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Lead and Calcium Binding to Fulvic Acids: Salt Effect and Competition

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Knowledge of the speciation of Pb in natural aquatic systems is important if we want to understand the bioavailability and mobility of Pb in polluted and natural environments. The results given in this paper were obtained under conditions as close as possible to natural conditions. These new data show that Pb strongly binds to fulvic acids. We also show that the competitive effect of Pb on Ca binding to the same fulvic acid is smaller than the salt effect on Ca binding to fulvic acids as pH varies from 4 to 8. All the data were analyzed with the NICCA–Donnan model developed to describe metal ion binding to natural organic matter. The model predictions of competitive and salt effects are excellent. Comparison of our results with previously published data suggests that metal ion binding strength is similar for fulvic acids from different origins. Thus, all data sets could be interpreted within the framework of a unified modeling approach.

Introduction

Anthropogenic emission of heavy metal ions in the environment during the last century has led to increasing accumulation of metal ions in soils and natural waters in both urban and rural areas. Accumulation of some heavy metal ions in soils indicates their relative immobility in the environment and that geochemical dispersion is not efficient. There is increased concern for the environmental impact of human activities on global climate change and for the impact of agricultural practices on the bioavailability of metal ions. It is, therefore, of primary importance to understand the geochemical processes that control the speciation and mobility of metal ions. The need for qualitative and quantitative descriptions of the chemical speciation of Pb in particular and other metal ions in general also is important because of increased mobilization of metal ions in water and soils due to acid deposition (1).

Pb is one of the most toxic metals especially for children (2). There is increased scientific interest in Pb geochemistry (3–5). With the help of Pb isotopic geochemistry, advances have been made concerning the nature of contamination sources and the mobility of Pb (6–8). Some papers address the problem of Pb binding by natural organic matter and minerals in soils and waters (9, 10). Recently, major advances have been made concerning the speciation of Pb at polluted

sites (11–13). The results of these spectroscopic studies show that organic matter is one of the major binding sites for Pb in soils (12, 13). Similar information on Pb speciation in aquatic systems is not available, but knowledge of Pb speciation in natural aquatic systems is important if we want to understand the bioavailability and mobility of Pb in polluted and natural environments. Data exist for the complexation of Pb with small organic molecules (i.e., acetate) (14) at various temperatures. However, small organic molecules are not the best analogues for NOM (15). Humic acids (HA) and fulvic acids (FA) provide better analogues for the reactive components of NOM in soils and rivers, and they can be used to model metal ion binding to NOM (15–17). Competitive interactions of H⁺, inorganic Pb species, and major cations (Ca²⁺, Mg²⁺) with NOM will affect the pH and Pb speciation. Hence, it is important to obtain reliable Pb binding data for organic ligands and to develop sound models to predict Pb speciation in natural, multicomponent systems (i.e., soils and rivers). The models should not only give information about the speciation of Pb but should also predict the net charge of the natural organic ligand since this is controlled by the extent of proton and metal ion binding.

Our aim in the present work is the prediction of the free metal ion concentrations in the presence of competing ions for various environmental conditions with the help of a unifying model because direct measurements are sometime difficult and time-consuming. To reach this goal, we present new data for Pb binding to one fulvic acid. The new data are obtained at experimental conditions closer to natural environments. For instance, using trace metal concentrations for Pb and an increase of salt concentration is significant of estuarine conditions. These new data sets and some previously published data (9) are analyzed using the new consistent bimodal NICCA–Donnan model (18) with a single set of parameters to describe Pb binding to different humic substances. Once the experimental data have been described with the NICCA–Donnan approach, we will show the effect of Ca competition on Pb binding.

Experimental Section

Proton Binding to LFA as a Function of Salt Concentration.

The Laurentian fulvic acid (LFA) was obtained from C. H. Langford. It is extracted from a podsol collected in the Laurentian Forest Preserve of Laval University, Quebec, Canada. Physicochemical characterization of the sample has been reported elsewhere (19).

Proton titrations were performed with a computer-controlled titration stand (20). Titrations were performed under pure nitrogen (99.99%) with CO₂ free KOH (0.0198 N) and HNO₃ (0.020 N). The titration method is described in detail in ref 21. It was modified to perform titrations at different ionic strengths on the same sample in a series of continuous up and down titrations. The titrations were carried out in a thermostated reaction vessel (25 °C) with solutions containing 125 mg L⁻¹ LFA. The pH was read with two pH Metrohm electrodes (6.0133.100) and a glass reference Metrohm electrode (6.0733.100) with a salt bridge (0.1 M KNO₃). The electrodes were calibrated by two different methods: (a) with NIST standard buffers of known pH values (4.008, 6.986, and 9.933) and (b) with solutions of known proton concentrations and ionic strengths. In the present work, the reported pH values correspond to calibrations made with solutions of known proton concentrations at the same ionic strength. The pH readings with the duplicate electrodes were averaged. After addition of acid or base, the rate of drift for both electrodes was measured over a 1-min interval, and

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readings were accepted when the drift was less than 0.25 mV min⁻¹. For each data point, the maximum time for monitoring pH drift was 20 min. Titrations of the LFA consisted of three up-and-down cycles conducted at ionic strengths of 0.01, 0.05, and 0.15 M (KNO₃). Before the first titration leg, the pH was read in the solution, and KNO₃ was added to reach the chosen ionic strength. Data points were collected at intervals of 5 mV in the -200 to +200 mV range (pH 3.5–10.6). At the end of the first leg (first acid), KNO₃ was added to reach the salt level for the second leg, and the titration was continued. Analysis of the titration data was performed as described in ref 21.

