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Contribution of Individual Sorbents to the Control of Heavy Metal Activity in Sandy Soil

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A multisurface model is used to evaluate the contribution of various sorption surfaces to the control of heavy metal activity in sandy soil samples at pH 3.7–6.1 with different sorbent contents. This multisurface model considers soil as a set of independent sorption surfaces, i.e. organic matter (NICA-Donnan), clay silicate (Donnan), and iron hydroxides (DDL, CD-MUSIC). The activities of Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+} in equilibrium with the soil have been measured using a Donnan membrane technique. The metal activities predicted by the model agree with those measured reasonably well over a wide concentration range for all the metals of interest except for Pb. The modeling results suggest that soil organic matter is the most important sorbent that controls the activity of Cu^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+} in these sandy soils. When metal loading is high in comparison with soil organic matter content, the contribution of clay silicates to metal binding becomes more important. Adsorption to iron hydroxides is found not significant in these samples for Cu, Cd, Zn, and Ni. However, for Pb the model estimates strong adsorption on iron hydroxides. The model predicts that acidification will not only lead to increased solution concentrations but also to a shift toward more nonspecific cation-exchange type binding especially for the metals Cd, Zn, and Ni. Lowering the pH has led to a loss of 56% of Cd, 69% of Zn, and 66% of Ni during 16 years due to increased leaching.

Introduction

In the decision making process concerning the protection of soil quality, it is necessary to make accurate assessments of heavy metal speciation. This is important for formulating heavy metal standards and choosing appropriate soil remediation techniques. Land use change from agricultural production to nature conservation will lead to gradual acidification of especially sandy soils. It is therefore of interest to be able to predict effects of natural acidification on metal ion behavior, especially since long-term agricultural use may have increased the metal content of these soils. It has been established that under most circumstances, free metal ion activity (or concentration) is the key factor in determining metal bioavailability and toxicity (*1*). The dissolved metal pool reflects the soil metal fraction that could potentially be leached from the soil to groundwaters and surface waters (*2*).

Soils and sediments usually contain mixtures of several adsorptive surfaces. Heavy metal adsorption to these surfaces is recognized as being important in controlling heavy metal activity. Colloidal particles of soil organic matter (SOM), clay silicates, and metal hydroxides, which have large surface area and are often electrically charged, are considered important adsorptive surfaces to bind heavy metals. Zachara et al. (*3*) reviewed the techniques that have been used to quantify the contribution of different sorbent phases to metal sorption in soils. These techniques include the following: (i) application of sequential extractions (*4, 5*), (ii) development of statistical relationships between the sorption and soil properties (*6–11*), (iii) observation of similarities in sorption on single sorbents and whole soils (*12, 13*), and (iv) comparison of sorption on natural and treated soils (*3*). As pointed out by Zachara et al. (*3*), all these methods have limitations. The contribution of individual sorbents may be difficult or impossible to experimentally identify (*14*).

Another approach is to try to predict the free metal activity in the soil solution using adsorption and ion-exchange models for the various soil constituents and compare these predictions with measurements. In this approach, one has to make a choice with respect to the types of adsorption models being used. One has to estimate the amount of reactive surface of each type sorbent, and one has to estimate the amount of metal in the solid phase, which is active in the competitive binding to these surfaces for each relevant metal. One also has to deal with competition of ions other than the heavy metal ions of interest. Some multisurface calculations have been done using various model approaches (*15–18*), but pure predictions of free metal activity using such an approach and comparing the results with measurements have so far not been published. The test of such an approach becomes more useful if a series of metals are included in the study. Since pH plays such an important role in metal adsorption and since the pH effect on metal ion binding is quite different for the different sorbents and for different metals, it is also important to use field soil samples that differ in pH.

In this paper, we propose and apply a multisurface model to predict the Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+} activities in the soil solution of sandy soil samples at pH 3.7–6.1. The predicted metal activities were compared with those measured using a soil column Donnan membrane equilibrium method (*19, 20*). The model approach also results in a calculated solid-phase speciation of the metals bound to the soil. The relative importance of soil sorbents, i.e. SOM, clay, and iron hydroxides, for the binding of heavy metals in sandy soils was studied.

Model Description

The multisurface model considers soil as a set of independent sorption surfaces, i.e. organic matter, clay silicate, and iron hydroxides (amorphous and crystallized). The metal speciation was predicted using models of adsorption and ion-exchange for each sorbent in combination with models of inorganic solution chemistry, precipitation of aluminum hydroxides [$Al(OH)_3$], and chloropyromorphite [$Pb_5(PO_4)_3$-Cl]. In the following, the models of adsorption and ion-exchange used in the multisurface model will be discussed.

Binding to Soil Organic Matter. Humic acid was used as an analogue for the reactive soil organic matter (SOM). The consistent Non Ideal Competitive Adsorption Donnan model (*21*), referred to as NICA-Donnan model, was chosen for metal binding to soil organic matter since it is one of the most advanced models for competitive metal ion binding to humic substances. It has recently been parametrized for the

