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Complexation with Dissolved Organic Matter and Solubility Control of Heavy Metals in a Sandy Soil

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The complexation of heavy metals with dissolved organic matter (DOM) in the environment influences the solubility and mobility of these metals. In this paper, we measured the complexation of Cu, Cd, Zn, Ni, and Pb with DOM in the soil solution at pH 3.7–6.1 using a Donnan membrane technique. The results show that the DOM-complexed species is generally more significant for Cu and Pb than for Cd, Zn, and Ni. The ability of two advanced models for ion binding to humic substances, e.g., model VI and NICA-Donnan, in the simulation of metal binding to natural DOM was assessed by comparing the model predictions with the measurements. Using the default parameters of fulvic and humic acid, the predicted concentrations of free metal ions from the solution speciation calculation using the two models are mostly within 1 order of magnitude difference from the measured concentrations, except for Ni and Pb in a few samples. Furthermore, the solid–solution partitioning of the metals was simulated using a multisurface model, in which metal binding to soil organic matter, dissolved organic matter, clay, and iron hydroxides was accounted for using adsorption and cation exchange models (NICA-Donnan, Donnan, DDL, CD-MUSIC). The model estimation of the dissolved concentration of the metals is mostly within 1 order of magnitude difference from those measured except for Ni in some samples and Pb. The solubility of the metals depends mainly on the metal loading over soil sorbents, pH, and the concentration of inorganic ligands and DOM in the soil solution.

Introduction

To protect the environmental quality of soil, sediment, groundwater, and surface water, it is necessary to make an accurate assessment of the toxicity and mobility of the heavy metals. It is known that the processes of precipitation, adsorption, and complexation are important in controlling heavy metal speciation in soils. In soil solution, heavy metals

can form hydrolysis species and complexes with inorganic ligands such as Cl^- and SO_4^{2-}. The importance of the hydrolysis species and inorganic complexes depends on pH and the concentration of metal and ligands. Ions of heavy metals also form complexes with dissolved organic matter (DOM) in soils, sediments, and aquatic systems. It has been shown that DOM can strongly bind heavy metals such as Cu, Pb, Cd, Zn, and Ni (*1–4*). It is therefore important to include the effect of DOM on the mobilization and transport of heavy metals and in the risk assessment of sites contaminated with heavy metals (*3*).

Efforts have been made to develop models to describe heavy metal speciation in soil and soil solution. Mostly, these models are of empirical nature (*2, 5–11*). Recently, a multisurface model was proposed by Weng et al. (*12*), which employs advanced adsorption and cation exchange models and default binding parameters. This type of process-oriented model is necessary to adequately describe the interaction of metals with the particulate and dissolved surfaces over a wide range of conditions. This multisurface model has been used to predict the free ion activity of Cu^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+} in a sandy soil over the pH range of 3.7–6.1 with reasonable success (*12*). However, if we want to apply this model for the estimation of metal solubility, the metal binding to DOM has to be accounted for.

Dissolved organic matter is a complex mixture of many molecules and is usually operationally defined as the organic matter that passes a 0.45-μm filter. Humic and fulvic acid are major components and represent up to 70% of DOM (*13*). Model VI (*14*) and nonideal consistent competitive adsorption (NICA)-Donnan (*15*) are two advanced models available for the description of the binding of proton and metal ions to humic substances. Both models consider the site heterogeneity, binding competition, and electrostatic effects. However, the strength of a model depends on its ability to deal with humic substances of different origin and structure and with varying solution chemistry (*16*). At present, there are few studies to evaluate how well these models with default parameters of purified humic and fulvic acid can predict the complexation of heavy metals with natural DOM (*1, 3, 17*). Until now there has been no study on the comparison of these two models using the same data set of metal complexation with DOM.

The aim of this paper is twofold: (i) to evaluate the ability of model VI and NICA-Donnan in the prediction of metal binding to DOM by comparing the predictions with the measurements using a Donnan membrane technique; (ii) to include the NICA-Donnan model for the description of metal binding to DOM in the existing multisurface model (*12*) and to evaluate the ability of this model in the estimation of the metal solubility in soil.

Model Description

Simulating Solution Speciation. The solution speciation of heavy metals is simulated with two advanced models for ion binding to humic substances, e.g., model VI (*14*) and NICA-Donnan (*15*), along with inorganic solution chemistry. Model VI has been described in detail by Tipping (*14*). In this model, fulvic and humic acids are pictured as rigid spheres of uniform size with ion-binding groups positioned on the surface. The model is a discrete binding site model including two types of sites (A and B), each having four different types of sites present in equal amount. Besides the site heterogeneity, model VI also includes the electrostatic effects via a Donnan expression and the competition among protons and metal ions. The default parameters of model VI have been derived