Ca Binding to LFA as a Function of pH. Ca concentrations in solution were measured potentiometrically using a Ca ion-selective electrode (Orion 93-20). Routine calibrations were performed under static pH conditions in the absence of fulvic acid with additions of 0.05–2 mL of 5.09 mM Ca(NO₃)₂ in 0.1 M KNO₃. Static pH experiments were carried out at pH 5, 6, and 8. A solution of LFA (65 and 125 mg/L) in 0.1 M KNO₃ was titrated to the static pH (± 0.004 pH) and then maintained for up to 1 h to stabilize the LFA before titration with Ca(NO₃)₂ in the concentration range of 5–200 μ M. The concentration of free Ca was measured after the static pH had been maintained for 15 min, and the Ca electrode deviation was less than 0.2 mV min⁻¹. This generally meant that there was a total time of 25–35 min between successive Ca additions. The total concentration of Ca species in the solution was then calculated, and the amount of bound Ca²⁺ was estimated by difference.

Ca binding to LFA (125 mg L⁻¹) at constant total Ca of 0.1 mM, a constant ionic strength of 0.02 M, and pH from 3 to 8 was measured. pH was varied with the same procedure used for the proton titrations (see above). The Ca concentrations in solution were measured potentiometrically using the Ca ion-selective electrode. Routine calibration was made at static pH 5.5 with additions of 0.05–2 mL of 5.09 mM Ca(NO₃)₂ in 0.02 M KNO₃.

Pb Binding to LFA as a Function of pH. The polarographic experiments were performed using an Autolab System (Eco Chemie) attached to a Metrohm 663 VA stand and to a personal computer using GPES 3.1 software (Eco Chemie). The electrodes were a static drop mercury working electrode, an Ag/AgCl reference electrode with a salt bridge and a platinum wire counter electrode. The experiments with LFA (125–250 mg L⁻¹) were done at pH 4, 4.5, and 5 and ionic strength 0.01 M. The total Pb concentration range was 0.01–10 μ M. Reverse pulse polarography (0.5–10 μ M) and anodic stripping (0.01–1 μ M) with small detection limits were applied.

Competitive Binding of Pb and Ca to LFA. Pb–Ca competitive binding to LFA (65 and 125 mg L⁻¹) at constant total Pb and Ca concentrations of 49 μ M and 0.1 mM, respectively, constant ionic strength of 0.02 M, and pH from 3 to 8 was measured. pH was varied with the same procedure used for the proton titrations (see above). Ca concentrations in solution were measured potentiometrically using the Ca ion-selective electrode. Routine calibration was made at static pH 5.5 with additions of 0.05–2 mL of 5.09 mM Ca(NO₃)₂ in 0.02 M KNO₃.

Model Description

Metal ions binding to humics is assumed to occur through specific interactions between cations and the “surface” functional groups and by nonspecific binding to any residual negative charge. The specific binding is described by the Non Ideal Competitive Adsorption model (NICA), and the nonspecific binding is described by the Donnan model (22–25). In this model, the affinity distributions for the different ions are not necessarily of identical shape. As well as a general heterogeneity exhibited by all ions, the NICA model includes

ion specific heterogeneity or nonideality. For humic and fulvic acids, the model is based on a bimodal quasi-Gaussian intrinsic affinity distribution for all ions with monodentate binding. The starting point for the derivation of the NICA model is the use of the Henderson–Hasselbalch or Hill equation as a local isotherm for the binding species *i*. The basic NICA equation for the overall binding of species *i* in the competitive situation is

$$\theta_{i,t} = \frac{(\bar{K}_i C_{D,i})^{n_i}}{\sum_j (\bar{K}_j C_{D,j})^{n_j} + 1 + (\sum_j (\bar{K}_j C_{D,j})^{n_j})^p} \quad (1)$$

where $\theta_{i,t}$ is the fraction of all of the sites occupied by species *i*, \bar{K}_i is the median value of the affinity distribution for species *i*, *p* is the width of the distribution, and $C_{D,i}$ is the concentration in the Donnan phase (see below). In the applications of the NICA model published so far (22–25), the amount of component *i* bound, Q_i , has been given by

