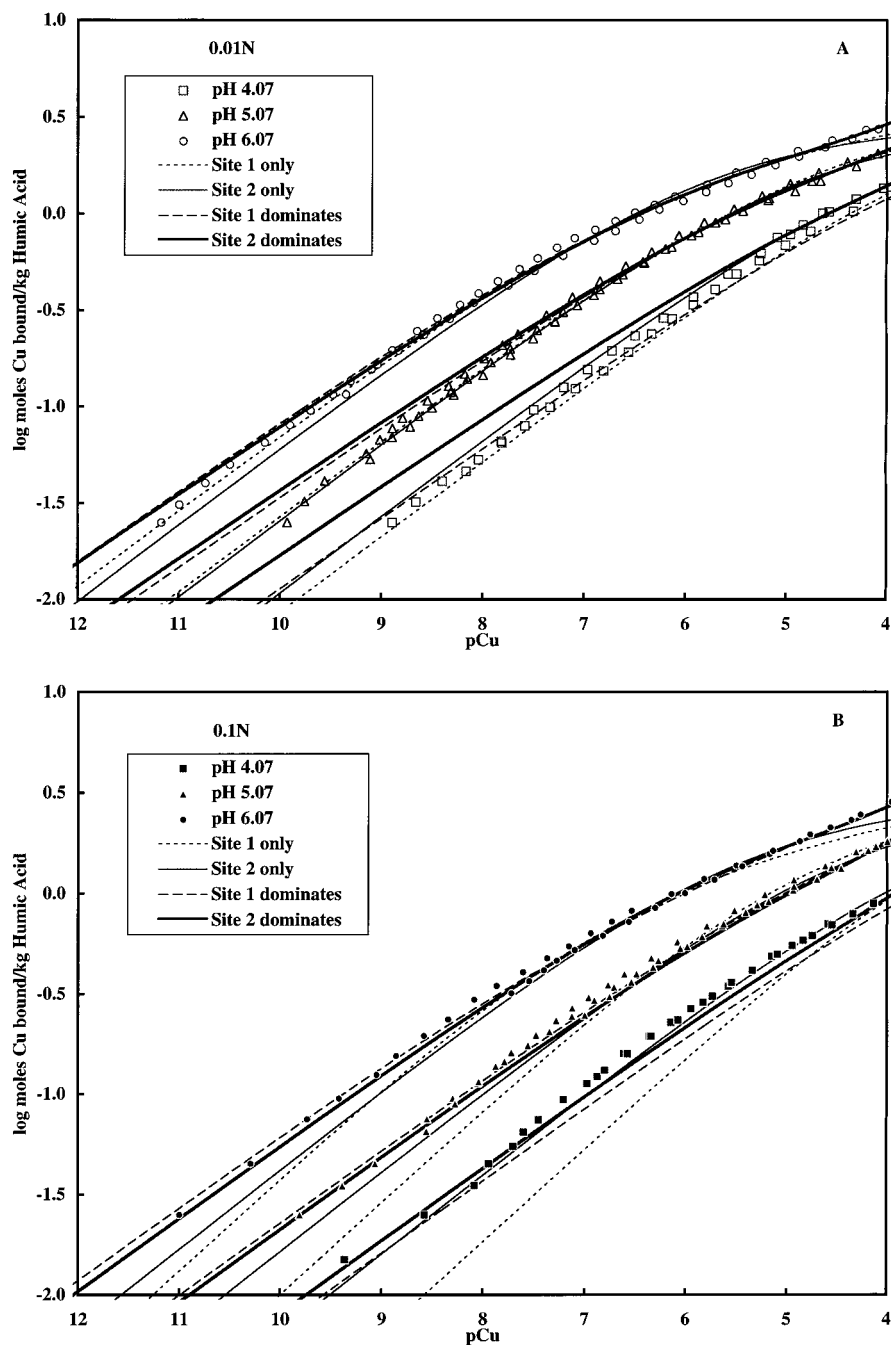


FIGURE 6. NICA model fits (Table 7) of humic copper binding data. Symbols represent data, lines represent model fits A. 0.01 N and B. 0.1 N.

100 functional groups. Such large entities may well have functional groups located throughout a three-dimensional structure (gel). However this humic's acid/base properties cannot be mimicked by a solute permeable, fixed volume gel.