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TABLE 1. Concentration of Total Dissolved and Free Ion of the Metals

soil	depth (cm)	pH 0.002 M Ca(NO₃)₂	DOC (mg L⁻¹)	metal concn in soil solution (0.002 M Ca(NO₃)₂) (-log M)					free ion concn (Donnan membrane analysis) (-log M)				
				Cu	Cd	Zn	Ni	Pb	Cu	Cd	Zn	Ni	Pb
1A	0−20	3.78	24.5	5.63	7.10	5.34	6.29	7.15	5.96	7.20	5.38	6.33	7.36
2A	0−20	3.86	22.5	5.23	7.08	5.28	6.18	7.27	5.52	7.15	5.32	6.25	7.49
3A	0−20	3.88	23.4	4.99	7.18	5.32	6.26	7.24	5.20	7.29	5.37	6.33	7.44
4A	0−20	3.76	22.5	4.77	7.33	5.47	6.48	7.14	4.94	7.42	5.47	6.54	7.33
1D	0−20	5.54	19.0	5.95	8.06	5.96	6.96	8.04	7.73	8.17	6.05	7.45	>9.8
2D	0−20	5.75	19.3	5.69	7.95	5.88	6.73	7.92	7.29	8.09	5.94	7.04	8.91
3D	0−20	5.59	18.6	5.52	7.98	5.93	6.64	8.16	6.96	8.12	5.93	6.82	9.13
4D	0−20	5.47	22.1	5.36	7.87	5.76	6.45	7.99	6.72	7.99	5.74	6.61	8.78
4A	20−30	3.73	33.9	4.60	7.06	5.19	6.25	7.09	4.76	7.05	5.27	6.36	7.27
4A	30−40	4.07	26.3	5.17	6.93	5.29	5.83	7.82	5.29	7.03	5.46	5.84	7.97
4A	40−50	4.19	17.1	5.70	7.02	5.33	5.93	8.00	5.96	7.10	5.46	6.00	8.73
4A	50−60	4.25	15.0	6.00	7.15	5.30	6.02	8.41	6.32	7.20	5.33	6.09	8.72
4A	60−70	4.26	14.2	5.91	7.21	5.22	5.92	8.26	6.17	7.29	5.20	5.99	8.47
4A	70−80	4.25	12.6	6.06	7.21	5.22	5.82	8.44	6.30	7.27	5.20	5.89	8.64
4A	80−90	4.29	13.3	5.80	7.14	4.62	5.69	8.20	5.99	7.18	4.63	5.76	8.47
4A	90−100	4.33	13.1	6.26	7.26	4.92	5.74	7.86	6.64	7.35	5.07	5.84	8.61
3D	20−30	5.61	26.6	5.59	7.94	5.72	6.61	8.39	6.90	8.14	5.71	6.73	9.02
3D	30−40	5.80	23.8	6.08	8.28	6.02	6.97	8.77	7.75	8.95	6.03	7.73	9.58
3D	40−50	5.70	12.4	6.75	9.06	6.41	7.56	8.92	>8	8.88	6.68	>8	>9.8
3D	50−60	5.64	10.0	7.19	9.06	6.70	7.37	9.62	>8	8.98	6.77	>8	>9.8
3D	60−70	5.88	8.4	6.74	9.06	6.74	7.65	9.62	>8	8.88	6.91	>8	>9.8
3D	70−80	5.87	6.9	7.27	>9.1	6.58	7.89	8.10	>8	>9	6.80	>8	>9.8
3D	80−90	5.98	6.7	6.46	>9.1	6.15	7.33	8.54	>8	8.89	6.14	7.70	>9.8
3D	90−100	5.92	8.7	6.92	>9.1	6.47	7.28	9.62	>8	>9	7.00	>8	>9.8
4D	20−30	5.49	28.4	5.45	7.81	5.70	6.39	8.44	6.70	8.25	5.69	7.03	8.64
4D	30−40	5.48	25.3	5.85	8.02	5.96	6.40	8.39	7.37	8.77	6.02	7.99	9.14
4D	40−50	5.46	14.1	6.45	8.88	6.49	7.24	8.50	>8	8.68	6.68	7.84	>9.8
4D	50−60	5.55	10.4	7.01	8.88	6.70	7.65	8.58	>8	>9	6.78	>8	>9.8
4D	60−70	5.70	8.5	6.81	9.06	6.74	7.62	8.66	>8	>9	6.96	>8	>9.8
4D	70−80	5.75	7.6	7.10	>9.1	6.79	7.71	8.34	>8	>9	6.80	>8	>9.8
4D	80−90	6.10	8.8	6.27	8.88	6.04	7.11	8.58	>8	>9	6.13	7.54	>9.8
4D	90−100	6.00	9.4	6.74	>9.1	6.50	7.23	8.58	>8	>9	6.99	7.81	>9.8

TABLE 2. Root-Mean-Square Residual (RMSR) between the Predicted and Measured Free Ion Concentration and Percentage of Free Ion in the Soil Solution

metals	RMSR free ion concentration (M)				RMSR percentage free ion/total dissolved (%)			
	model VI 30% HA, 30% FA	model VI 65% FA	NICA-Donnan 30% HA, 30% FA	NICA-Donnan 65% FA	model VI 30% HA, 30% FA	model VI 65% FA	NICA-Donnan 30% HA, 30% FA	NICA-Donnan 65% FA
Cu	0.39	0.40	0.29	0.28	20.1	15.3	18.0	12.8
Cd	0.26	0.26	0.33	0.35	32.2	31.9	14.8	15.7
Zn	0.14	0.15	0.14	0.16	21.8	24.4	22.1	25.6
Ni	0.44	0.44	0.35	0.42	43.8	43.7	23.7	38.0
Pb	0.37	0.38	0.92	0.71	38.2	36.8	27.4	18.2

by fitting using published data (*14*) (see Table 1, Supporting Information).