$$Q_i = \theta_{i,t} Q_{\max} \quad (2)$$

where it is assumed that species *i* reacts with one site and Q_{\max} is the site density obtained from proton titrations. It has been recently shown that the combination of eqs 1 and 2 leads, in general, to a thermodynamically inconsistent set of equations for the competitive binding of species *i* (26, 27). The combination of eq 1 with eq 2 is only consistent if all values of n_i are equal (18, 26, 27). Stoichiometric consistency is obtained by scaling according to n_i/n_H (18):

$$Q_i = \theta_{i,t} (n_i/n_H) Q_{\max} \quad (3)$$

Q_{\max} is the maximum binding capacity for protons. Substituting eq 1 into eq 3 to give eq 4 defines a stoichiometrically consistent version of the NICA model. We call this the Consistent NICA or NICCA model. In the absence of metal ions, i.e., protons only, $n_i/n_H = 1$, and the NICCA model reduces to the Langmuir–Freundlich (LF) isotherm. This reinforces the point that n_i and *p* in eq 1 can only be separated using multicomponent data. Data for metal ion binding are necessary to split the apparent heterogeneity into a generic or intrinsic heterogeneity part seen by all ions (*p*) and an ion-specific nonideality part seen by each particular ion (n_i).

The Donnan model used in combination with NICCA 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. This point is discussed in some detail for acid–base titration experiments with humic and fulvic acids in refs 23 and 28, and it is concluded that the Donnan volume is most sensitive to changes of ionic strength. It does not appear to vary greatly with changes of charge during simple acid–base chemistry. This assumption was confirmed recently by viscosimetric measurements (28, 29). Since there is not as yet sufficient data to say how the Donnan volume varies with the concentration of specifically bound metals, we have assumed here that it varies with ionic strength and have used the empirical relationship between ionic strength and Donnan volumes given in ref 24.

The total amount of metal bound ($Q_{M,t}$ in mol kg⁻¹) measured experimentally corresponds to the sum of the specifically bound metal ion and the amount of metal ion bound in the Donnan phase and is given by

$$Q_{M,t} = Q_i + V_D(C_{D,i} - C_i) \quad (4)$$

where C_i is the concentration of the metal ion in the bulk solution in mol L⁻¹.

Results and Discussion

Experimental Data. Proton. The base titrations data are shown in Figure 1. General proton data have been discussed

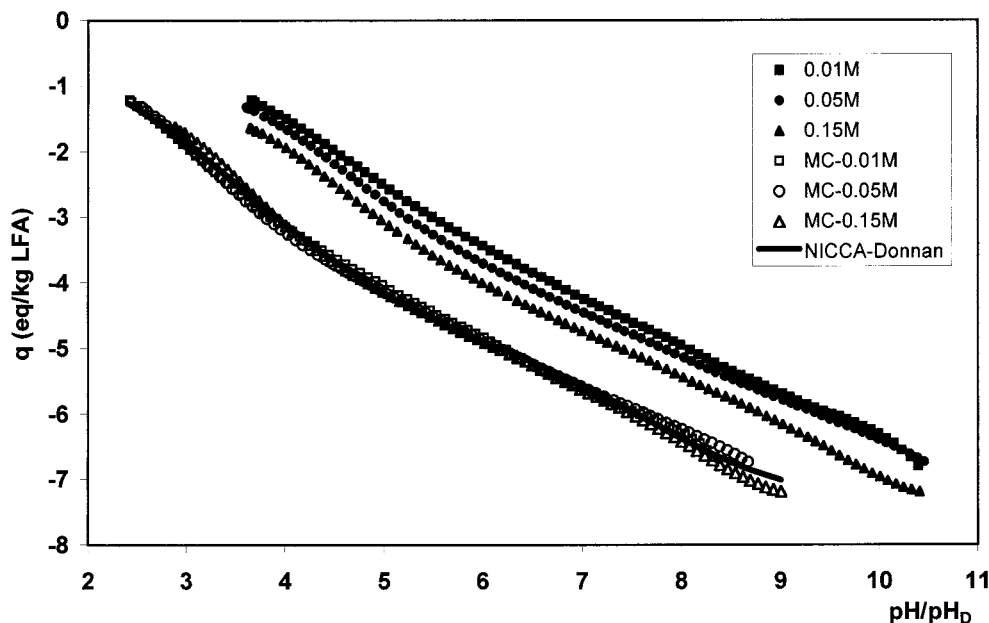


FIGURE 1. Effect of ionic strength on the proton binding curve. pH_D corresponds to the data corrected for salt effects with the Donnan model developed by Benedetti et al. (23). MC master curve in open symbols. The absolute position of the charge was obtained with an initial charge value of -1 equiv/kg as discussed in ref 21.

