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Effect of Aluminum Competition on Lead and Cadmium Binding to Humic Acids at Variable Ionic Strength

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Complexation of Al^{3+} by NOM will change the speciation of Al and influence its toxicity. Competitive binding data between Al and metal ions to humic acids are needed to understand changes in speciation and mobility. We also need to investigate the effect of changes in electrolyte concentration on the binding of Al, Pb and Cd to humic acid. Competition experiments were performed at various pH and electrolyte concentrations using Cd and Pb ion selective electrodes to measure free metal ion concentrations. The effect of aluminum on the lead binding is important; it can reduce the amount of lead bound by a factor of 2 to 3. In the absence of Al, an increase of ionic strength also leads to a reduction of Pb bound. For cadmium, similar results are obtained. The NICA-Donnan model is used to describe the Al and Pb binding to humic acids and to predict Pb−Al as well as Cd−Al competition without parameter adjustment. With NICA-Donnan model, we calculate the speciation of the metal ions in the system and quantify the contribution of specific binding and electrostatic binding as pH, electrolyte and metal ion concentrations change during the experiments. In a natural environment, Al competition will have an effect on Pb toxicity and on Cd transport.

Introduction

Aluminum, the third most abundant element in the earth's crust, is involved in many processes of increasing interest in both terrestrial and aquatic ecotoxicology and in soil and water quality assessment. Natural organic matter (NOM) plays a major role in the speciation and geochemistry of aluminum in natural systems (*1*). For example, $Al^{3+} - H^+$ exchange reactions and hydrolysis of Al^{3+} on organic matter exchange sites are important sources of pH buffering in soils and control the Al^{3+} activity in acid soils (*2, 3*). Phosphate fertilizer retention in acid soils is also believed to occur through binding of PO_4^{3-} on organic matter complexes via Al bridges (*4*).

The toxicity of Al in natural environments is believed to be directly related to the $[Al^{3+}]$ concentration and is an important limiting factor for plant growth and root development in acid soils (*5*). Complexation of Al^{3+} by NOM will change the speciation of Al and influence its toxicity. Moreover, NOM is an important target in water treatment (*6*). Generally, NOM is removed by coagulation with an Al or Fe salt (*7*). Therefore, a knowledge of the speciation of Al is important because it can give information about the mechanism of NOM removal during water treatment (*7*). The need for a qualitative and quantitative description of the chemical speciation of Al in particular, and other metal ions in general, is also important because of the increased mobilization of metal ions in water and soils due to acid deposition (*8*).

The competitive interactions of H^+, inorganic Al species, and major cations (Ca^{2+}, Mg^{2+}, ...) with NOM will affect the pH, Al speciation, and the NOM solubility (as well as its cation exchange capacity) (*9*−*11*). These interactions can influence chemical weathering, Al transport and toxicity, and the buffering of acidity (*9*). Hence, it is important to obtain reliable Al binding data for both inorganic and organic ligands and to develop sound models which can be used to predict Al speciation in natural, multicomponent systems (i.e. soils, rivers). The models should not only give information about the speciation of Al but also should predict the net charge of the natural organic particles since this is controlled by the extent of proton and metal ion binding.

High quality data for Al complexation with inorganic ligands are already available (*12, 13*). There is also data for the complexation of Al with small organic molecules (i.e. acetate) (*14*−*16*) at temperatures ranging from 25 °C to 200 °C. However, small organic molecules are not always good analogues for NOM (*17*). 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 the metal ion binding to NOM (*17*−*19*).

Several data sets for metal ion binding to HA and FA are available (see refs in *17, 20*−*25*) for different salt levels and pH values. However, these data sets are frequently not interpreted in the framework of a unifying modeling approach which results in diverse and controversial binding constants. Studies integrating competitive binding effects with the influence of Al binding on the charge of the humic particles are rare (*10, 20, 24*).

In this paper we present new data for Pb/Al and Cd/Al competitive binding to a humic acid. We also investigate the effect of changes in electrolyte concentration on the binding of Al, Pb and Cd to a humic acid. This competitive binding is used to derive new Al and Pb parameters within the NICA-Donnan unifying approach. Effect of salt and Al competition on the binding of Pb and Cd will be discussed within the framework of the NICA-Donnan model (*24*).

Experimental Section

The Purified Peat Humic Acid (PPHA) extracted from an Irish moss peat was obtained from D. Kinniburgh (British Geological Survey, Wallingford UK). Physicochemical characterization of the sample has been reported elsewhere (*25*).

Titrations were performed using a computer controlled titration stand (*25*) under pure nitrogen (99.99%) bubbling in a thermostated reaction vessel (25 °C). The pH was measured using two pH Metrohm electrodes (6.0133.100) and a Ag/AgCl glass reference Metrohm electrode (6.0733.100) with a salt bridge (same as the solution).