TABLE 1. Soil Characteristics, Total Metal Contents, and Metal Activities

soil	depth (cm)	pH 0.002 M Ca(NO₃)₂	CEC-BaCl₂ (mmol kg⁻¹)	clay (<2 µm) (%)	OM (%)	Fe-oxalate (g Fe kg⁻¹)	Fe-DCB (g Fe kg⁻¹)	metal content (2 M HNO₃ extraction) (µmol kg⁻¹)					metal activity (Donnan membrane analysis) (−log M)				
								Cu	Cd	Zn	Ni	Pb	Cu	Cd	Zn	Ni	Pb
1A	0−20	3.78	18.7	4.2	3.7	2.08	2.34[a]	461.2	1.13	55.7	9.1	116.8	6.13	7.37	5.55	6.50	7.53
2A	0−20	3.86	21.0	4.1	3.9	1.96	2.34[a]	958.7	1.22	56.5	10.0	115.7	5.69	7.32	5.49	6.42	7.66
3A	0−20	3.88	20.7	4.2	3.9	2.03	2.34[a]	1331.6	0.98	50.7	8.8	115.9	5.36	7.45	5.53	6.49	7.60
4A	0−20	3.76	20.5	4.2	3.9	2.02	2.34	1713.6	0.68	39.4	6.7	115.4	5.10	7.58	5.63	6.70	7.49
1D	0−20	5.54	42.1	4.2	4.0	2.23	2.28[a]	519.0	2.20	155.2	19.2	111.4	7.93	8.37	6.25	7.65	>10
2D	0−20	5.75	41.2	4.8	4.1	2.21	2.28[a]	1042.7	2.45	175.9	25.1	124.3	7.49	8.29	6.14	7.24	9.11
3D	0−20	5.59	40.6	4.3	4.1	2.10	2.28	1685.9	2.18	143.5	26.2	107.1	7.15	8.31	6.12	7.01	9.32
4D	0−20	5.47	40.1	4.5	4.0	2.08	2.29	2247.0	2.33	170.1	31.4	123.4	6.92	8.19	5.94	6.81	8.98
4A	20−30	3.73	19.4	4.5	3.8	1.80	2.36	1625.6	0.84	51.0	7.5	97.0	4.92	7.21	5.43	6.52	7.43
4A	30−40	4.07	21.7	4.1	2.4	1.19	4.11	744.5	1.35	46.2	14.0	31.5	5.45	7.19	5.62	6.00	8.13
4A	40−50	4.19	11.6	3.2	1.0	0.57	1.84	235.6	0.99	42.0	11.2	12.6	6.11	7.25	5.61	6.15	8.88
4A	50−60	4.25	9.0	2.6	0.4	0.29	1.38	80.9	0.61	25.5	8.4	5.6	6.47	7.35	5.48	6.24	8.87
4A	60−70	4.26	16.0	2.5	0.4	0.30	1.57	115.5	0.58	52.8	11.2	8.9	6.32	7.44	5.35	6.14	8.62
4A	70−80	4.25	10.1	2.1	0.4	0.16	1.34	52.5	0.50	51.8	12.2	5.7	6.45	7.42	5.35	6.04	8.79
4A	80−90	4.29	12.6	2.1[a]	0.5	0.19	1.34[a]	102.3	0.59	155.4	16.7	8.5	6.14	7.33	4.78	5.91	8.62
4A	90−100	4.33	13.3	2.1[a]	0.4	0.15	1.34[a]	45.1	0.49	81.3	17.8	6.5	6.79	7.50	5.22	5.99	8.76
3D	20−30	5.61	39.8	4.9	4.1	2.18	2.13	1369.6	1.96	135.4	24.7	95.0	7.10	8.34	5.91	6.93	9.22
3D	30−40	5.80	33.1	4.5	3.1	1.51	4.14	307.2	1.01	83.2	16.5	46.4	7.94	9.14	6.22	7.92	9.77
3D	40−50	5.70	20.0	4.0	1.2	0.74	1.39	36.8	0.24	21.5	6.4	11.6	>8.2	9.05	6.85	>8.2	>10
3D	50−60	5.64	13.4	2.8	0.6	0.30	0.88	5.7	0.09	4.0	4.3	5.7	>8.2	9.15	6.94	>8.2	>10
3D	60−70	5.88	12.2	2.6	0.6	0.27	0.83	24.9	0.11	11.7	4.5	6.2	>8.2	9.04	7.07	>8.2	>10
3D	70−80	5.87	13.4	2.8	0.5	0.15	0.53	8.8	0.06	14.0	4.5	4.8	>8.2	>9.2	6.96	>8.2	>10
3D	80−90	5.98	13.5	2.8[a]	0.5	0.19	0.53[a]	51.4	0.11	48.2	7.8	6.5	>8.2	9.04	6.29	7.85	>10
3D	90−100	5.92	19.4	2.8[a]	0.5	0.14	0.53[a]	17.0	0.07	20.6	8.0	6.0	>8.2	>9.2	7.15	>8.2	>10
4D	20−30	5.49	41.7	4.9	4.2	2.09	2.36	2192.9	2.30	183.3	35.5	116.5	6.91	8.46	5.90	7.24	8.85
4D	30−40	5.48	30.2	4.9	2.9	1.32	2.14	360.0	1.02	108.6	21.1	50.1	7.57	8.97	6.22	8.19	9.34
4D	40−50	5.46	19.8	3.4	1.4	0.63	1.60	72.8	0.30	26.9	8.3	14.9	>8.2	8.85	6.85	8.01	>10
4D	50−60	5.55	12.1	2.5	0.7	0.21	0.81	8.5	0.08	19.2	4.5	6.0	>8.2	>9.2	6.94	>8.2	>10
4D	60−70	5.70	12.8	2.5	0.7	0.22	0.70	39.4	0.11	19.9	5.1	7.4	>8.2	>9.2	6.96	>8.2	>10
4D	70−80	5.75	14.1	2.6	0.4	0.14	0.54	7.2	0.07	11.8	5.3	5.5	>8.2	>9.2	6.96	>8.2	>10
4D	80−90	6.10	13.2	2.6[a]	0.6	0.21	0.54[a]	67.9	0.11	67.3	7.7	7.6	>8.2	>9.2	6.29	7.70	>10
4D	90−100	6.00	16.6	2.6[a]	0.5	0.15	0.54[a]	23.0	0.06	28.7	10.4	6.7	>8.2	>9.2	7.15	7.97	>10

[a] Values that are missing and estimated as the same as in the similar samples.

most extensive data set available (22, 23). The model accounts for proton and multimetal binding, binding site heterogeneity, ion specific nonideality, variable stoichiometry, cation-exchange, and electrostatic effect (21). This type of model has been used previously to describe metal binding to natural organic matter in soil and solution (24−28). In the multisurface model, the NICA-Donnan parameters of generic humic acid (22, 23) were used in the model calculations (see Table 1, Supporting Information).