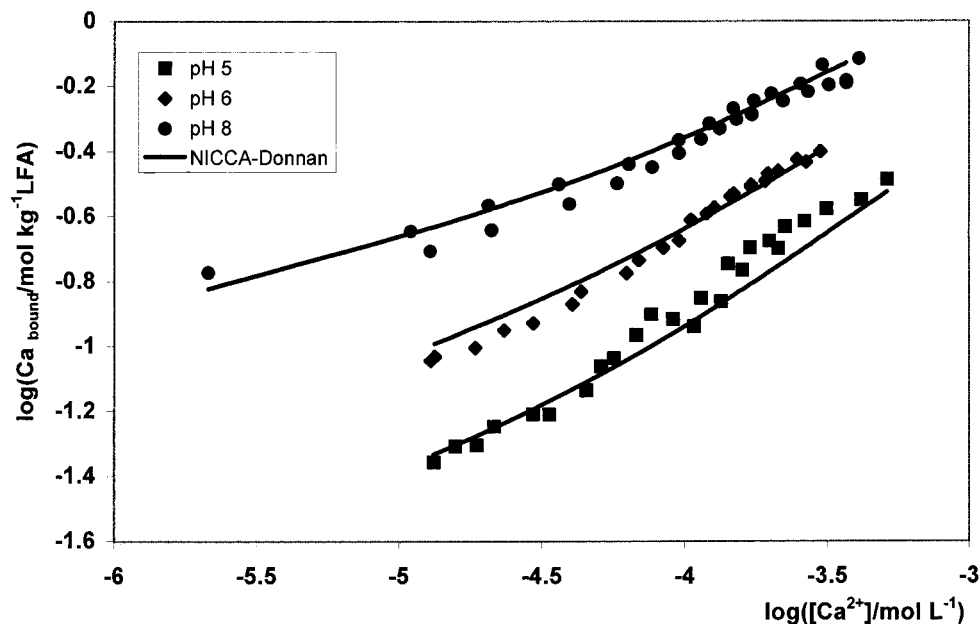


FIGURE 2. Ca binding (mol of Ca/kg of LFA) to LFA as a function of pH as measured during static pH experiments with a Ca ISE. The ionic strength is constant ($I = 0.1$ M KNO_3). Data points correspond to different total amounts of LFA (i.e., 65 or 125 mg/L). The data points were used to obtain NICCA-Donnan parameters given in Table 1 and correspond to the fitted model lines.

extensively (21, 23), but since the proton charging curve is used to derive the proton parameters, the major results are summarized here. Surface charge versus pH curves for LFA measured at different ionic strengths could be modeled reasonably well with the master curve approach (30). However, Figure 1 shows that above pH 9.5 the salt effect causes a clear deviation from the expected behavior, presumably due to (a) the low fulvic acid concentration used in the experiment (low buffer capacity) and (b) the hysteresis between acid and base titrations as previously reported (31, 32).

Metal Ions. Figure 2 shows the Ca binding data, $\log[\text{Ca}_{\text{bound}}]$ as a function of the free Ca concentration, $\log[\text{Ca}^{2+}]$, for pH values of 5, 6, and 8. The Ca binding is strongly pH dependent, with more Ca bound at higher pH. The data show

no effect of the varying LFA concentrations from 65 to 125 mg/L on the binding at a given Ca to ligand ratio. The separation between the pH 6 and pH 8 curves in the log-log plot is similar to the one measured for Ca binding to a purified peat humic acid (33). The unusual slope for the Ca isotherms in Figure 2 could be the result of the dominant nonspecific binding of Ca to the fulvic acid or to deviation of the Ca electrode with respect to the calibration at low free Ca concentrations.

Figure 3 shows the Ca binding as function of pH at constant total Ca and LFA concentrations. We also show three data points from the static pH experiments 5, 6, and 8 (Figure 2) corresponding to the same amount of total Ca. It can be seen that the ionic strength effect is very important for Ca binding. Another significant difference observed in