The NICA-Donnan model (*15*) accounts for the site heterogeneity by including two types of sites (types 1 and 2) each having a continuous distribution. Similar to model VI, the electrostatic effects are described with the Donnan approach. The NICA-Donnan model includes the competition between protons and metal ions, the ion-specific nonideality, and variable stoichiometry. The default parameters for generic humic and fulvic acids have been derived against published data (*18, 19*) (see Table 2, Supporting Information).

It has been found that most of DOM is humic substance, and the fraction of humic and fulvic acid in DOM varies in soil samples. Therefore, the model calculation was carried out with two separate assumptions as to the composition of DOM: (i) 30% of DOM is humic acid, 30% is fulvic acid, and 40% is inert; (ii) 65% of DOM is fulvic acid and 35% is inert. The calculations were executed with the computer program WHAM (*20*) and ECOSAT (*21*) for model VI and NICA-

Donnan, respectively. The measured data of pH, DOM, total dissolved concentrations of major cations, Al, Fe, and heavy metals of interest were used as the input data. The DOM concentration was calculated as 2 times that of dissolved organic carbon (DOC), because humic and fulvic acids contain on average ~50% carbon. The competition of ion binding including Ca, Al, and Fe was taken into account.

Simulating Solid−Solution Distribution. As mentioned in the Introduction, we have developed a multisurface model to predict metal activities in soil considering soil as a set of independent sorption surfaces in the solid phase (*12*). In this model, metal binding to the soil organic matter, to clay, and to the amorphous and crystalline iron hydroxides is calculated by using respectively the NICA-Donnan model, a Donnan cation exchange model, two site surface complexation diffuse double-layer model (*22*), and the charge distribution multisite complexation (CD-MUSIC) model (*23, 24*). In this paper, we included the NICA-Donnan for the description of metal binding to DOM into the multisurface model. As to the composition of DOM, we used the first assumption discussed
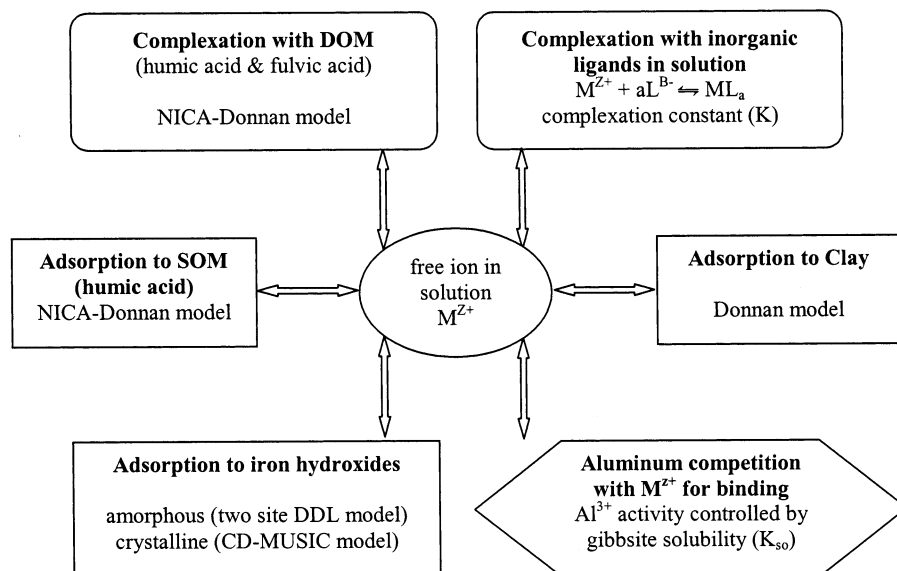
FIGURE 1. Conceptual structure of the reactions and models used in the multisurface model.

above; e.g., 30% of DOM is humic acid, 30% is fulvic acid, and the rest is inert. Figure 1 depicts the important components considered and models used in the multisurface model.

The calculation was done with the computer program ECOSAT (*21*). The HNO_3 (2 M)-extractable metal is assumed to be the amount of metal in soil that is active in adsorption/desorption processes (*12*). The way that amount of soil surfaces and their site density was estimated was described in the previous paper (*12*). The other input data, such as pH, ionic strength, and soil solution ratio, are the same as in the Donnan membrane analysis (see the Experimental Section). The calculation was done in two steps. First the concentrations of free metal ions were calculated by considering metal binding to the solid surfaces. Thereafter, using the free metal concentrations as input, the concentrations of the dissolved metal were predicted taking metal binding to DOM into account. In the calculation, it is assumed that the solubility of gibbsite $(Al(OH)_3)$ controls Al^{3+} activity and the competition of Al^{3+} to metal binding was considered. The competition of Fe^{3+} to the binding was not accounted for. Due to the relatively low concentration of Fe, the difference of metal speciation calculated with or without taking Fe into account is small.