For all experiments, the pH electrodes were calibrated with CO_2 free KOH (0.099 M) and HNO_3 (0.100 M) at the ionic strengths of 0.005, 0.03 and 0.1 M. The duplicate values

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were averaged. After addition of acid or base, the rate of drift for both electrodes was measured over 1 min, and readings were accepted when the drift was less than 0.25 mV min^{-1}. For each data point the maximum drift monitoring time was 20 min. The pH electrodes were also calibrated with N.I.S.T. standards buffers pH (4.008, 6.986). During the pH stat experiments the pH was controlled with KOH (0.099 M) and HNO_3 (0.100 M).

Pb(II) Binding to PPHA in the Absence and Presence of Aluminum at pH 4.5. Pb^{2+} concentrations in solution were measured potentiometrically using a Pb ion-selective electrode (Radiometer ISE 25Pb). Routine calibrations were performed at pH 4.5, in the absence of humic acid, with total $Pb(NO_3)_2$ concentration ranging from 1 μM to 100 μM in either 0.005 M or 0.1 M KNO_3 (Pb ISE calibration: Eo = 178.5 ± 1.5 mV, slope 28.7 ± 0.1). Titrations were performed in the absence of aluminum at ionic strength (I) 0.005 M and in the presence of 30 μM $Al(NO_3)_3$ at I = 0.005 and I = 0.1 M. An additional experiment was the addition of aluminum (from 1 to 31 μM) to a mixture of 10 μM Pb and 65 mg L^{-1} of PPHA at pH 4.5 and I = 0.005 M.

A solution of PPHA 65 mg L^{-1} was titrated to pH 4.5 (± 0.004 pH) and then maintained for up to 30 min to stabilize the PPHA before titration with $Pb(NO_3)_2$ in the concentration range 2 μM to 100 μM. At each step the concentration of the Pb^{2+} was measured after the pH had been maintained at 4.5 for 10 min, and the drift of the Pb electrode was less than 0.1 mV min^{-1}. This resulted in 15−25 min interval between each Pb addition. The total concentration of Pb species in the solution was then calculated, and the amount of bound Pb(II) was estimated by difference.

Cd(II) Binding to PPHA in the Presence and Absence of Aluminum at pH 4 and 4.5. Cd concentrations in solution were measured potentiometrically using the Cd ion-selective electrode (Methrom 6.052.110). Routine calibrations were performed under pH stat conditions (pH 4 and 4.5) in the absence of humic acid with total $Cd(NO_3)_2$ concentration ranging from 1 μM to 100 μM in 0.005 M KNO_3 (Cd ISE calibration: Eo = −38 ± 1.5 mV, slope 29.8 ± 0.1). Titrations were performed in the absence of aluminum and in the presence of 30 μM $Al(NO_3)_3$ at I = 0.005 M. An additional experiment was the addition of aluminum (from 1 to 31 μM) to a mixture of 30 μM cadmium and 65 mg L^{-1} of PPHA at pH 4 and I = 0.005 M.

A solution of PPHA 65 mg L^{-1} was titrated to the stat pH (± 0.004 pH) and then maintained for up to 30 min to stabilize the PPHA before titration with $Cd(NO_3)_2$ in the concentration range 0.3 μM to 100 μM. At each step the concentration of Cd^{2+} was measured after the stat pH had been maintained for 10 min, and the drift of the Cd electrode was less than 0.1 mV min^{-1}. This resulted in 15−25 min interval between each Cd addition. The total concentration of Cd species in the solution was then calculated, and the amount of bound Cd(II) was estimated by difference.

Competitive Binding of Al and Cd to PPHA: pH Titration at Different Salt Levels. Cd−Al competitive binding to PPHA ([65 mg L^{-1}]) was measured at constant total Cd and Al concentrations of 30 μM and 31 μM, respectively, over the pH range from 3 to 5.5. The titration of the consisted of 3 cycles conducted at ionic strengths of 0.005, 0.03, and 0.1 M. Each cycle involved titration with base from pH 3 to pH 5.5, followed by a reverse acid titration. At the end of each cycle the ionic strength was increased by addition of 1 M KNO_3.

Model Description. Metal ions binding to humic substances 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 NICA model and the nonspecific binding by the Donnan model (*24, 26−30*). In the NICA model the affinity distributions for the different ions are not necessarily of identical shape. As well as a general heterogeneity that is seen by all ions, the NICA model includes ion specific heterogeneity or nonideality. The NICA equation for the overall binding of species i in the competitive situation is

$$\theta_{i,t} = \frac{(\tilde{K}_i C_{D,i})^{n_i}}{\sum_i (\tilde{K}_i C_{D,i})^{n_i}} \times \frac{(\sum_i (\tilde{K}_i C_{D,i})^{n_i})^p}{1 + (\sum_i (\tilde{K}_i C_{D,i})^{n_i})^p} \quad (1)$$

where $\theta_{i,t}$ is the fraction of all sites occupied by species i, $\tilde{K}_i$ is the median value of the affinity distribution for species i, p is the width of the distribution, n_i an ion-specific nonideality coefficient, and $C_{D,i}$ the concentration in the Donnan phase (eq 4). For humic and fulvics acids, the model is based on a bimodal quasi-Gaussian intrinsic affinity distribution for all ions. In the applications of the NICA model (*24, 30*), the amount of component i bound to a given type of site, i.e., carboxylic COOH and/or phenolic OH type groups, Q_i, is given by