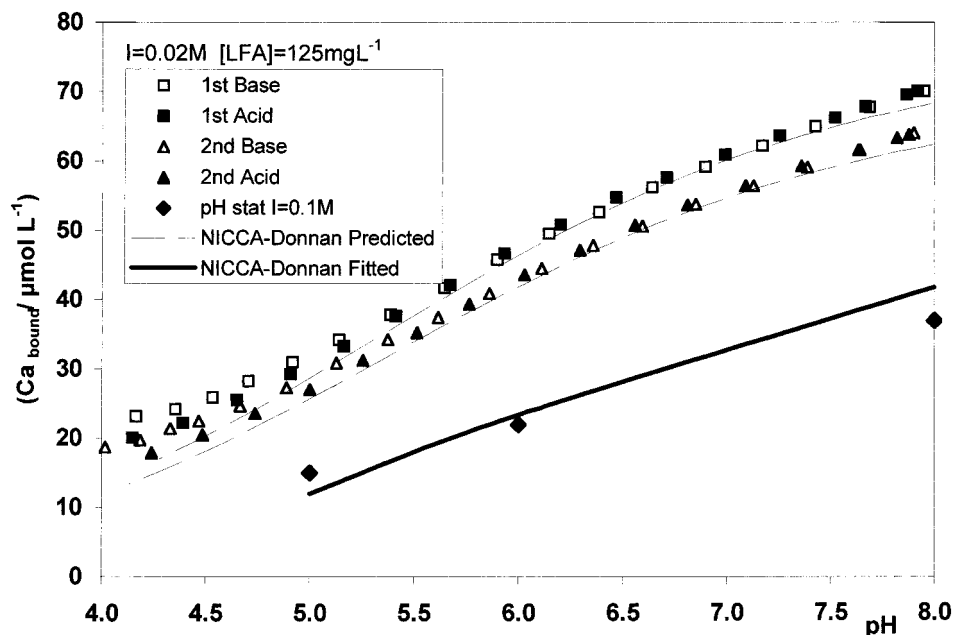


FIGURE 3. Ca binding (μmol of Ca/L) to LFA as function of pH as measured during acid–base titrations at constant ionic strength ($I = 0.02\text{ M}$), Ca concentration ($[\text{Ca}]_i = 0.1\text{ mM}$), and LFA concentration (125 mg/L). Also reported are three data points from the static pH experiments from Figure 2 showing the salt effect on the Ca binding to LFA. The solid line corresponds to the NICCA–Donnan fit from Figure 2. The dotted line corresponds to the model prediction of the experiments using the parameters from Table 1.

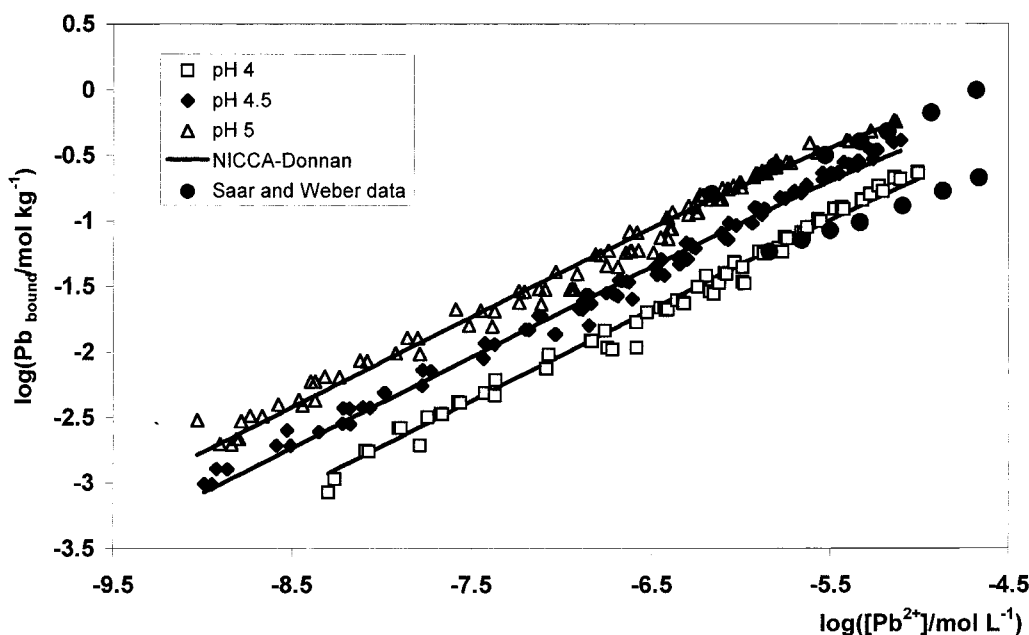


FIGURE 4. Pb binding (mol of Pb/kg of LFA) to LFA as function of pH as measured by voltammetry. The ionic strength is constant ($I = 0.01\text{ M}$). Data points correspond to different total amount of LFA (i.e., 125 or 250 mg/L). The data points are used to obtain NICCA–Donnan parameters given in Table 1 and correspond to the fitted model lines. The solid circles correspond to Pb binding to water-derived fulvic (WFA) as measured by Saar and Weber (9) at pH values of 5 and 4 and $I = 0.1\text{ M}$.

this figure is the dilution effect between the first and second leg of the experiment, which is not related to binding since the metal to ligand ratio remains the same.

Figure 4 shows $\log [\text{Pb}_{\text{bound}}]$ as a function of the free Pb concentration, $\log [\text{Pb}^{2+}]$, for pH values of 4, 4.5, and 5 at $I = 0.01\text{ M}$. Also reported are the data from Saar and Weber (9) for a water-derived fulvic acid at pH 4 and pH 5 at $I = 0.1\text{ M}$. Like Ca, Pb binding is pH dependent, and the total amount of Pb bound is much higher than Ca bound under similar conditions. The data show no effect of the varying LFA concentrations from 125 to 250 mg/L on the binding at a given Pb to ligand ratio. Combining our data together with

data of (9) shows that Pb binding is similar for both fulvic acids despite the different salt concentrations.