The EA model requires no assumptions about humic structure and is directly compatible with standard chemical models which use components and species, eg., FITEQL. Its use requires no assumptions about, or assessments of, humic structure. For this humic the model reasonably replicates acid/base data but poorly replicates the copper binding behavior. This failure is due to both a lack of low concentration site classes and the inability of site classes to mimic observed copper binding pH and ionic strength dependencies. The former weakness could be alleviated by breaking a single proton affinity class into multiple copper affinity

classes. The latter weakness derives from the model's assumption that humic ligands behave like simple solution ligands, i.e., complexation of an ion ( $H^+$ ,  $Cu^{2+}$ ) by one ligand has no effect on solution properties adjacent to a second ligand. For polyelectrolytes ionic strength and ion sorption can influence electrostatic properties in ways that depend in a complex fashion on solution conditions and polyelectrolyte structure and composition. Thus the pH, ionic strength, and sorbent loading dependencies for polyelectrolyte complexation can differ substantially from those of simple ligands.

The basic NICA model also incorporates no assumptions regarding humic structure. Fits are conditional, i.e., good for a single ionic strength. For a given ionic strength any variability in electrostatic properties due to pH or sorbent loading are subsumed in the calculated affinity distribution

for a sorbing component. At each ionic strength both the acid/base and copper binding data for this humic can be reasonably replicated by the NICA model using *multiple* parameter combinations. This suggests that, in the absence of independent supporting data, one must be careful in ascribing physical significance to the NICA fits.

The proton release data and analysis (Figure 3) show proton exchange greater than that expected from binding to a simple monodentate ligand. For ligand-to-copper ratios of 1000, Stone (36) showed that a number of common, monodentate, carboxylic ligands bind roughly 10% of the copper. At similar ratios this humic acid bound 98 to >99.99% of added copper. Multidentate copper complexation may be important, and fits incorporating bidentate humic/copper complexes have been successfully employed by some researchers (37, 38). However electrostatic effects may significantly increase both the probability of binding by monodentate ligands and the observed proton release (13, 27); therefore, the data reported here do not provide conclusive evidence.

Our work suggests that a reasonable representation of humic polyelectrolyte properties is necessary for successful replication of humic ion binding behavior over wide ranges of solution conditions. Recently the NICA model has been coupled with a variable volume gel model to describe behavior of humics and other organic polymers (9, 13, 39). Tipping and co-workers (17, 37, 40, 41) have modeled multiple ionic strength humic behavior assuming a small number of discrete affinity site classes (similar to the EA model) coupled with an empirical electrostatic relation whose two fitting parameters are derived from acid/base titration data (model V). Both the NICA Donnan model and Tipping's model V can fit acid/base data that is consistent with the following relationship (similar to eq 8)

$$\text{pH}_b(\alpha_0, I_1) - \text{pH}_b(\alpha_0, I_2) = \text{pM}_b(I_1) - \text{pM}_b(I_2) - V^* = C_{12}^* \quad (8b)$$

where  $V^*$  depends only on the two ionic strengths. In the NICA Donnan model

$$V^* = \log \left( \frac{V(\alpha_0, I_2)}{V(\alpha_0, I_1)} \right) \quad (8c)$$

where  $V(\alpha_0, I)$  represents the specific volume of the gel phase ( $\text{L}^3/\text{mol}$  or  $\text{L}^3/\text{g}$  of humic). Acid/base data which fits an equation like 8b are consistent with a variable volume gel, whose specific volumes depends on ionic strength but not on degree of protonation. For a  $C_{12}^*$  equal to 0.6 our acid/base data can be fit to eq 8b quite well. This suggests a gel whose volume at  $I = 0.01 \text{ N}$  is twice its volume at  $I = 0.1 \text{ N}$ .

Experimental binding isotherms for metal cation/humic systems often include humic metal loadings as low as 0.1% of total humic acidity (8, 9, 13, 26, 42, 43). As shown in Figure 6 and Table 4, low concentration, high affinity site classes may be important in determining shapes of such isotherms. Analyses of acid/base data may not suggest their presence because 1. site concentrations may be of the order of, or smaller, than experimental error and 2. minor site acid/base properties may be very similar to those of higher concentration site classes. The NICA model can incorporate low concentration, high affinity sites because affinity distributions are independently determined for each binding cation considered. For discrete site models inclusion of additional or subdivision of site classes determined from acid/base analyses may be necessary to successfully replicate both metal and proton behavior over a wide range of solution conditions.

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## Supporting Information Available

Additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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