Experimental Section

The sample set used in this paper is the same as in the paper in which the free metal ion activities were predicted using the multisurface model (*12*). In this paper, we will provide the concentration of the total dissolved metal and DOC in addition to the concentrations of the total (including solid phase) and free metal that have been published before. The soil samples were collected in June 1998 from a field near Wageningen in The Netherlands (Wildekamp site). In 1982, the field site was established as a randomized block design of four pH adjustments (nominal pH (KCl): (A) 4.0, (B) 4.7, (C) 5.4, and (D) 6.1) and four copper concentrations ((1) 0, (2) 250, (3) 500, and (4) 750 kg of $CuSO_4$ hectare^{-1}). Samples from the lowest pH (soil A) and highest pH (soil D) were taken for different soil layers in the range of 0−100 cm. The field soil samples were air-dried and sieved (<2 mm) before analysis. The major soil characteristics have been measured and reported in the previous paper (see Table 1 in Weng et al. (*12*)).

The concentrations of the free metal ion in these soils were measured using the Donnan membrane technique

(*25−28*). A 100-g air-dried soil sample was used in the soil column Donnan membrane analysis. A 200-mL 0.002 M $Ca(NO_3)_2$ solution was used as the salt solution in the donor side and 18 mL in the acceptor side. After 24 and 48 h, the donor and acceptor solutions were sampled. pH was measured with a pH meter in all the samples. The donor solution was filtered over a 0.45-μm nitrate−cellulose membrane filter (Schleicher & Schuell, NC45). DOC content in the donor solution was measured with a fully automated TOC/DOC analyzer (SK12, Skalar). The carbon leached from the filter (∼1 mg L^{-1}) was measured, and the DOC concentration in the filtered solution was corrected. The concentrations of macroelements in the donor and acceptor solution were measured by ICP-OES (Spectros, Spectro Flame), and concentrations of microelements were measured by ICP-MS (Perkin-Elmer, Elan 6000).

Results and Discussion

Solution Speciation. In the soil solutions, the concentration of the DOC is between 7 and 34 mg L^{-1} (Table 1). The total dissolved concentrations of Cu, Cd, Zn, Ni, and Pb in the soil solution are in the range of $10^{-7.3}$−$10^{-4.6}$, $<10^{-9.0}$−$10^{-6.9}$, $10^{-6.8}$−$10^{-4.6}$, $10^{-7.9}$−$10^{-5.7}$, and $10^{-9.6}$−$10^{-7.1}$ M, respectively (Table 1). The free Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+} are measured to be <2−76, <18−92, 30−100, <3−98, and <10−70% of the total dissolved metal. Note that the detection limit for the concentration of free ion and dissolved metal can be different as a result of the different diluting ratios in the experiment. Due to small experimental error when almost 100% of metal exists as free ion or when the concentration is close to the detection limit, more than 100% of free ion over total dissolved metal is measured. Because of the small concentration of the anions such as SO_4^{2-} and Cl^- in these samples (SO_4^{2-} < 10^{-4} M, Cl^- < 10^{-3} M), and the low pH (<6.1), the inorganically complexed metals including hydrolyzed and carbonate species can be neglected. After subtracting the free metal ion from the total in soil solution, the metal left in the solution is regarded as DOM-complexed. The DOM-complexed metals comprise from almost 0% to more than 98% of the dissolved metal. The complexation with DOM is found to be more significant for Cu and Pb than for Cd, Zn, and Ni. Similar results have been observed in other studies (*8, 29, 30*).