Figure 5 shows the effect of added Pb on Ca binding as function of pH at constant LFA concentration. For comparison, Ca binding in the absence of Pb (data from Figure 3) is also shown. The presence of Pb decreases the binding of Ca to LFA, as expected. The decrease is slightly pH dependent, with a stronger decrease at higher pH values. Another significant difference observed in Figure 5 is the dilution effect between the first and third leg of the experiment, which is not related to binding since the metal to ligand ratio remains the same. Comparing Figures 3 and

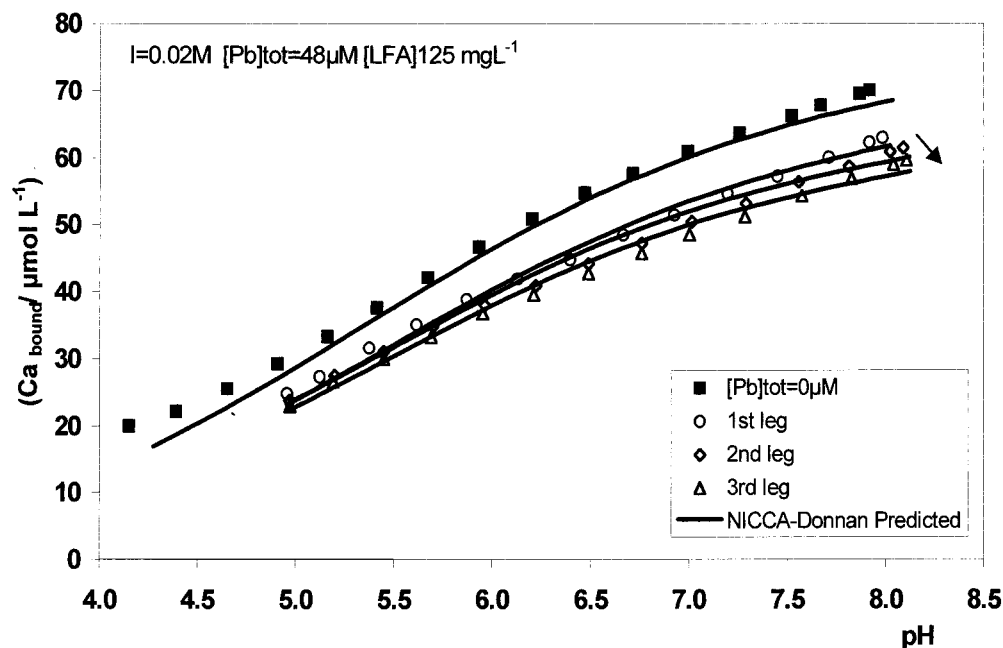


FIGURE 5. Ca/Pb competitive binding as a function of pH as measured during acid–base titrations at constant ionic strength ($I = 0.02$ M), constant Ca and Pb concentrations ($[Ca]_i = 0.1$ mM, $[Pb]_i = 49$ μ M), and LFA concentrations (65 or 125 mg/L). The data points correspond to the acid part of a titration leg. The solid lines correspond to the NICCA–Donnan model predictions using parameters from Table 1. The arrow shows the dilution effect during the acid–base titrations.

TABLE 1. Parameters Derived Using the NICCA–Donnan Model^a

	Proton Binding		
	Q_{\max}	m^b	$\log \bar{K}_H$
type 1 site	5.17	0.41	3.59
type 2 site	2.22	0.58	7.78
type 1 site for i	Metal Ion Binding		
	n_i	$\log \bar{K}_i$	p
H	0.60	3.59	0.68
Ca	0.28	-2.98	0.68
Pb	0.69	1.26	0.68

^aDonnan effects were simulated using the empirical relationship between V_0 and salt level described in ref 24. ^b m is the proton exponent in the double Langmuir–Freundlich (LF) equation used to describe the proton titration data; see ref 27 for extended definition.

5 shows that the effect of increasing ionic strength is much larger than the competitive effect of Pb on Ca binding to LFA.

Modeling. The full NICCA–Donnan model has a large number of parameters that were estimated using an unconstrained nonlinear least-squares fitting program.

Proton parameters were obtained by fitting the master curve data from Figure 1. Parameters are given in Table 1, and the line fit ($r^2 = 0.997$) is shown in Figure 1. The parameters are very similar to those previously obtained for fulvic material (see Table 3 in ref 23). As expected for humic substances, it was necessary to use a bimodal distribution with median affinity constant for type 1 and type 2 sites of $\log \bar{K}_1 = 3.59$ and $\log \bar{K}_2 = 7.78$, respectively. We identify these two distribution as low (COOH type) and high affinity types of sites (OH type or bidentate or SH, ...).

Ca and Pb data were used simultaneously in the fitting procedure to obtain the intrinsic heterogeneity parameter (p) of the LFA (18, 22). Model lines ($r^2 = 0.98$) for Ca and Pb are given in Figures 2 and 4, respectively. For the ranges of pH and metal to ligand ratio covered, only the low affinity

sites were needed to get a reasonable description of the experimental data (Table 1). When the high affinity sites were used in the fitting procedure, no significant improvements were obtained unless some arbitrary choices were made for some parameter values. Moreover, when using both types of sites, it was found that the majority of the bound metal ions was located on the low affinity sites. Therefore only the low affinity sites were used for fitting. This result is a consequence of the limited pH range explored by our calibration experiments for Pb (4–5) and the lack of data at lower free Ca^{2+} and free Pb^{2+} .