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

where it is assumed that species i reacts with one site and Q_{max} is the maximum site density for proton binding to one type of site (COOH or OH). n_i and p in eq 1 can only be separated using multicomponent data. Therefore, data for metal ion binding is necessary in order to split the apparent heterogeneity into the generic or intrinsic heterogeneity, 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 NICA 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 both humic and fulvic acids in refs *29* and *31*, 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 titration. This assumption was supported recently by viscosimetric and Atomic Force Microscopy observations (*31, 32*). Therefore, we have used the empirical relationship between ionic strength and Donnan volumes given by ref *29*.

The total amount of metal bound ($Q_{Mi,t}$ in mol kg^{-1}) measured experimentally corresponds to the sum of the specifically bound metal ion to the COOH and OH type site and the amount of metal ion bound in the Donnan phase and is given by

$$Q_{Mi,t} = Q_i + V_D(C_{D,i} - C_i) \quad (3)$$

where C_i is the concentration of the metal ion in the bulk solution (mol L^{-1}) and is related $C_{D,i}$ by the Boltzmann factor

$$C_{D,i} = c_i \exp(-z_i F\psi_D/RT) \quad (4)$$

where z_i is the charge of the metal ion, ψ_D is the Donnan potential inside the Donnan gel, F is the Faraday constant (C mol^{-1}), R is the gas constant (J mol^{-1} K^{-1}) and T is the temperature (K).

Results and Discussion

Experimental Data. *Lead Binding to PPHA in the Absence and Presence of Aluminum*. The lead potentiometric titrations of PPHA are shown in Figure 1. The amount of Pb(II) bound is in the range of previously published data for Pb binding to PPHA (*24, 33*) at pH 4.5 and 4.95 (Figure 2). The effect of aluminum on the lead binding is significant since at a constant [Pb^{2+}], the addition of 31 μmol of aluminum

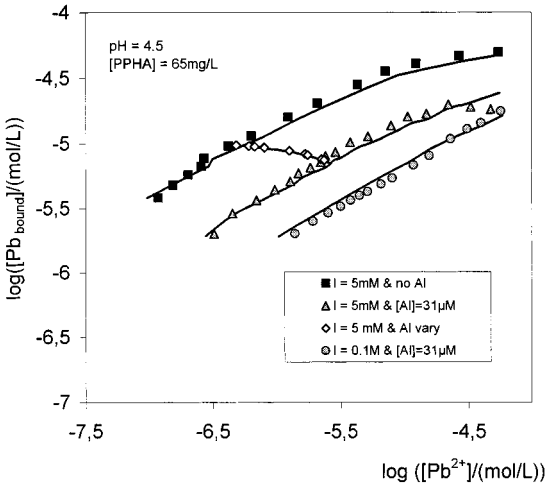

FIGURE 1. Al−Pb competitive binding to PPHA at pH 4.5 and two salt concentrations. The Pb binding (mol Pb/L) to PPHA was measured with Pb ISE. All data points correspond to a total amount of 65 mg PPHA/L. The effect of a fixed total aluminum concentration (31 μM) is shown for two salt concentrations (i.e. 5 mM and 0.1 M KNO_3). The effect of varying the total aluminum concentration from 0 to 31 μM at I = 5 mM is also shown. The data points corresponding to experiments made in the absence of Al and with a constant total Al (31 μM) concentration are used to obtained NICA-Donnan parameters given in Table 1 for aluminum alone, corresponding to the fitted model lines.

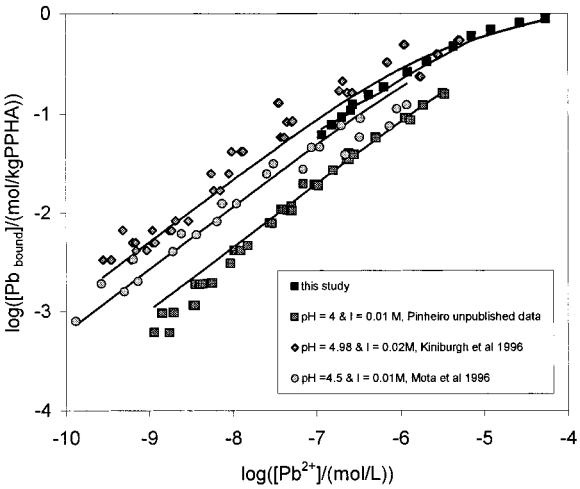

FIGURE 2. Pb binding (mol Pb/kg PPHA) to PPHA as a function of pH and ionic strength. Data points correspond to different experimental sets previously published for Pb binding to the same PPHA and include the data set from this study. The data points are used here to obtain NICA-Donnan parameters given in Table 1 for Pb alone, corresponding to the fitted model lines.

decreases the concentration of lead bound by a factor of 2−3 for the range of $[Pb^{2+}]$ explored in this experiment. The figure also shows the effect of changes in the ionic strength (from 0.005 to 0.1 M) on the Pb(II) binding. The effect is of similar magnitude to the effect of addition of aluminum, i.e decrease of factor 2 to 3. This result demonstrates that explicit electrostatic terms are necessary when modeling systems where salt effects may be important, such as in saline soils or estuarine conditions.