Metal complexation with DOM in the soil solutions, for which the concentrations of the free ions are measurable (see Table 1), is simulated using model VI and NICA-Donnan
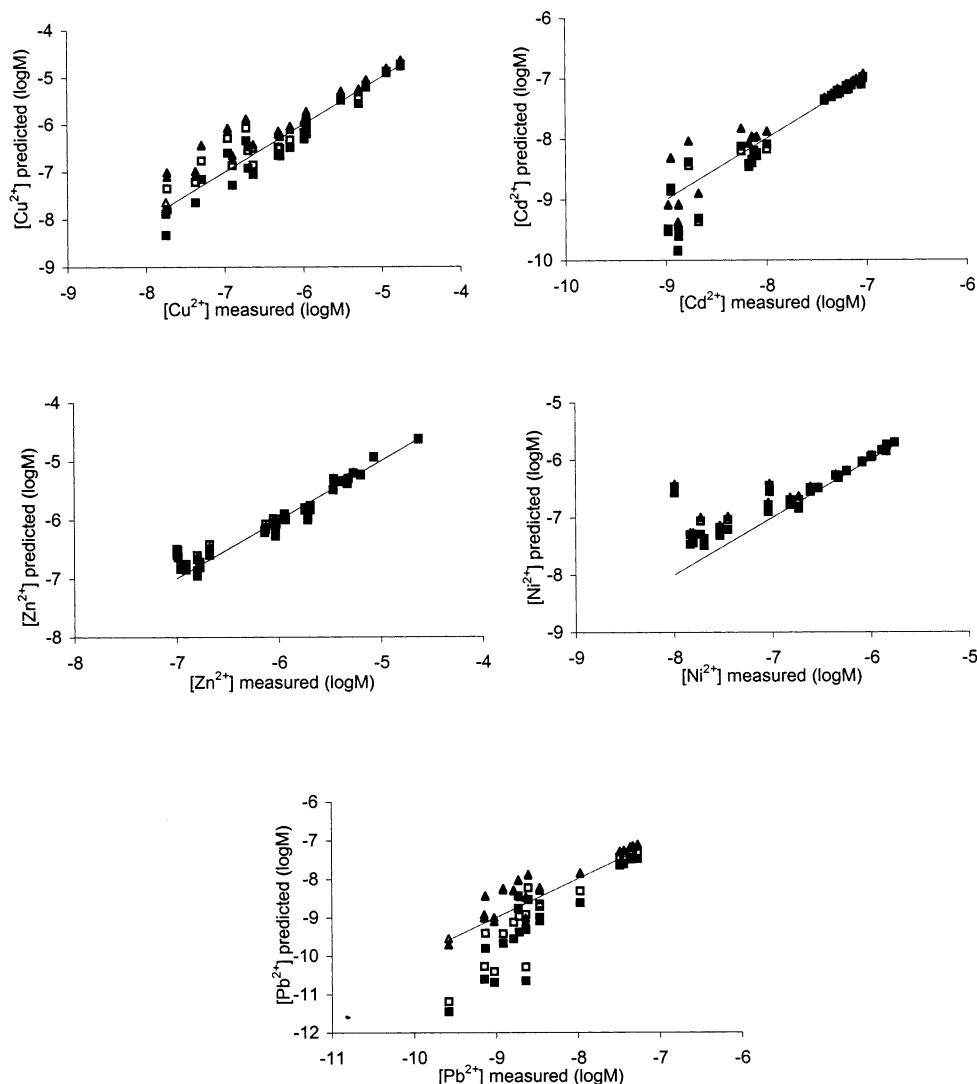
FIGURE 2. Comparison of the free ion concentration in the soil solutions measured and predicted using model VI and NICA-Donnan: ▲, prediction with model VI, 30% humic acid, 30% fulvic acid; △, prediction with model VI, 65% fulvic acid; ■, prediction with NICA-Donnan, 30% humic acid, 30% fulvic acid; □, prediction with NICA-Donnan, 65% fulvic acid; —, 1 to 1 line;

under two assumptions about DOM composition (see Model Description). Figure 2 and Figure 3 compare the free ion concentration and percentage of free ion over total dissolved concentration measured and predicted from the solution speciation. In Table 2, the root-mean-square residuals (RMSRs) between the predicted and measured free metal ion concentration and percentage of free ion are given. As shown in Figure 2, the predicted concentrations of free metal ions using the two models are within 1 order of magnitude difference from the measured concentrations except for Ni^{2+} in one sample and Pb^{2+} in four samples.

The ability of the two models to predict metal complex-ation with DOM differs to a certain extent with respect to metals and assumptions regarding the composition of DOM. As a general feature, NICA-Donnan predicts lower free metal ion concentration, e.g., more binding to DOM, than model VI. The two assumptions for the DOM composition have generally minor effects on the predictions by model VI, whereas the effects are larger for the NICA-Donnan model (Figure 3). Generally, the NICA-Donnan model predicts more complexation of Cu, Zn, Ni, and Pb with DOM (smaller free ion concentration) under the first assumption, e.g., 30% of DOM is humic acid, 30% is fulvic acid, and 40% is inert, than under the second assumption, e.g., 65% DOM is fulvic and the rest is inert. However, for Cd, the NICA-Donnan predicts less binding and larger free Cd^{2+} concentration under the

first assumption. By assuming that DOM is a mixture of humic and fulvic acids (the first assumption), the predictions by the NICA-Donnan model are generally closer to the mea-surements for the metals of Zn and Ni than assuming only fulvic acid present (the second assumption). But it is the opposite for Cu and Pb; e.g., the second assumption leads to better prediction. For Cd, the difference between the two assumptions is small. The metal binding predicted with the NICA-Donnan model is generally stronger for HA than for FA. For the strongly bound Cu and Pb, the NICA-Donnan model mostly overestimates the binding. Therefore, assuming only FA in DOM produces better results for these metals. For Zn and Ni, the model underestimates the binding, therefore assuming that HA presence gives better predictions.

