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Modeling Sorption of Cd, Hg and Pb in Soils by the NICA-Donnan Model

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Metal adsorption is an important process at the soil-solution interface that controls metal bioavailability and toxicity. In this study, batch adsorption experiments were conducted to investigate the binding of Cd, Hg and Pb in soils collected from around metal smelters in Quebec and Ontario, Canada. It was found that soil organic matter enhanced the retention of Cd, Hg and Pb. Assuming that the surfaces of soil particles behaved similarly to organic matter, we used the Non-Ideal Competitive Adsorption (NICA)-Donnan model to derive the parameters for surface complexation of the three metals. The shape of the Cd, Hg and Pb adsorption isotherms are briefly discussed with respect to the results of the experimental measurements and the model predictions. The average values of the NICA-Donnan model parameters could be used to give reasonable predictions of metal sorption in the soils of this study.

Keywords Trace metals, soil contamination, adsorption, thermodynamic equilibrium, modeling.

Introduction

Cadmium (Cd), mercury (Hg) and lead (Pb) are common toxic metals emitted from smelters. As a result of aerial deposition, the concentrations of these metals in soils surrounding the smelters have been elevated, potentially causing adverse effects on the environment (Hutchinson and Whitby, 1977; Freedman and Hutchinson, 1979; Derome and Lindroos, 1998). The risks associated with the metal pollution are closely related to metal mobility and bioavailability, which in turn are controlled by the chemical reactions taking place in soil solutions and on the surface of soil particles (Huang *et al.*, 1998).

Soils have a finite capacity to attenuate trace metals through their multiple reactive mineral and organic components, which are involved in metal retention by forming inner- and outer-sphere complexes (Evans, 1989). Clay minerals, metal oxides and organic matter

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are key constituents of soil particle surfaces and possess different sites for metal retention; consequently, metals may be found in various forms in the soil solid phase: (i) on nonspecific ion exchange sites; (ii) on functional groups of organic matter and metal oxides; (iii) in the structure of primary and secondary minerals (Duquette and Hendershot, 1990). The strength of metal sorption is dependent on the affinity of metals, the composition of soil solutions and the nature of the surface sites (Harter and Naidu, 1995).

In boreal temperate regions such as the Canadian Shield, soils often possess podzolic characteristics due to the acidic soil environment and the alluviation process (leaching of Al, Fe and organic matter). Organic matter usually accumulates in the surface and subsurface layers of the soil profile, present as either bulk materials or coating on particulate matter (McKeague *et al.*, 1986). Organic matter is an important reactive component in such soils capable of retaining the metal cations (Temminghoff *et al.*, 1997). In some studies involving metal adsorption in mineral-humic mixtures, it was shown that the amount of bound metals was increased compared to the metal binding on the mineral alone (Matínez and McBride, 1999; Vermeer *et al.*, 1999). Further, in a surface charge study (Ge and Hendershot, 2004), organic matter was found to be significantly correlated with the binding site concentration of soils collected from Quebec and Ontario, Canada. These findings indicate that organic matter may be the primary sorbent for trace metals in the soils of this region.

Recently, a semi-mechanistic Non-Ideal Competitive Adsorption (NICA)-Donnan model was developed to describe the proton and metal binding on organic substances (e.g., purified humic acid (HA) and fulvic acid (FA)) (Benedetti *et al.*, 1996a; Kinniburgh *et al.*, 1996). With the parameters calibrated under well-defined laboratory conditions, this model reasonably predicted the partition of Cd and Cu between the soil solution and solid phase of two soils with different properties (Benedetti *et al.*, 1996a). An improved version, the consistent NICA-Donnan model, corrected the H^+/M^{z+} molar exchange ratio in the metal binding and thus ensured the thermodynamic consistency of the model (Kinniburgh *et al.*, 1999).