Binding to Clay Silicates. In the model, illite was taken as a representative of clay silicate, because it is an important aluminum silicate mineral in most soils of The Netherlands (29). The adsorption of metals to clay silicates can be attributed to two kinds of processes. At lower pH, nonspecific cation-exchange type binding based on the electrostatic interaction of the metal ions with the negatively charged clay particles is the dominant process. At higher pH, the adsorption of heavy metals seems to be more specific, which may be related to the chemical binding to the edge phases of the clay (30). Because of the relatively low pH (<6.1) of the samples, it was assumed that electrostatic interaction is the main process for binding of cations to the clay silicates. The cation-exchange process of clay domains can be described using a Donnan approach (16). The advantage of such a model is that there is no need to select ion-exchange coefficients from literature, since they are implicit in the model. Metal concentration in the Donnan phase is related to the concentration in the solution according to the Boltzmann accumulation factor.

Binding to Iron Hydroxides. In the multisurface model, metal binding to two types of iron hydroxides, i.e. amorphous and crystalline, was considered. Hydrous ferric oxide (HFO) and goethite were assumed as the model substances of the soil amorphous and crystalline iron hydroxides, respectively.

Goethite is in general the most dominant crystalline iron hydroxide in many soils. Metal binding on HFO was described by a two site surface complexation diffuse double layer (DDL) model (31). Metal binding to goethite was calculated with the Charge Distribution Multi-Site Complexation (CD-MUSIC) model (32, 33). The model parameters of DDL and CD-MUSIC were taken from Dzombak and Morel (31) and Hiemstra and Van Riemsdijk (32−34), respectively (see Tables 2 and 3, Supporting Information). The influence of phosphate on metal binding on goethite was taken into account.

The calculation was done with the computer program ECOSAT (Equilibrium Calculation Of Speciation And Transport) (35), since it has the possibility to use all the models relevant in this study. HNO₃ (2 M) extractable metal was used as the total metal content that is assumed to be active in adsorption processes. The other chemical conditions, such as pH, ionic strength, and soil solution ratio, are the same as in the soil column Donnan membrane analysis (see Experimental Section). The competition between Al^{3+}, Ca^{2+}, and the metal ions of interest for binding to SOM was considered. The effect of competition by Fe^{3+} was not taken into account explicitly but is implicitly accounted for in the CEC determination since iron bound to SOM is not easily exchangeable. Iron may be one of the reasons for the lower site density of SOM compared to humic acid, as will be discussed in the Results and Discussion section. The PO_4^{3-} activity was calculated using the measured total P in the soil solutions and pH. The Cl^- activity was estimated from the total soil solution Cl measured.

Experimental Section

Soil Samples. The soil samples were collected in June 1998 from a field near Wageningen in The Netherlands (Wildekamp site). This area was used as permanent pasture for at least

TABLE 2. Model Estimation of Individual Sorbents Contribution to Metal Adsorption in the Soils (Percent of Total Sorbed)