In Figure 3, we show the Cd(II) binding to the PPHA at two pH, with and without aluminum, at I = 0.005 M. The data show that the effect of aluminum competition is important and can be bigger than the pH effect when Cadmium binds to PPHA. The aluminum competition appears to be slightly more important at pH 4 than at pH 4.5.

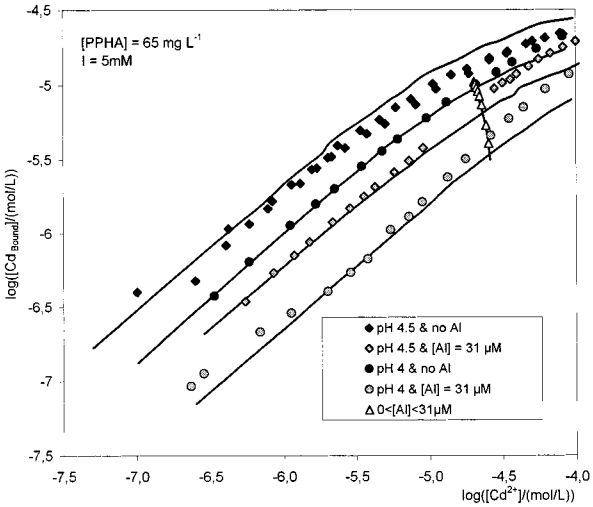

FIGURE 3. Al−Cd competitive binding to PPHA at pH 4 and 4.5 and I = 5 mM. The Cd binding (mol Cd/L) to PPHA was measured with Cd^{2+} ISE. All data points correspond to a total amount of 65 mg of PPHA/L. The effect of a fixed total aluminum concentration (31 μM) is shown for pH (i.e. 4 and 4.5). The effect of varying the total aluminum concentration from 0 to 31 μM at pH = 4 is also shown. In the present figure all lines correspond to predicted model lines using NICA-Donnan parameters given in Table 1.

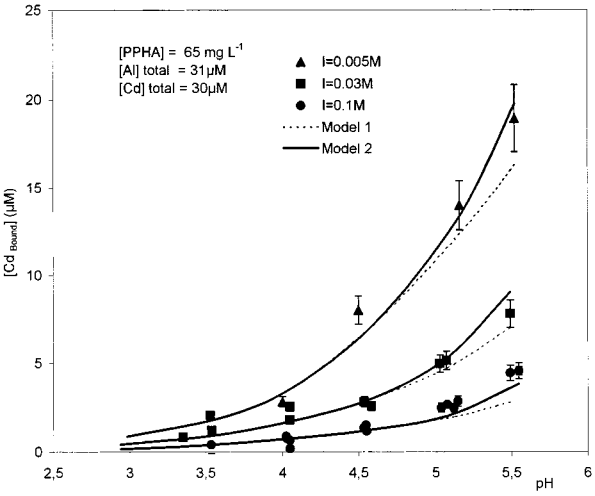

FIGURE 4. Al−Cd competitive binding as function of pH as measured during acid base titrations at variable ionic strengths (i = 5 mM, 0.03 M and 0.1 M KNO_3), constant Al and Cd concentrations ($[Al]_t$ = 31 μM, $[Cd]_t$ = 30 μM) and constant PPHA concentrations (65 mg/L). The dotted lines (model 1) correspond to the NICA-Donnan model predictions using parameters from Table 1. The plain lines (model 2) correspond to the NICA-Donnan model predictions using parameters from Table 1 including aluminum hydroxide ($Al(OH)_3$) precipitation during the experiment. In model 2 a log K_s of −33.5 was used for the $Al(OH)_3$ solubility.

This could be due to the increased competitive effect of at low pH and/or to increased Al^{3+} competition due to the decrease of hydrolyzed Al species concentration with decreasing pH.

Figure 4 shows the results of cadmium binding experiments, at different pH and electrolyte concentrations, with a constant total amount of aluminum. The data clearly show the strength of the nonspecific (outer-sphere) binding of the cadmium. For instance, at pH 5.5, the concentration of cadmium bound decreases by a factor 4 when the ionic strength increases from 0.005 to 0.03 M. This effect will be important for estuarine conditions or saline soils where electrolyte concentrations are high, even if the concentrations

TABLE 1. Parameters Derived from Competitive Metal Ion Binding Using NICA-Donnan Model[a]

type 1 site for *i*	n_i	log $\tilde{K}_i$
Al	0.25	2.00
Cd[b]	0.66	0
Pb	0.65	1.52

[a] Donnan effect were simulated using the empirical relationship between V_D and salt level as described in ref *29*. [b] Cd parameters were taken from ref *24*.

of Cd or Pb added in the experiments are 1 to 2 orders of magnitude higher than in pristine environments. Moreover, it shows that changes in electrolyte concentrations can be as large as the pH effect observed at a low ionic strength (Figure 4).