Metal Ion Speciation. It is important in metal ion speciation to distinguish between specific and nonspecific binding. This can only be done if models incorporate this important difference (16, 26). Our modeling approach allows this distinction. Ca speciation is dominated by nonspecific binding. At constant total Ca concentration, the specific binding increases with pH, and at a given pH it decreases with increasing total Ca. The huge salt effect on Ca binding observed in Figure 3 supports the importance of the nonspecific binding. This result agrees with previous work on Ca binding to purified humic substances (25). However, this finding does not agree with the recent assumption made for Ca binding to Suwannee River fulvic acid (34) where it was proposed that Ca binding could take place via specific binding (i.e., inner-sphere complex) to the fulvic molecule. Such modeling could not explain the large salt effect shown in Figure 3.

The dotted line in Figure 3 represents a model prediction of the change in Ca bound with pH obtained from the fitted parameters (Table 1). The model gives a reasonable prediction of the data for pH ranging from 5 to 8. The discrepancy observed at lower pH may be due to poor response of the Ca ISE in this pH range, probably caused by proton interference (35) or simply due to model deviation caused by overestimation of the proton Ca competition for low affinity sites. The goodness of the prediction emphasizes the importance of incorporating nonspecific binding in models to adequately describe the large salt effect.

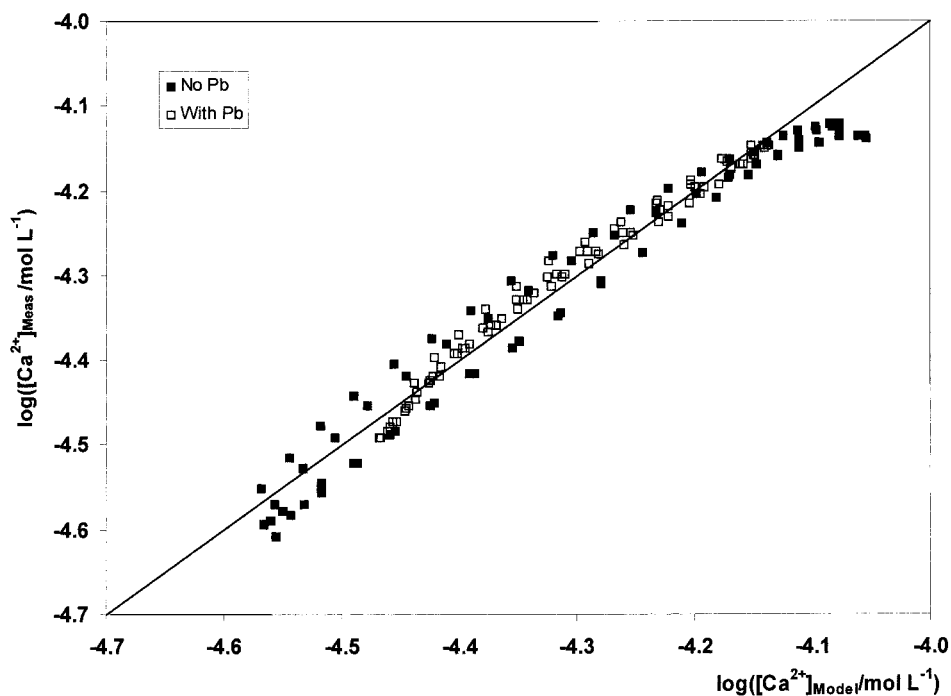


FIGURE 6. Ca concentrations measured by ISE as a function of Ca concentrations obtained from the NICCA–Donnan model. Points correspond to both competitive (with Pb) and noncompetitive (no Pb) experiments described in Figures 3 and 5.