treatment	depth (cm)	Cu SOM specific	gel	clay	iron oxides	Cd SOM specific	gel	clay	iron oxides	Zn SOM specific	gel	clay	iron oxides	Ni SOM specific	gel	clay	iron oxides	Pb SOM specific	gel	clay	iron oxides
1A	0−20	99.60	0.22	0.13	0.05	82.08	11.32	6.59	0.00	77.12	14.44	8.42	0.02	91.77	1.88	6.35	0.00	61.27	16.43	9.56	12.74
2A	0−20	99.36	0.37	0.20	0.07	82.49	11.42	6.09	0.00	77.82	14.45	7.71	0.02	92.12	1.98	5.90	0.00	62.34	16.36	8.70	12.60
3A	0−20	99.05	0.54	0.30	0.11	82.66	11.12	6.22	0.00	77.09	14.67	8.22	0.02	91.63	2.03	6.34	0.00	59.30	16.51	9.23	14.97
4A	0−20	98.73	0.72	0.41	0.14	84.08	10.19	5.72	0.00	78.79	13.56	7.63	0.02	92.25	1.87	5.88	0.00	60.42	17.20	9.65	12.73
1D	0−20	99.51	0.01	0.00	0.48	97.67	1.60	0.56	0.17	93.84	3.48	1.22	1.46	98.66	0.28	0.82	0.25	10.76	0.09	0.03	89.11
2D	0−20	99.35	0.03	0.01	0.61	97.09	2.06	0.74	0.10	92.93	4.55	1.65	0.88	98.24	0.46	1.16	0.14	12.91	0.15	0.06	86.88
3D	0−20	99.37	0.09	0.04	0.50	95.05	3.48	1.43	0.05	90.31	6.62	2.70	0.38	96.89	0.94	2.11	0.07	27.09	1.34	0.58	70.98
4D	0−20	99.14	0.11	0.05	0.71	95.02	3.52	1.43	0.03	89.45	7.25	2.94	0.36	96.62	1.04	2.30	0.04	24.69	0.79	0.32	74.20
4A	20−30	98.70	0.70	0.37	0.23	83.61	10.69	5.70	0.00	77.03	14.95	7.99	0.04	92.49	1.70	5.81	0.00	62.40	16.40	8.73	12.47
	30−40	98.37	0.43	0.33	0.87	76.69	13.22	10.07	0.02	72.55	15.33	11.69	0.44	84.36	4.42	11.22	0.00	59.77	9.72	7.40	23.11
	40−50	98.61	0.30	0.42	0.67	69.41	12.72	17.85	0.02	62.05	15.55	21.83	0.57	75.60	3.91	20.48	0.00	53.50	6.88	9.65	29.97
	50−60	98.06	0.23	0.65	1.06	59.19	10.69	30.07	0.05	51.68	12.35	34.77	1.20	60.79	4.13	35.07	0.01	43.25	4.55	12.79	39.42
	60−70	98.55	0.32	0.89	0.24	59.19	10.90	29.90	0.02	44.82	14.72	40.39	0.07	59.97	2.95	37.07	0.01	36.35	4.69	12.85	46.11
	70−80	99.37	0.17	0.37	0.09	63.37	11.25	25.36	0.01	48.04	15.95	35.96	0.05	62.90	3.58	33.51	0.00	52.17	6.19	13.95	27.69
	80−90	98.93	0.20	0.30	0.56	70.31	11.82	17.84	0.04	45.49	21.20	32.01	1.30	72.35	1.94	25.70	0.00	56.93	7.15	10.79	25.13
	90−100	98.87	0.13	0.28	0.72	66.84	10.27	22.85	0.04	45.04	16.62	36.96	1.38	61.87	3.45	34.68	0.00	55.76	6.74	15.00	22.49
3D	20−30	98.90	0.03	0.01	1.06	97.64	1.62	0.60	0.13	94.03	3.58	1.34	1.05	98.14	0.54	1.11	0.21	10.41	0.08	0.03	89.48
	30−40	98.83	0.01	0.00	1.16	98.36	0.95	0.41	0.28	92.99	2.25	0.97	3.79	98.15	0.43	0.95	0.46	7.80	0.03	0.01	92.15
	40−50	99.76	0.00	0.00	0.24	97.92	0.93	0.90	0.25	93.78	1.92	1.86	2.44	96.48	0.71	2.32	0.50	8.55	0.03	0.03	91.40
	50−60	99.95	0.00	0.00	0.05	97.89	0.84	1.14	0.13	96.85	0.94	1.28	0.93	92.39	3.24	4.06	0.31	11.52	0.05	0.07	88.37
	60−70	99.55	0.00	0.00	0.45	98.49	0.59	0.71	0.20	92.94	1.70	2.08	3.28	95.31	0.95	3.14	0.60	8.05	0.02	0.03	91.91
	70−80	99.83	0.00	0.00	0.17	97.56	0.76	1.49	0.18	88.75	2.46	4.86	3.93	92.56	0.95	6.02	0.48	10.09	0.04	0.08	89.80
	80−90	99.29	0.00	0.01	0.71	98.66	0.53	0.69	0.12	85.50	4.04	5.28	5.18	94.55	0.52	4.39	0.54	10.07	0.03	0.04	89.85
	90−100	99.87	0.00	0.00	0.13	98.56	0.59	0.77	0.08	91.59	2.62	3.43	2.36	93.60	1.40	4.70	0.30	14.74	0.06	0.08	85.12
4D	20−30	98.72	0.06	0.02	1.20	97.10	2.05	0.77	0.08	92.43	4.91	1.83	0.83	97.53	0.79	1.53	0.15	14.49	0.19	0.07	85.25
	30−40	99.55	0.01	0.01	0.44	97.58	1.52	0.81	0.09	92.61	4.01	2.14	1.25	97.42	0.65	1.78	0.15	13.95	0.11	0.06	85.88
	40−50	99.71	0.01	0.00	0.28	97.63	1.31	0.97	0.09	93.45	2.94	2.18	1.43	96.43	0.98	2.41	0.18	17.73	0.17	0.13	81.97
	50−60	99.93	0.00	0.00	0.07	97.74	0.98	1.20	0.08	89.65	3.54	4.36	2.46	95.07	0.73	4.07	0.14	17.58	0.12	0.15	82.16
	60−70	99.90	0.00	0.00	0.10	97.56	0.95	1.41	0.08	91.16	3.15	4.59	1.10	93.32	1.20	5.36	0.12	17.89	0.12	0.20	81.79
	70−80	99.93	0.00	0.00	0.07	97.23	0.94	1.75	0.08	91.63	2.71	5.06	0.60	91.54	1.53	6.77	0.16	17.95	0.13	0.25	81.67
	80−90	97.73	0.00	0.00	2.27	99.18	0.29	0.35	0.18	83.54	3.39	4.03	9.03	94.25	0.32	3.22	2.21	7.58	0.02	0.03	92.37
	90−100	99.83	0.00	0.00	0.17	98.86	0.49	0.59	0.06	92.40	2.96	3.58	1.07	93.96	1.29	4.46	0.29	15.81	0.07	0.08	84.04
range of prediction	min. ±	0.14		0.01	0.10	1.34		1.12	0.00	5.42		2.60	0.01	2.69		2.54	0.00	3.70		0.01	3.67
	max. ±	4.64		2.82	4.63	26.21		26.20	0.45	27.85		27.84	5.36	27.57		27.56	1.43	21.79		14.28	11.44

30 years till 1978. From 1978, the soil has been used for crop production. During 1978–1981, liquid cattle manure and mineral fertilizers were applied. There after, only mineral fertilizers have been used. In 1982, the field site was established as a randomized block design of four pH adjustments (coded A, B, C, and D for nominal pH of 4.0, 4.7, 5.4, and 6.1, respectively) and four copper concentrations (coded 1, 2, 3, and 4 for copper treatments of 0, 250, 500, and 750 kg $CuSO_4$ hectare^{-1}, respectively). pH levels were established using calcium carbonate or sulfur. pH and Cu levels were adjusted in the plough layer. In 1988, pH levels were readjusted to their nominal values (36, 37).