It is found that organically bound species are important for Cu and Pb. Compared with the measurements, both model VI and NICA-Donnan capture the main trend in the big changes in the extent of Cu complexation with DOM (free Cu^{2+} is 2−76% of the total dissolved Cu) (Figure 3). The RMSR of free Cu^{2+} concentration is less than 0.4 and 0.3 log unit for model VI and NICA-Donnan, respectively. The RMSR of the percentage of free Cu^{2+} is around or less than 20% (Table 2). The free Cu^{2+} concentration predicted with model VI is mostly higher than with NICA-Donnan. As to Pb, the quality of the prediction is less good than for Cu (Table 2). The trend is captured reasonably by NICA-Donnan especially when
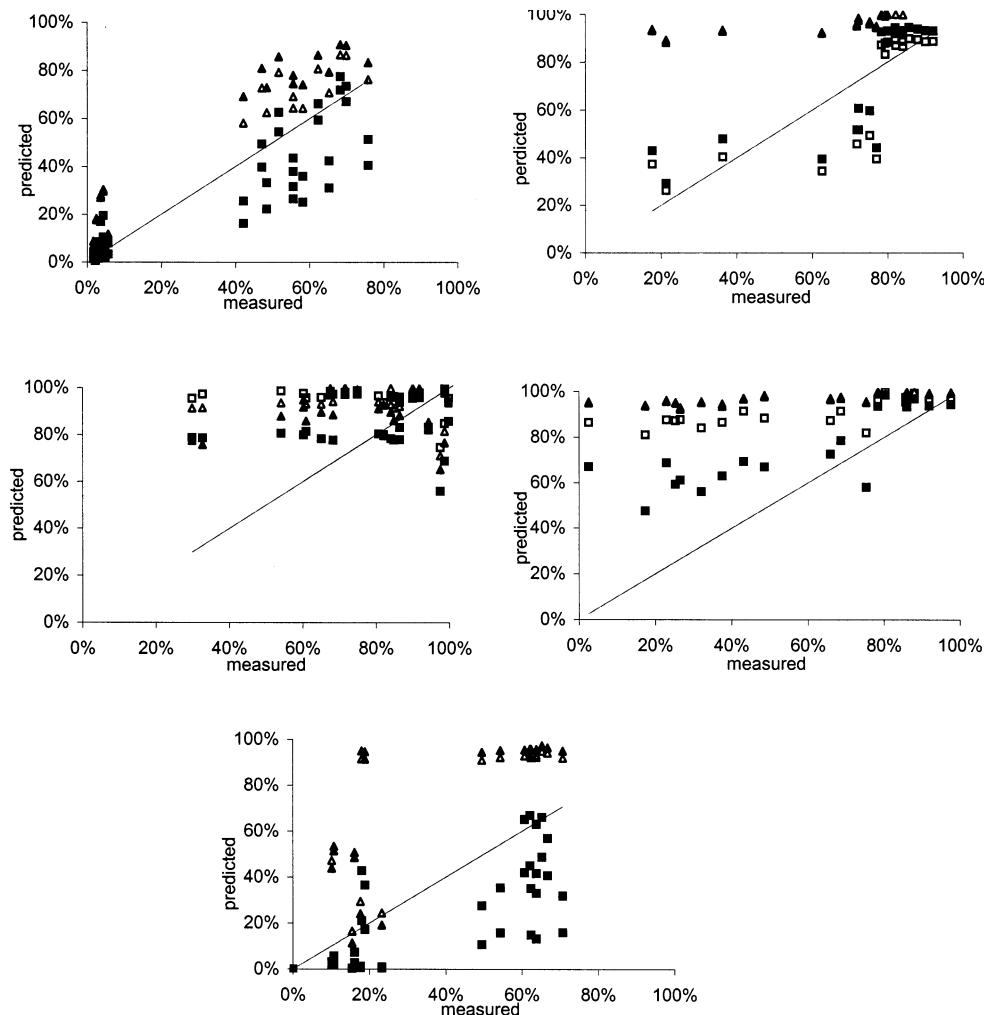
FIGURE 3. Comparison of the percentage of free ion concentration in the soil solutions measured and predicted using model VI and NICA-Donnan: ▲, prediction with model VI, 30% humic acid, 30% fulvic acid; △, prediction with model VI, 65% fulvic acid; ■, prediction with NICA-Donnan, 30% humic acid, 30% fulvic acid; □, prediction with NICA-Donnan, 65% fulvic acid; —, 1 to 1 line;

assuming 65% of DOM as fulvic acid. However, in a few samples with relatively high pH, the free Pb^{2+} concentration predicted with NICA-Donnan is much lower than measured, which leads to a larger RMSR of free Pb^{2+} concentration than with model VI. Model VI predicts little binding of Pb at relatively low pH. Complexation of Pb predicted with model VI increases fast at relatively high pH and becomes closer to those measured. Model VI generally underestimates the binding of Pb, and the NICA-Donnan model does the opposite (Figures 2 and 3).

For Cd, according to the measurements, 18–92% of Cd in the soil solution is in the form of free ion. There are four samples in which the measured free Cd^{2+} concentration is larger than the total dissolved concentration (Table 1), due to the experimental error when the concentration is very close to the detection limit. These four samples are not considered in the comparison of the percentage of free ion. The RMSR for free Cd^{2+} concentration (including those four samples mentioned above) is about 0.26 and 0.34 log unit with model VI and NICA-Donnan, respectively (Table 2). The range of the fraction of free ion in solution is better predicted with the NICA-Donnan model with the RMSR below 15%. Model VI tends to underestimate Cd binding to DOM.

For Zn and Ni, it is believed that complexation with DOM is less important than for Cu and Pb. Still, in the analysis, a considerable proportion of Zn and Ni is found to exist in complexed form in the soil solution, especially at relatively high pH. With both NICA-Donnan and model VI, the fraction

of free Zn^{2+} in the soil solution is overestimated (underestimation of complexation). However, because substantial Zn in the solution is uncomplexed, the RMSR of the free ion concentration predicted and measured is only ∼0.15 log unit using both models. Similar to Zn, both NICA-Donnan and model VI underestimate the complexation of Ni in the soil solution, although the predictions with NICA-Donnan are closer to the measurement. The residuals for both the free Ni^{2+} concentration and percentage of free Ni^{2+} are bigger than for Zn.