Modeling. *New NICA-Donnan Parameters for Al and Pb Binding to PPHA.* We will first discuss the parameters values already published by (*24*) for both Pb and Al. Using these parameters values, although it was possible to describe Pb/Al competitive binding to PPHA, we failed to account for the Cd/Al competitive experiments given in Figures 3 and 4 (these simulations are not given here). This can easily be understood since Kinniburgh et al. (*24*) supposed that both Pb(II) and Al(III) binding took place at high affinity sites or phenolic type sites. However, it was also seen by the same authors that cadmium binding at low pH (pH < 6) and high cadmium concentrations ($[Cd^{2+}] > 10^{-6}$ M) was dominated by low affinity or carboxylic type sites. Similar conclusions were reached by Li and co-workers (*34*) with Cd^{113} NMR studies. If most of the aluminum binding is located on the OH type sites, then almost no competitive effect is obtained when simulating a Cd(II)/Al(III) competitive binding experiment. The lack of agreement between model simulation and experimental data is an indirect proof of aluminum binding to COOH. Al binding to carboxylic acid group was suggested by Luster and co-workers (*35*) based on multiwavelength molecular fluorescence spectrometry for quantitative characterization of Al(III) complexation by organic matter. Therefore, to be able to account for competition data we have redetermined NICA-Donnan parameters for Al and Pb. Proton and cadmium parameters are taken as given by (*24*) since with them we were able to give a good description of the cadmium binding data in absence of aluminum (Figure 3). The small discrepancy at high cadmium loading at pH 4.5 could be due to differences between ISE calibrations in this work and in the original Cd binding data set (*34*) used to calibrate the model (*24*).

To obtain lead parameters, we used a combination of available datasets for Pb(II) binding to PPHA (Figure 2) in the absence of aluminum. The best fit ($r^2 = 0.96$) was obtained when Pb(II) binding was ascribed to the low affinity or COOH type of sites. The fitted values of n_{Pb} and log $\tilde{K}_{Pb}$ are given in Table 1. They are similar to those obtained for copper, a divalent cation with a known high affinity for humic substances (*17, 18*). The parameters for aluminum binding to COOH type sites were obtained by fitting the Pb−Al competitive experiments presented in Figure 1 using the ECOSAT computer code (*37*). In this figure, it can be seen that a reasonable description of the competition can be achieved since the solid lines, representing the model, are in good agreement with experimental data points. Figure 1 shows that the Donnan model, used to describe the electrostatic effects on the binding, is robust and can successfully account for salt effects even in the presence of highly charged metal ions such as Al^{3+}. Owing to the relatively low pH of our experiments we did not need to consider explicitly the binding of hydrolyzed species such as $AlOH^{2+}$. At higher pH, specific binding of hydrolyzed species may need to be considered (*24*). The very low value for n_{Al} (Table 1) may here reflect not only the partial correlation between affinity distributions (*24*) but also chelation and reaction stoichiometry (i.e. bi- or tridendate Al binding) as proposed by (*9*−*11*).

Model Predictions: Cd/Al and Previous Pb/Al Competitive Experiments. The NICA parameters for aluminum can be validated by simulating, rather than fitting, the results of the competitive Cd binding experiments and comparing with with the experimental data. This is illustrated in Figures 3 and 4 where the simulated model lines are in good agreement with the experimetal data. The importance of Al competition and the validity of the approach is reinforced in Figure 4 when small changes in the free aluminum concentration are taken into account increasing the quality of the simulated lines (model 2 versus model 1). In model 1 no aluminum hydroxide precipitation was allowed above pH 4, where it is well-known that $AlOH_3$ solubility can control the free aluminum concentration ($[Al^{3+}]$) (*13*). If ignored, this leads to an overestimation of the free aluminum in the system and by consequence to an overestimation of the competitive effect on Cd(II) binding. A much better prediction of the data is achieved when $AlOH_3$ precipitation is allowed (Figure 3, model 2). This is especially true for data points corresponding to the lowest ionic strength (0.005 M) and highest pH values which are relevant to natural systems. The agreement between model simulation and experimental data does suggest that Al binds to COOH (*35*) for a range of total Al concentrations which are similar to the range found in natural rivers, lakes or soil solutions.

One of the purposes of the modeling is the prediction of the free metal ion concentration in the presence of other metal ions for various environmental conditions. We have assessed the ability of the present modeling approach to predict free metal ions in a competitive environment. In Figure 5, the measured Pb^{2+} and Cd^{2+} concentrations are reported as a function of the calculated Pb^{2+} and Cd^{2+} concentrations. The data points cluster around the one to one line meaning that the increasing competitive effects with the increasing total aluminum concentration are adequately simulated by the model.