Samples from the lowest and highest pH (treatments A and D) were taken from different soil layers in the range of 0–100 cm. The field soil samples were air-dried and sieved (<2 mm) before analysis. Soil organic matter (SOM) content was measured by loss-on-ignition at 550 °C. Clay content (<2 μm) was measured by sieve and pipet method. Cation exchange capacity (CEC) was determined by unbuffered 0.01 M $BaCl_2$ method (38). Fe fraction in DCB (dithionite-citrate-bicarbonate) and ammonium oxalate–oxalic acid extractions and metal content in 2 M HNO_3 (SSR = 1:10) extractions were measured with ICP-OES (Spectros, Spectro Flame).

Donnan Membrane Method. The Donnan membrane method is based on a Donnan membrane equilibrium using a cation exchange membrane to separate the substrate solution (donor) and a blank salt solution (acceptor) (19, 20, 39). The charge corrected activity ratios of the cations on both sides of the membrane are equal at the Donnan membrane equilibrium. In one measurement the free metal ion activity of all cations can be determined simultaneously.

One hundred grams of air-dried soil sample was used in the soil column Donnan membrane analysis. Two hundred milliliters of 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. The composition of the donor solution will be determined by the buffering behavior of the soil that is stored in the soil column and linked to the donor side of the membrane, since the amount of ions added to the system is small compared to the ions bound to the solid-phase matrix. The column percolation speed was 2 mL minute^{-1}. 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 (D-37582, Dassel, Germany). The concentrations of macroelements were measured by ICP-OES, and concentrations of microelements were measured by ICP-MS (Perkin-Elmer, Elan 6000).

Results and Discussion

Analytical Results. The analytical data show that there is a wide variation in most soil characteristics (Table 1). The organic matter content and the clay fraction (<2 μm) are between 0.4%–4.2% and 2.1%–4.9%, respectively. The soil CEC is in the range of 9.0–42.1 mmol kg^{-1}. Down a soil profile, the organic matter content, the clay content, and the CEC decrease with depth. The decrease of the organic matter content is stronger than the decrease of the clay content. Therefore the contribution of clay to soil CEC is more significant at the bottom of the profile.

The total Cu in the 2 M HNO_3 extraction is between 6 and 2247 μmol kg^{-1}, which reflects the treatments of Cu levels. The 2 M HNO_3 extractable Cd, Zn, Ni, and Pb are 0.06–2.45, 4–183, 4–36, and 5–124 μmol kg^{-1}, respectively (Table 1). When comparing the total Cu content in the surface layer (0–20 cm) at the same level of Cu treatment for the low pH soils (soils A) and the high pH soils (soils D), it follows that the amount in the low pH soils is 8–24% lower, indicating an enhanced Cu leaching by acidification during the 16 year period. If we assume that the original content and later input

of the other metals is the same for all the treatments in the field, the data show an even stronger leaching of Cd, Zn, and Ni at lower pH. The average total Cd, Zn, and Ni content in the surface layer (0–20 cm) for the low pH (soils A) is only 44%, 31%, and 34%, respectively, of that at high pH (soils D). It means that acidification has led to an excess removal of Cd, Zn, and Ni of approximately 56%, 69%, and 66% of the "initial" amount over a period of 16 years. As for Pb, there is little difference observed in the average total Pb content in the surface layer at the low and high pH, suggesting that there is hardly leaching of this metal. It can be shown that these leaching data are roughly expected based on the amount of water available for leaching in this area (about 1 mm day^{-1}) and the measured metal concentrations in the solid and solution phases. We intend to analyze these data in more detail in a forthcoming paper.

The Cu^{2+} activity measured varies from <$10^{-8.2}$ to $10^{-4.9}$ M, Cd^{2+} activity varies from <$10^{-9.2}$ to$10^{-7.2}$ M, Zn^{2+} activity is between $10^{-7.2}$–$10^{-4.8}$ M, Ni^{2+} activity ranges from <$10^{-8.2}$ to $10^{-5.9}$ M, and Pb^{2+} activity varies from <10^{-10} to $10^{-7.4}$ M. For some soil samples, the metal activity was below the detection limit of the ICP-MS (Table 1). In general, the metal activity decreases with increasing pH. Among these metals, Pb has the lowest free ion concentration in comparison with total Pb. Less than 0.04% of the total 2 M HNO3 extractable Pb exists as free Pb^{2+}, whereas for Cu, this was less than 2.4%. Compared to Pb and Cu, the soil has much lower affinity for Cd, Zn, and Ni. This is in agreement with the observation that more Cu and Pb are retarded in the upper layer of the soil profile than the other metals (Table 1). Lower solubility of Pb and Cu in soil has been observed previously (40–42).

Site Density of Soil Sorbents. Before being able to do the model calculations, it is essential to make a reasonable estimation of the amount and the site density of soil sorbents. In our model, the clay content (<2 μm) measured in the samples was used as the estimation of the clay silicate content in the soil samples. The charge of clay was assumed to be the same as the CEC of illite, which is normally in the range of 0.1–0.4 mol kg^{-1} (43). The charge of clay was assumed in the model to have a constant value independent of pH. In the calculation, we used the average and the extreme values of 0.1, 0.25, and 0.4 mol kg^{-1} for the charge of clay resulting in a range of the predictions. The Donnan volume of illite was estimated as 1 L kg^{-1} using the interlattice distance (10 Å) and the surface area (80–150 m² g^{-1}) of illite (43).