Considering the range of the degree of metal complexation with DOM and the degree of variation between prediction and measurement, the predictions with model VI for Cu and with the NICA-Donnan model for Cu and Cd are reasonable. The predictions for the other metal ions are less good. The variation in the composition of DOM from sample to sample makes it essentially impossible with the approach followed for the models to produce exact predictions using the default parameters of purified humic and fulvic acids. Additional studies of the composition, charge characterization, and Al and Fe content of DOM may yield more information on the model performance. The model description might, however, still be improved by updating the model parameters once more data for their adsorption to humic substances become available. For Zn and Ni, and maybe also for Pb, the existence of other species such as those bound to mineral colloidal, which is not accounted for in the modeling, could be one of the possible reasons to explain the discrepancy.
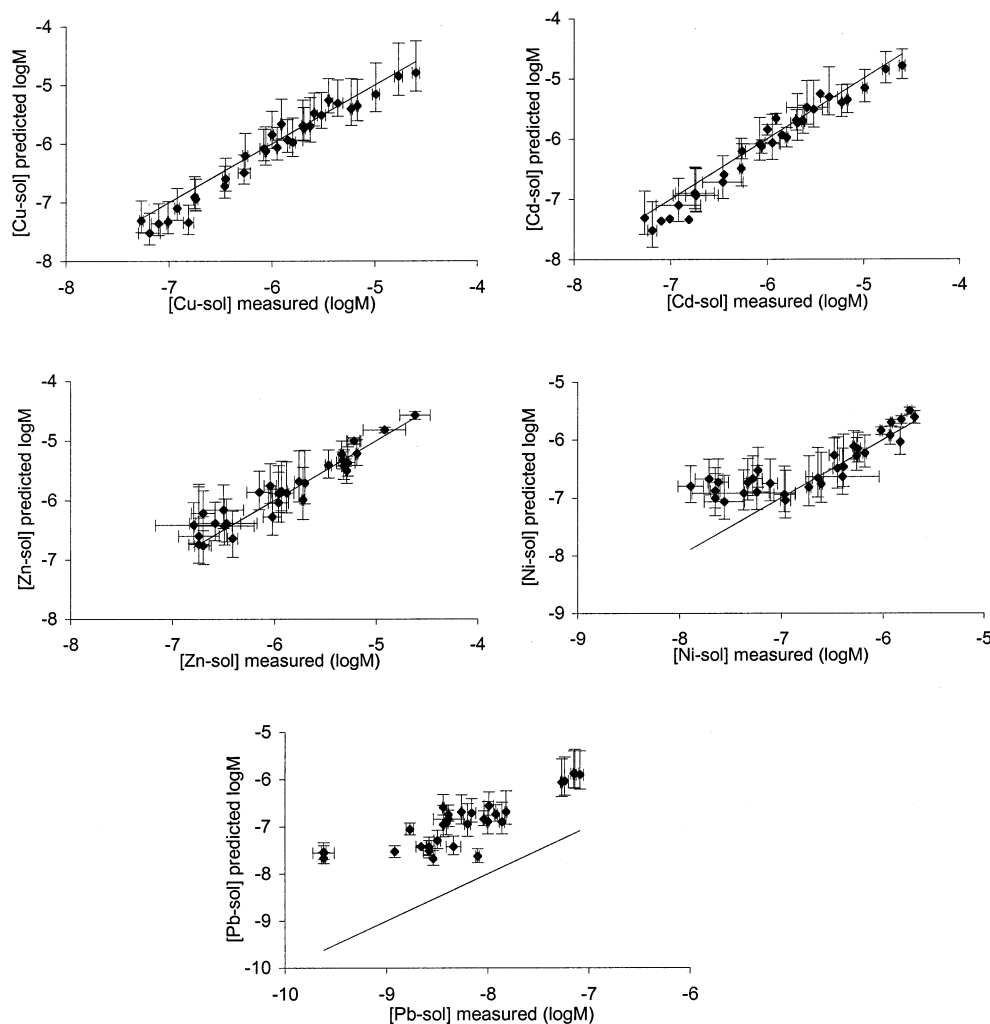
FIGURE 4. Comparison of dissolved metal content predicted and measured in the soil solution: ◆, model predictions at the mean clay charge of 0.25 mol kg^{-1} and site density of SOM equal to 31% of the generic humic acid. The vertical error bars are model predictions with extreme clay charge and site density of SOM. The horizontal error bars are the standard deviations of the metal activity measured; —, 1 to 1 line.

Simulating Solid–Solution Distribution. The solid–solution partitioning coefficient (K_d), which has often been used to describe the solid–solution distribution of metals, is the ratio of the total metal adsorbed in the solid phase relative to that found in the solution phase. The K_d values found in the soil samples varied widely between the metals and for the same metal. The K_d values are in the range of 58–616 L kg^{-1} for Cu, 6–274 L kg^{-1} for Cd, 3–140 L kg^{-1} for Zn, 6–347 L kg^{-1} for Ni, and 469–32085 L kg^{-1} for Pb. A larger K_d value indicates smaller solubility. However, the partitioning coefficient is conditional and depends on the physicochemical situation.