Mota and co-workers (*33*) studied the competitive binding of Pb and Al to the same PPHA but at a higher electrolyte concentration. These data provide a further test to validate the Pb and Al parameters derived from this study. A reasonable agreement is obtained between the model predictions using the parameters in Table 1 and the experimental data, especially at the low free lead concentrations which are relevant for natural systems (Figure 6a). Only data obtained with the highest total humic acid concentration (124 mg L^{-1}) are reported in Figure 6a. Data obtained with a lower humic acid concentration are available (*33*). All the data are presented in Figure 6b which shows measured $[Pb^{2+}]$ by ASV (*33*) as function of the simulated $[Pb^{2+}]$. This figure seems to confirm the hypothesis regarding the binding of Al to the low affinity type sites since the points cluster nicely along the one to one line. The discrepancy between data and model lines at high total lead concentrations could perhaps be attributed to dilution, which is not taken into account in the model predictions. Dilution would result from base addition during the experiments in order to keep pH constant. It has been shown previously (*38*) that small scale dilution can affect the results of the modeling if not taken into account correctly.

Competition and Salt Effect. Mota et al. (*33*) concluded that Al competition was not only due to the decrease of available binding sites as for Ca/Pb or Ca/Zn (*39*) competition but also could be the result of an electrostatic influence of Al^{3+}, affecting the overall charge of the humic acid molecule. An important strength of models which explicitly consider electrostatic effects (like Model VI (*20*) or the NICA-Donnan

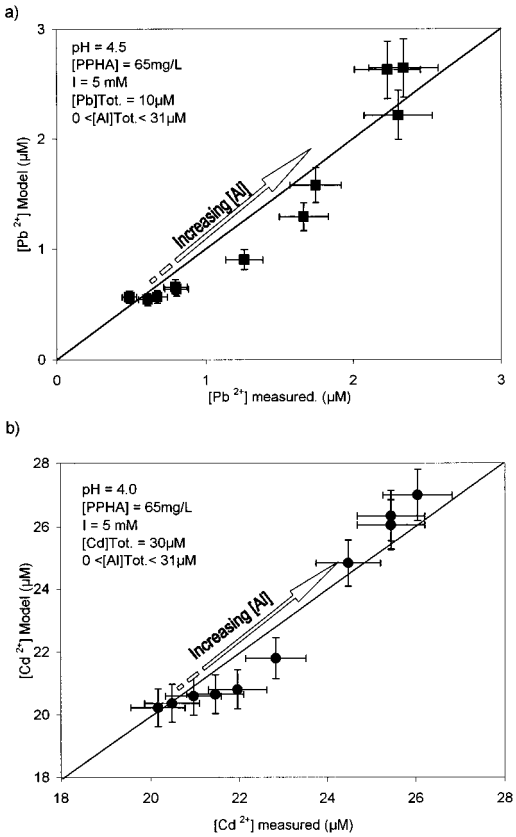

FIGURE 5. Modeled free metal ion concentrations vs measured free metal ion concentrations for Al competitive experiments at one pH, I = 5 mM and increasing total aluminum concentrations. (a) Showing free Pb^{2+} (μM) obtained from NICA-Donnan predictions as function of free Pb^{2+} (μM) measured by ISE at pH 4.5 with total [Al] increasing from 0 to 31 μM. Error bars correspond to a 10% error on Pb−ISE measurements. (b) $[Cd^{2+}]$ (μM) obtained from NICA-Donnan predictions as function of $[Cd^{2+}]$ (μM) measured by ISE at pH 4 with total [Al] increasing from 0 to 31 μM. Error bars correspond to a 10% error on Cd−ISE measurements.

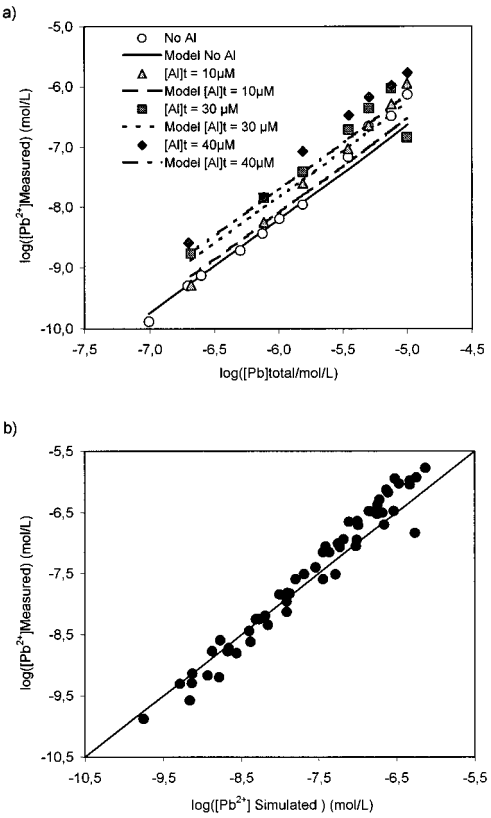

FIGURE 6. Lead aluminum competition as measured by ref *32*. (a) Pb^{2+} measured by ASV as function of total lead in the system at pH = 4.95, I = 0.01 M KNO_3 and [PPHA] = 124 mg L^{-1}. Lines correspond to NICA-Donnan Model predictions based on Al and Pb parameters given in Table 1. (b) Pb^{2+} concentrations (log scale) as function of simulated Pb^{2+} concentration (log scale) given by the NICA-Donnan model. Data points correspond to 2 concentrations of PPHA in the experiments, 124 mg L^{-1} and 62 mg L^{-1}.