The content of SOM was measured using loss-on-ignition. In the modeling, all the NICA-Donnan parameters for the generic humic acid were used and kept constant except for the site density (22, 23). The site density needs to be estimated in a reasonable way because besides humic substances, SOM contains other subcomponents such as plant residual and microorganism biomass, which may have a metal binding reactivity differing from the humic substances. In addition, the interaction of SOM with soil minerals will also result in changes in site density for metal binding compared to the purified humic acid. The site density of SOM in comparison with generic humic acid was estimated in the following way: (i) calculate the contribution of clay to soil-CEC by multiplying the chosen clay charge (0.1, 0.25, or 0.4 mol kg^{-1}) with the clay content in each soil sample, (ii) calculate the CEC of SOM by subtracting clay-CEC from the measured soil-CEC, (iii) calculate the ratio of SOM-CEC to that of the generic humic acid under the same conditions, and (iv) the thus estimated relative site density of SOM has a high uncertainty in case the SOM contributes little to the CEC (mainly samples at larger depth); we therefore take the average of the ratio as the relative site density of SOM in comparison with the generic humic acid. The results of this calculation show that at the clay charge of 0.1–0.4 mol kg^{-1}, the site density of SOM varies between 46% and 16% of that of the generic
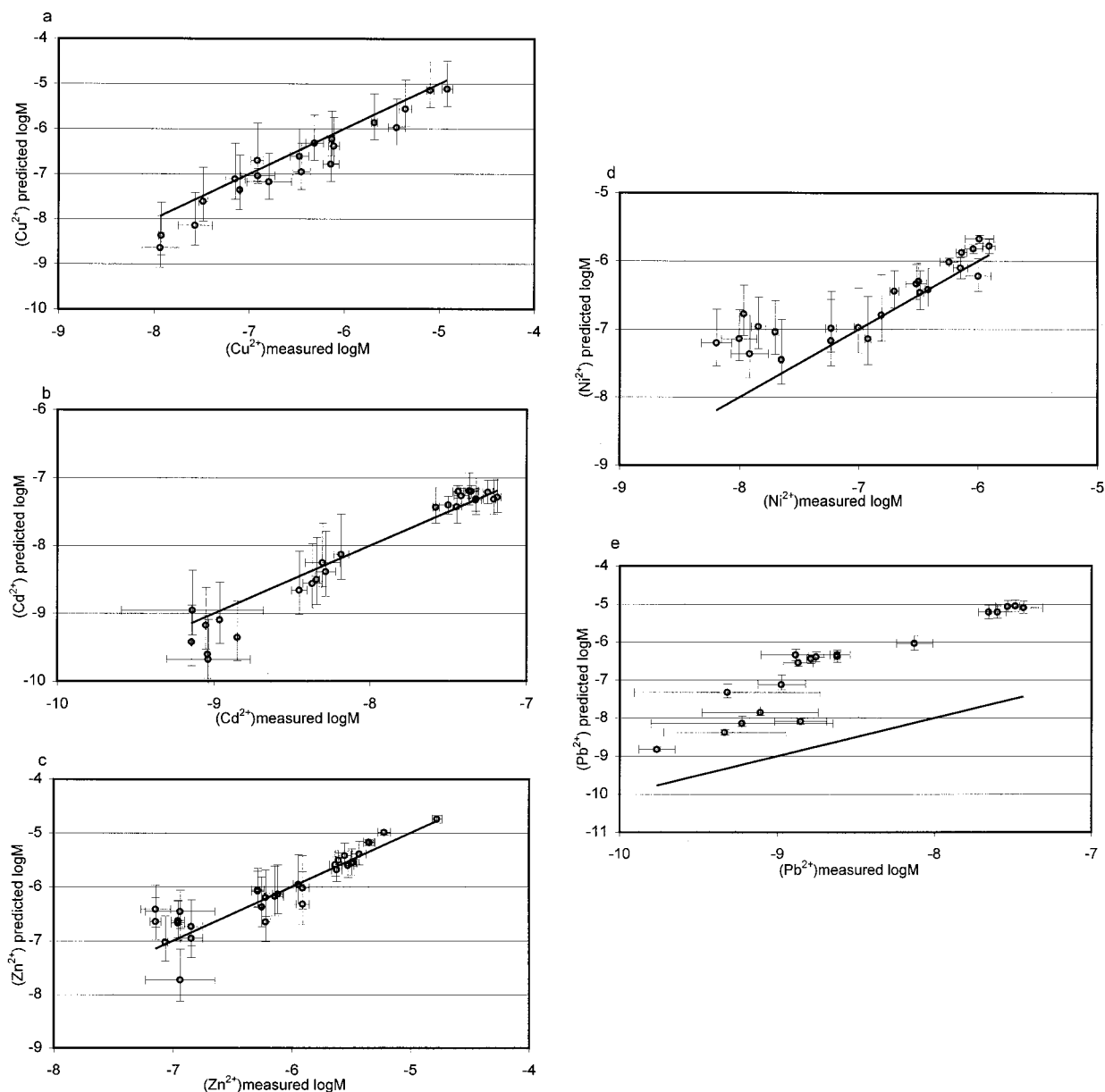
FIGURE 1. Comparison of predicted and measured metal activities. (○) Model predictions at the mean clay charge of 0.25 mol kg^{-1}and site density of SOM equals to 31% of the generic humic acid. The vertical error bars are model predictions with extreme clay charge and site density of SOM. The horizontal error bars are the standard deviations of the metal activity measured. (—) One to one line.

humic acid. At the average value of clay charge of 0.25 mol kg^{-1}, the site density of SOM was 31% of that of the generic humic acid.