In Figure 4, the predicted concentrations of dissolved Cu, Cd, Zn, Ni, and Pb using the multisurface model are compared to those measured. The model gives dissolved metal concentrations between a low and a high boundary by taking the clay charge of 0.1, 0.25, and 0.4 mol kg^{-1} and corresponding site density of SOM (46, 31, and 16% of generic humic acid) (see Weng et al. (12)). At 0.1 mol kg^{-1} clay charge and 46% site density of the generic humic acid for SOM, the model predicts a smaller concentration of dissolved metal than using a higher clay charge and a lower site density of SOM. This is due to the stronger affinity of SOM for the metals than that of the clay.

The agreement between the model predicted and the measured dissolved concentrations of Cu and Cd is very good (Figure 4). This can be expected from the reasonable prediction of the free ion activities (12) and the complexation with DOM of these metals. For Zn and Ni, the estimated concentrations of dissolved metal agree with the measurements reasonably well for most of the samples, except for some samples of soil 3D and 4D at larger depth. For these samples, the model predicts a larger concentration than measured. The overestimation of Zn and Ni solubility is largely due to the overestimation of their free ion activity in these soils (12). In the previous paper, we suggested that a possible reason for the discrepancy between the predicted and measured Zn^{2+} and Ni^{2+} activity in these samples might be the formation of Zn–Al and Ni–Al layered double hydroxide (LDH), which are more stable at near-neutral pH values (31, 32). The predicted concentration of the dissolved Pb is generally 0.5–2.1 log units larger than measured. The disagreement is due to the overestimation of Pb^{2+} activity and the overestimation of Pb complexation with DOM. The Pb^{2+} activity predicted with the model is generally 0.2–1.4 log units larger than the measurement. Note that in our previous paper the discrepancy found was 0.5–2.5 log units (12), and it is incorrect. This is because the NICA-Donnan parameters used for Pb were incorrect due to an error in the previous version of the database. The overestimation of adsorbed metal using the amount in 2 M HNO$_3$ extraction can be one of the reasons that leads to the discrepancy for Zn, Ni, and Pb.

Besides the prediction of the dissolved metal concentrations, the multisurface model gives an estimation of each sorbent contribution to metal solubility control in soils. The model predicted that the metal that is bound by DOM is only a small fraction of the metal that is bound to all the soil sorbents (SOM, clay, iron hydroxides, DOM). Among the total bound metal, only $0.3-2.9\%$ Cu, $0.6-4.8\%$ Cd, $0.3-2.1\%$ Zn, $0.3-2.0\%$ Ni, and $0.2-2.8\%$ Pb are DOM-complexed. Compared to metal bound to the other soil sorbents, the contribution of DOM is not important. The free ion activity in these soils is therefore largely determined by metal binding to the solid phase (*12*). Sauvé et al. (*11*) found that the addition of the dissolved organic matter to their equation $pCd^{2+} = 5.14 + 0.61pH - 0.79 \log(\text{total Cd})$ improved R^2 by less than 2%. The relative contribution of SOM, clay, and iron hydroxides to the metal activity control was discussed previously (*12*).

Although metal binding to DOM does not contribute significantly to the control of metal activity in soil, it can affect the solubility of metals to a considerable extent. The measurements show that the complexation with DOM can increase the concentration of dissolved metals by more than 2 orders of magnitude. Due to the nonlinearity and pH dependency of the metal binding to DOM, the effects of the complexation with DOM are more significant at lower free metal activity and at higher pH. Any factors that lead to an increase in the DOM concentration will enhance the solubility and mobility of the metals.

The significance of DOM complexation in soil solution influences the pH dependency of the solid–solution distribution of metals. When the DOM-complexed species is the dominant fraction of the metal in the solution, the pH effects on the solid–solution distribution of the metal will be less obvious than that on the free ion activity. The data (Table 1) show that the difference in the pH dependency of the dissolved and free ion concentration is bigger for Cu and Pb, for which the DOM-complexed fraction is more important, than for Cd, Zn, and Ni, where the complexation with DOM is less significant. Sauvé et al. (*33*) studied the pH dependency of the partitioning coefficient (K_d) of Cu, Cd, Zn, Ni, and Pb and found that the pH dependency of K_d values is in the order of Cu < Pb < Cd < Zn < Ni. As has been noted in our previous paper (*12*), the increased solubility of metals by acidification is more significant for the metals such as Cd, Zn, and Ni, which have larger solubility and are less complexed with DOM, than for the metals such as Cu and Pb, which have smaller solubility and are more in the DOM-complexed form.

In the multisurface model at this stage, we consider only the adosprtion/desorption processes. The binding of metals is calculated as the additive results to the various surfaces. The interactions between the various surfaces and their effects on the metal binding are neglected. In addition, metal binding to oxides and clay are treated in a simpler way compared to the organic matter. The effects of the binding of many anions on the metal binding to oxides are not yet accounted for. The other processes, such as precipitation and kinetics, which might be important for some metals under certain conditions, are not yet included. The reasonable success of the model at this stage makes it a promising starting point. Further research is necessary to improve the modeling approach and to make it closer to the situation in the field.

Acknowledgments

Supporting Information Available

The parameters of model VI and NICA-Donnan. The other model parameters used in this paper can be found in the Supporting Information of Weng et al. (*12*). This material is available free of charge via the Internet at http://pubs.acs.org.

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