model) is that they can be used to understand the respective contribution between specific binding to COOH or OH type sites and electrostatic effects. Moreover, this knowledge is extremely important since the metal ion speciation is needed to understand and predict mobility and bioavailability in the natural environment with data from field systems and or from laboratory experiments (*17, 40*). According to the NICA model, the binding of Pb(II) and Cd(II) by humic substances is very different (*24, 41*). Pb(II) binding is stronger than Cd(II) binding and in the range pH 3−5.5 Pb(II) binds to COOH type group, while Cd(II) binding mainly occurs via electostatic interactions in the Donnan phase (*24*).

Using the results of competitive binding experiments it was possible to investigate the effect of Al competition on the nature of Cd and Pb binding at the different ionic strenghts. Speciation calculations were carried out at constant pH and constant total aluminum and PPHA concentration. Figure 7a shows the speciation calculated with the NICA-Donnan model for the lead experimental data given in Figure 1. We can see that in this purely Pb system, 78% of the total Pb in the system is bound specifically. This calculated speciation is in agreement with EXAFS speciation data obtained for lead organic matter systems studied in the laboratory and in the field (*42, 43*). In Figure 7b, the speciation of lead in the presence of a fixed amount of aluminum (31 μM) is shown together with the corresponding Al speciation. Comparing with Figure 7a, it can be seen that Al competition reduces the amount of Pb specifically bound to COOH type sites (from 78% to 46% of total Pb). The reduction is due to Al bound to PPHA, either in the Donnan phase or specifically. The amount of Pb bound via electrostatic interactions (i.e. in the Donnan phase) is reduced to 4% due to the large amount of Al now present in the Donnan phase (30%).

The impact of increasing background electrolyte concentration is shown in Figure 7c. It has a drastic effect on lead specific binding, which is reduced to 27%. Most of the lead remains in the solution as Pb^{2+}. The explanation is found by comparing the aluminum speciation in Figure 7b,c. The increase in ionic strength mainly affects aluminum located in the Donnan phase: at high background electrolyte the electrostatic contribution becomes negligible (<5%). Therefore, aluminum is removed from the Donnan phase because of the lower potential induced by the higher charge screening capacity of the electrolyte (*28*). The increased amount of available aluminum becomes a stronger direct competitor of lead for specific binding sites because of its high affinity for the COOH type sites (*36*). The residual part of the aluminum remaining in the solution (as Al^{3+}, $AlOH^{2+}$, ...) now represents 34% of the total aluminum stock.

A similar type of simulation can be used to understand cadmium and aluminum competition and the effect of changes in ionic strength on both metal ions binding to PPHA (Figure 8). In the absence of aluminum we can see that cadmium speciation is different from lead speciation. Only 16% of the Cd is bound specifically and more than 50% of the total cadmium remains uncomplexed in the solution (Figure 8a). This calculated speciation is in agreement with measured cadmium speciation in soils solutions (*44*). Unlike

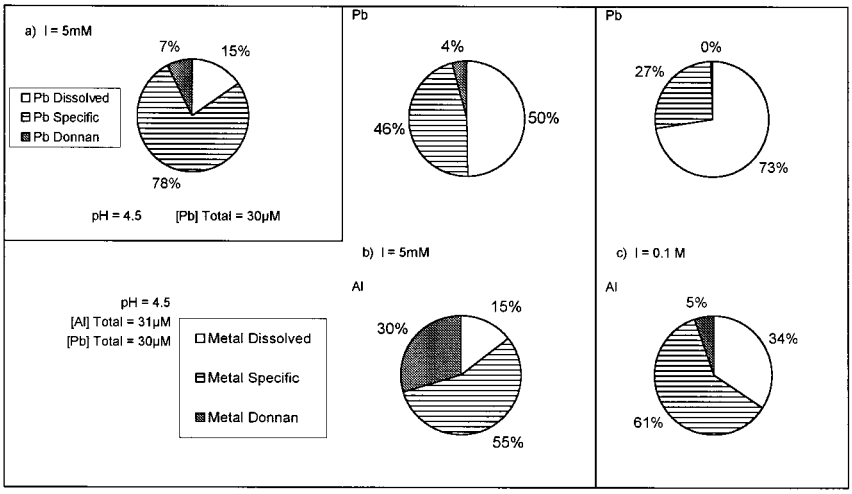

FIGURE 7. Effect of Salt and Al competition on lead and aluminum speciation. Dissolved corresponding to free and inorganic metal ion complex − Specific corresponding to metal binding calculated with eq 2 − Donnan corresponding to Metal ion located in the Donnan gel as calculated with eq 3. (a) Pb speciation at pH 4.5, I = 5 mM, PPHA = 65 mg L^{-1} and total Pb = 30 μM; (b) showing the effect of Al competition on Pb speciation as well as Al speciation at pH 4.5 and I = 5 mM and total Al = 31 μM; and (c) showing the effect of increasing background electrolyte concentration.