The amount of amorphous iron hydroxides was estimated from the oxalate extractable Fe, after subtracting the Fe that is calculated to be bound to SOM. The organically bound Fe was calculated with the NICA-Donnan model assuming that amorphous iron hydroxide controls Fe^{3+} activity. The solubility product of amorphous iron hydroxide used was $10^{-42.02}$ (44). The organically bound Fe was calculated to be $10-29\%$ of the oxalate extractable Fe. The surface area of amorphous iron hydroxides was assumed to be the same as that of HFO, i.e. 600 m^2 g^{-1} (31). The amount of crystalline iron hydroxides was estimated as the difference between DCB and oxalate extractable Fe. The surface area of crystalline iron hydroxides was assumed to be 100 m^2 g^{-1}. Ni adsorption on crystalline iron hydroxides was not considered due to the lack of the CD-MUSIC parameters for Ni.

Comparison Between Free Metal Activity Predicted and Measured. In Figure 1, the predicted Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+},

and Pb^{2+} activities using the multisurface model are compared to those measured. By taking the clay charge of 0.1, 0.25, and 0.4 mol kg^{-1} and the corresponding site density of SOM, i.e. 46%, 31%, and 16% of the generic humic acid, the model gives three predicted metal activities for one soil sample. At 0.1 mol kg^{-1} clay charge and 46% site density of the generic humic acid for SOM, the model predicts lower metal activities than using higher clay charge and lower site density of SOM. This is due to the higher affinity of SOM for the metals than that of the clay.

The bandwidth of Cu^{2+} activity predicted by the model at the extreme clay charges and SOM site density is $1-1.2$ log-unit. All the measured Cu^{2+} activities fall within this interval. The agreement between the model predicted and the measured Cu^{2+} activity is good (Figure 1a). For Cd^{2+}, Zn^{2+}, and Ni^{2+}, the bandwidth of predictions is narrower, and it is about $0.1-1$ log-unit. The interval is much smaller at higher metal activity than at lower metal activity (Figure 1b–d). Cd, Zn, and Ni form less strong complexes with SOM than Cu. At high metal activity, the adsorption to SOM is

relatively more determined by the nonspecific Donnan ion-exchange part of the NICA-Donnan model, and the model assumptions concerning CEC distribution between clay and SOM have therefore much less effect on the prediction of metal activity than at low metal activity. The predicted Cd^{2+} activity agrees with the measured well and all the measured Cd^{2+} activities are within the range of model predictions (Figure 1b). For Zn^{2+} and Ni^{2+}, the measured activities agree with the predictions reasonably well for most of the samples, except for some samples of high pH (soil 3D and 4D) at larger depth (Figure 1c,d). For these samples, the model predicts higher Zn^{2+} and Ni^{2+} activity than measured. A possible reason for the discrepancy for these samples could be the formation of Zn−Al, Ni−Al layered double hydroxide (LDH) which are more stable at near neutral pH values (45, 46).

The bandwidth of the model predictions for Pb^{2+} activity is less than 0.3 log-unit (Figure 1e). According to the model, Pb adsorption onto iron hydroxides is very important; therefore, the change of the site density of clay and SOM has little influence on the predicted Pb^{2+} activities. The predicted Pb^{2+} activities are about 0.5−2.5 log-unit higher than measured. The discrepancy cannot be explained by the hypothesis that Pb^{2+} activity is controlled by Pb phosphate minerals (44). The possibility of the existence of Pb phosphate minerals is excluded by comparing the ion activity product of Pb^{2+}, PO_4^{3-}, and Cl^- to the solubility of the most insoluble Pb phosphate mineral, chloropyromorphite $[Pb_5(PO_4)_3Cl]$ (44). The measured Pb^{2+} activity was lower than those calculated using the solubility product. In addition to the uncertainties involved in the adsorption models and model parameters, there are other possible causes for the failure of the model for Pb^{2+} activity prediction. The irreversibility of Pb adsorption can be one of the explanations. Another possible reason can be the adsorption on other soil surfaces, for example manganese oxides, which we did not consider in the model (47).

The failure of the model in predicting reasonable Pb^{2+} activities shows that the model approach is not necessarily adequate. Considering the fact that the predictions are fully based on models developed in the laboratory for individual sorbents and that no fitting has been involved in the calculations, the quite reasonable prediction for Cu^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+} are therefore rather encouraging.

Individual Sorbents Contribution to Metal Binding. Besides the prediction of the free metal ion activity, the multisurface model gives an estimation of each sorbent contribution to metal adsorption in soils. In Figure 2, the model predictions of the sorbents contribution to Zn binding in the soil samples at low pH (4A) and high pH (4D) are shown as an example. Extensive results are available in Table 2. In Figure 2, Table 2, and in the following discussions, we refer to the model predictions using the average charge of clay (0.25 mol kg^{-1}) and accordingly estimated SOM site density (31% of the generic humic acid). At the end of Table 2, the uncertainty ranges of the predictions under the extreme cases of clay charge and SOM site density are given. This uncertainty range is smaller for Cu than for other metals, due to the very strong affinity of SOM to Cu. The prediction is in general more sensitive to assumptions of CEC distribution between the SOM and clay when the SOM is more or less saturated with the metal in respect to its binding capacity.