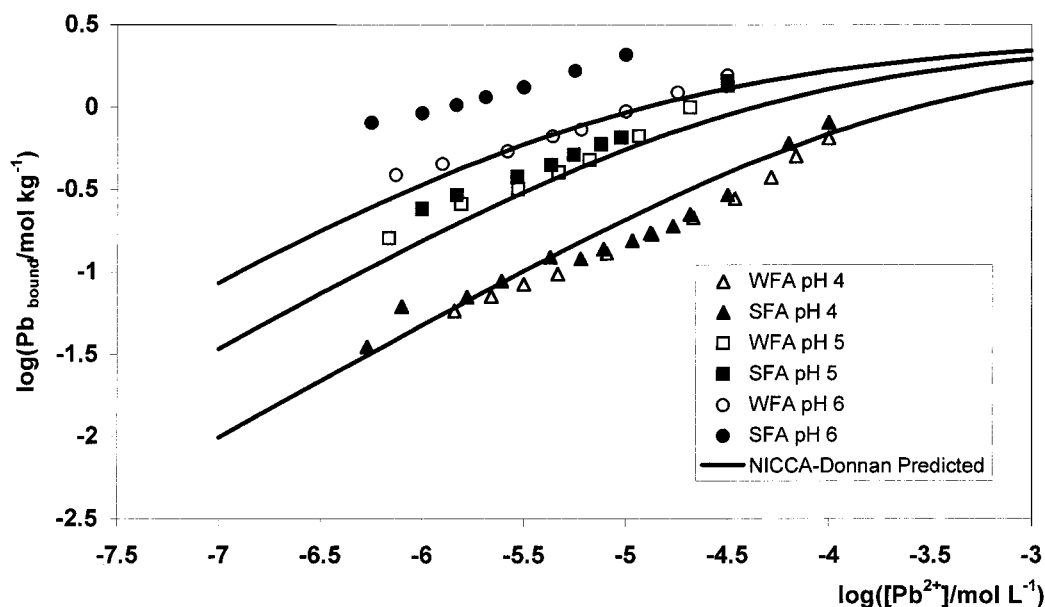


FIGURE 7. Pb binding to fulvic acids as measured by Saar and Weber (9) at constant ionic strength ($I = 0.1$ M) as a function of pH. WFA refers to water-derived fulvic acid data. SFA refers to soil-derived fulvic acid data. Lines correspond to NICCA–Donnan simulations using parameters from Table 1 derived for LFA.

In the case of Pb, the specific binding is dominant and the nonspecific binding is never larger than 10% of the total binding irrespective of the pH and the total Pb concentration used in the experiments.

Model Predictions and Competition. The validity of the modeling approach was discussed above with respect to salt effects (Figure 3). Note that with the present approach minor effects such as the dilution observed between the two legs of the titration are predicted.

One of the purposes of modeling is the prediction of free metal ion concentrations in the presence of other metal ions for various environmental conditions because direct measurements of all the free metal ion concentrations can be difficult and time-consuming (15). Consequently, it is

important to check the ability of the present model to predict free metal ion concentrations in a competitive environment. Our competitive experiment with Ca and Pb as a function of pH can be used for this purpose. In Figure 6, the measured free Ca is reported as a function of the free Ca as given by the model. The agreement between model-predicted values and measured values is excellent. Most of the data points cluster around the one to one line. This means that both pH and competitive effects are adequately simulated by the model. This can also be seen in Figure 5, where the effect of Pb and pH on Ca binding is shown. In this figure, the model predictions take into account the dilution effect observed for the three titration legs.

Similarities among Different Humic Substances. Figure 3 includes the Pb binding data from Saar and Weber (9) for different fulvic acids (FA) at the same pH and ionic strength. The very similar binding strength and pH effect (9) when compared to our data suggest that the binding strength and the pH effect could be the same for all FA for a given metal ion irrespective of the origin of the FA. It also confirms that the specific binding is dominant for Pb and that nonspecific binding is much less important (see above metal ion speciation). Similar behavior has been reported (15, 16, 23, 28, 32, 36) for humic substances (HS). Different proton titration data from various humic substances show very similar behavior irrespective of the origin of the HS (23, 28, 32). Earlier studies (15, 16) analyzing metal binding to different humic substances using one unifying modeling approach showed that binding affinity constants and heterogeneity parameters were similar for FA or HA of different origins. Very recently a similar behavior was also reported for Cu binding to fulvic acids (37). We can suggest two reasons for such behavior. First, this behavior could result from the extraction procedure used to recover the HS. The process (38) could homogenize the binding properties of the extracted material by only extracting molecules with similar types of binding groups (39). In this case structural differences could be preserved, but the resulting binding properties would be the same due to the overall chemical heterogeneity. The second reason could result from the presence of the same binding groups (i.e., COOH and OH type groups) with similar binding affinity constants and heterogeneity in the HS molecules coming from different environments. Although structural differences may exist between HS with various origins as reported in structural studies (40, 41), these structural differences would not affect the metal ion binding due to similar chemical heterogeneity of the different HS molecules. This reasoning is also supported by the Pb binding data of Saar and Weber (9) shown in Figure 7 where different FA have the same binding strength and experience the same pH effect although the FA have different origins. In Figure 7, we also show the simulated Pb binding to FA using the parameters from Table 1 derived from our experimental data. It can be seen that NICCA–Donnan approach gives a reasonable prediction of the Pb binding as well as the effect of pH for both types of FA. A better description could be obtained by just changing the value of the first proton affinity constant in Table 1 (i.e., $\log K_1 = 3.11$ instead of 3.59). Such a difference will not significantly affect the goodness of the model description for our experimental data (Figure 4).

These findings support the idea of using one unifying modeling approach (16, 26) to describe data for various materials with one set of model parameters. This can only be done if the modeling accounts for salt effects, competition, and the chemical heterogeneity of the ligands.

Acknowledgments

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