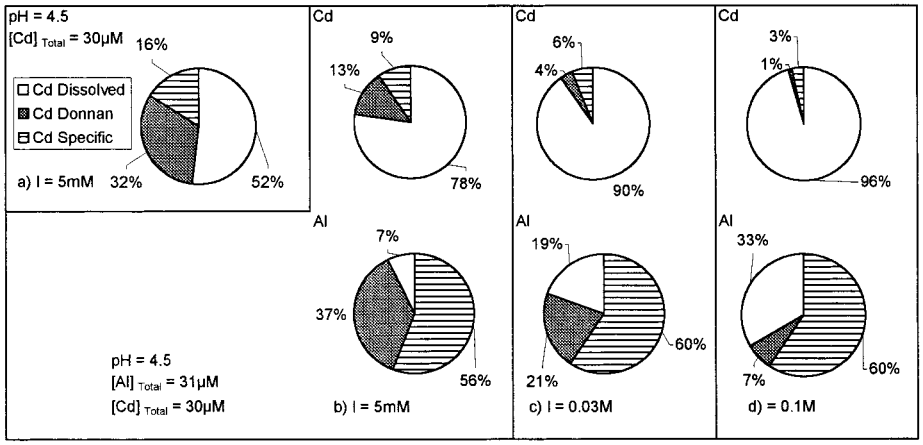

FIGURE 8. Effect of salt and Al competition on cadmium speciation. Dissolved corresponding to free and inorganic metal ion complex − Specific corresponding to metal binding calculated with eq 2 − Donnan corresponding to metal ion located in the Donnan gel as calculated with eq 3. (a) Cd speciation at pH 4.5, I = 5 mM, PPHA = 65 mg L^{-1} and total Cd = 30 μM. (b−d) Showing the effect of Al competition on Cd speciation as well as Al speciation at pH 4.5 and the effect of increasing background electrolyte concentration: I = 5 mM, 0.03 M and 0.1 M with total Al = 31 μM.

lead, however, cadmium is mainly bound to humic acids via electrostatic interactions in the Donnan gel (32%). Once aluminum is added in the system (Figure 8b) the amount of cadmium bound (specific + Donnan) is reduced to 22% and Cd specific and Donnan contributions are similar. This is the result of direct competition with aluminum for the COOH or low affinity type of sites but also direct competition between Cd^{2+} and Al^{3+} in the Donnan gel. Comparing Figure 8b and Figure 7b, we have an illustration of the lack of competitive effect of lead on the aluminum speciation due to the excess of binding sites. We can also see that in absence of a major competitor the amount of aluminum bound in the Donnan phase is quite similar (37% instead of 30%). The smaller amount of aluminum in the Donnan phase is the consequence of the larger amount of lead specifically bound compared to amount of Cd bound. Like Al, Pb could reduce the overall charge of the humic acid molecule thus lowering the Donnan potential inside the gel phase and the amount of Donnan bound metal ions.

The effect of salt on cadmium and aluminum speciation is illustrated in Figure 8c,d. As for lead, the increase of the ionic strength reduces the specific and the nonspecific binding. In the Donnan gel the potential is controlled mainly by changes in the ionic strength and the overall charge of the humic acid molecule (*28*). Changes in the Donnan potential affect both nonspecific binding (equation 3) and specific binding (equation 2 combined with 3). This combined effect accounts for the drastic reduction of cadmium bound as salt level increases as well as the decrease of the aluminum bound nonspecifically as shown in Figure 8c,d.

This study provides a better understanding of the nature of Al binding sites to humic substances in a competitive environment. In the pH 3 to 5.5 range, Al^{3+} competition toward divalent metal ions such as Pb(II) occurs primarily at carboxylic type groups. Owing to the different binding of Pb and Cd to humic substances (Pb(II) specific binding; Cd(II) electrostatic binding) the aluminum competition affects the two metal ions in a different ways. The Al(III) competition largely modifies the [Pb^{2+}] in solution ([Pb^{2+}] in Figure 7b versus [Pb^{2+}] in Figure 7a) and reduces the amount of Pb (II) bound. For Cd(II), the aluminum competition mainly affects the Cd(II) bound, with only smaller changes in the [Cd^{2+}] (Figure 8a versus Figure 8b). Thus Al(III) competition is likely to increase Pb(II) toxicity and bioavailability and Cd(II) transport.

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