The model calculation confirmed the common recognition that soil organic matter is an important sorbent for heavy metals in soils, especially for Cu. For all the soil samples, the modeling results show that the organically bound Cu is more than 98% of the total adsorbed Cu. Only less than 2% of adsorbed Cu is attributed to clay and iron hydroxides. The predominant role of organic matter for Cu adsorption in soils has been observed previously using different methods (48, 49). The model predicted that the Cd bound to organic
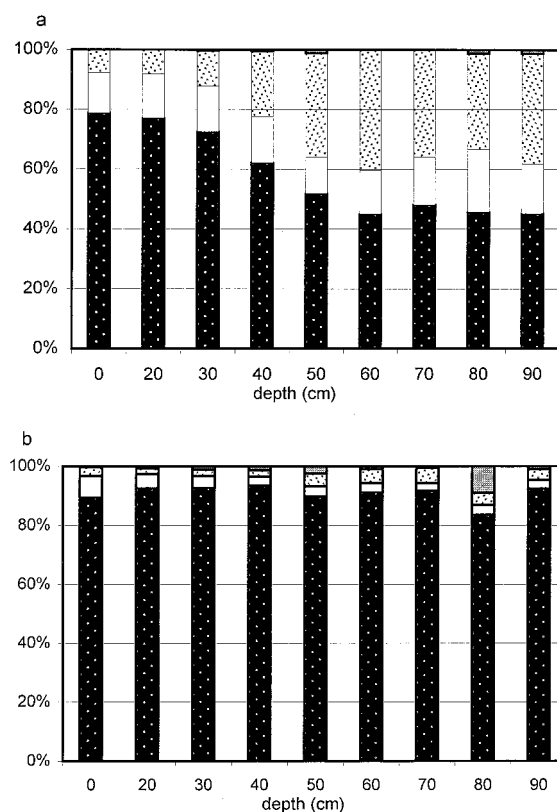

FIGURE 2. Contribution of soil sorbents to Zn adsorption in soil 4A (0−100 cm) (a) and in soil 4D (0−100 cm) (b) (model predictions at the mean clay charge of 0.25 mol kg^{-1} and site density of SOM equals to 31% of the generic humic acid). Bars with black background and white dots: specifically bound to SOM; white bars: bound in the Donnan gel of SOM; bars with white background and black dots: bound to clay; grey bars: bound to iron hydroxides.

matter accounts for about 70−99% of the total adsorbed Cd. The organically bound Zn and Ni accounts for about 60−99% of the total adsorbed Zn and Ni. The intrinsic affinity of organic matter for these metals is not as strong as for Cu. However, the soil organic matter is still the most important surface that adsorbs Cd, Zn, and Ni in these soils.

Although the model shows for Cd, Zn, and Ni that SOM is a dominant sorbent, it is still possible that under certain conditions a considerable fraction of metal is adsorbed to the clay minerals. In these soil samples, the Cd bound to clay can be as high as 30% of total adsorbed Cd. The clay bound Zn and Ni can be as high as about 40% of total adsorbed Zn and Ni. The highest contribution of clay to Cd, Zn, and Ni adsorption was found in the soil sample 4A (low pH) at larger depth. It suggests that metal adsorption to clay minerals is more important under the conditions of low pH and low organic matter content, when the soil organic matter is relatively saturated for metal adsorption.

From Figure 2 it can be seen that Zn bound to clay and to the Donnan part of SOM is more important in soil with low pH (4A) than in soil with high pH (4D). This also holds for other metals (Table 2). The specific binding of metals to SOM increases with increasing pH. Acidification thus leads to a shift in the binding of metal from specific binding to a more nonspecific ion-exchange binding. The effect of acidification on the shift in the type of binding is quite significant for Cd, Zn, and Ni and not significant for Cu.

In the literature, there is normally a lack of correlation between the soil cation exchange capacity (CEC) and the heavy metal binding. The importance of clay silicates as heavy metal adsorbents is uncertain (3). The multisurface model can be used to explain the contradictory findings in some

previous work. Gray et al. (*10*) concluded that pH and organic matter at high soil Cd content (i.e. 1.3 mg kg^{-1}) had little effect on the concentration of Cd in solution, with total soil Cd being the dominant controlling factor. However, at smaller Cd concentrations (i.e. 0.3 mg kg^{-1}), pH and organic matter play a much greater role in the controlling of the concentration of Cd in solution. According to our model calculation, Cd binding on organic matter is dominant at lower metal loading. When the metal loading is high, the binding to clay minerals becomes more important; therefore, little effect of pH and organic matter is expected for such conditions. Because the relative importance of clay on metal binding is conditional, it is understandable that no correlation can be found between metal binding and soil CEC or soil clay content in studies such as the one with Cd by Gray et al. (*10*).

According to the model, Cu, Cd, Zn, and Ni adsorbed on iron hydroxides is less than 6% of their total amount bound in these samples. The model estimates that iron hydroxides are not important sorbents for Cu, Cd, Zn, and Ni in these soils, which have relatively low pH and low content of the iron hydroxides compared to SOM and clay silicates. However, for soils with low organic matter content and high pH, metal binding to metal hydroxides can still be important, as was found by Zachara et al. (*3*).

The model failed to give a reasonable prediction of free Pb^{2+} activity. However, the model prediction of individual sorbents contribution to Pb adsorption can still be an indication of the relative importance of various soil surfaces. The model results show that 8$-$79% of the total sorbed Pb is in association with SOM. The adsorption to organic matter is more important in soil samples A, which all have a relatively low pH. In soil samples D, which have a relatively high pH, the adsorption of Pb to iron hydroxides is calculated to be more significant. Pb adsorbed to iron hydroxides can be as high as 92% of the total adsorbed Pb. Pb adsorbed on clay can amount to 15%, and it is only important in soil samples A, where the pH is low. Iron oxides and organic matter have a high capacity to adsorb Pb and concomitantly maintain a low Pb^{2+} activity in solution (*11*).

The model predicts that the acidification of sandy soils will not only result in a decreased binding affinity for metals in general but will also lead to a shift of specific binding toward more nonspecific binding. The change will not only lead to higher solution activities but will also make the metal activity more susceptible to the change of salt level. The model gives good results for Cu, Cd, Zn, and Ni of the effect of acidification on the resulting metal activity.

Acknowledgments

Supporting Information Available

Tables of the model parameters used in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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