In this study we hypothesized that the NICA-Donnan model can be used to simulate the metal adsorption in soils. This hypothesis is reasonable, as the surface charge study (Ge and Hendershot, 2004) showed that the surfaces of the soils behaved similarly to organic matter. A bimodal proton binding distribution was clearly observed from the surface variable charge curves, which were successfully fit by the NICA-Donnan model (Ge and Hendershot, 2004). Thus the objectives of this study are:1) to investigate the retention of Cd, Hg and Pb in eastern Canadian soils with a range of soil properties; 2) to derive parameters of the NICA-Donnan model using the metal adsorption data; and 3) to predict the metal adsorption in soils with the derived parameters.

Theoretical Background

A detailed description of the NICA-Donnan model has been given by D. G. Kinniburgh and coworkers (Kinniburgh *et al.*, 1996, 1999). This model implicitly assumes a continuous distribution of affinities for each site, where cation complexation with humic substances occurs through specific binding to the negatively charged surface functional groups and nonspecific coulombic sorption to the residual negative charge of the organic molecule (Kinniburgh *et al.*, 1996). The specific, monodendate binding (Eq. 1) is described by the NICA model and the nonspecific binding by the Donnan model.

$$\begin{aligned} S^- + H^+ &= SH^0 \\ S^- + M^{z+} &= SM^{(z-1)+} \end{aligned} \tag{1}$$

where S^- is negatively charged sites on soil surface particles and M^{z+} is metal cations. The NICA equation for the overall binding of species i in the competitive situation is:

$$\theta_{i,t} = \frac{(K_i c_i)^{n_i}}{\sum_i (K_i c_i)^{n_i}} \times \frac{\left[\sum_i (K_i c_i)^{n_i}\right]^p}{1 + \left[\sum_i (K_i c_i)^{n_i}\right]^p} \tag{2}$$

where $\theta_{i,t}$ is the fraction of all the sites occupied by species i, K_i is the median affinity constant for species i. The non-ideal behavior of ion i is reflected by n, which ranges from 0 to 1. The ion non-ideality shows a specific chemical heterogeneity of the sorbent toward the ion (Benedetti *et al.*, 1995). A smaller n means a more non-ideal ion behavior. The parameter p ($0 < p < 1$) refers to the intrinsic heterogeneity of the binding phase. A smaller p stands for a more heterogeneous site. The amount of component i bound, Q_i, is given by:

$$Q_i = \theta_{i,t}(n_i/n_\mathrm{H})Q_\mathrm{max} \tag{3}$$

where Q_max is the maximum binding capacity for protons.

The nonspecific, electrostatic interactions are incorporated into the NICA model by using the concentration of ions near the binding sites (Donnan phase) rather than the concentration in the bulk solution. Therefore, the cation adsorption on the organic molecule can be illustrated by the following isotherm equation:

$$Q_i = Q_\mathrm{max}(n_i/n_\mathrm{H}) \frac{(K_i c_{Di})^{n_i}}{\sum_i (K_i c_{Di})^{n_i}} \times \frac{\left[\sum_i (K_i c_{Di})^{n_i}\right]^p}{1 + \left[\sum_i (K_i c_{Di})^{n_i}\right]^p} \tag{4}$$

where c_{Di} is the concentration of uncomplexed cation i present in the Donnan phase in mol L^{-1}. It is related to its concentration in bulk solution, c_i, by a Boltzmann factor, χ:

$$c_{Di} = \chi c_i = \exp(-z_i \mathrm{F}\Psi_\mathrm{D}/\mathrm{RT}) c_i \tag{5}$$

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

The Donnan phase is considered to be an electrically neutral phase (Benedetti *et al.*, 1996b) having a particular volume (V_D, in L kg^{-1}). An empirical parameter, b, is used to describe how the Donnan volume varies with ionic strength (I):

$$\log V_\mathrm{D} = b(1 - \log I) - 1 \tag{6}$$

The electroneutrality condition in the Donnan phase is given by Eq. 7:

$$q/V_\mathrm{D} + \Sigma z_i (c_{Di} - c_i) = 0 \tag{7}$$

where q is the net charge of the humic substance (equiv kg^{-1}) and z_i refers to the charge of i, including sign.

Materials and Methods

Soil Sampling and Preparation

Thirty-one soils were taken from Rouyn-Noranda (northern Quebec), Valleyfield (southern Quebec) and Sudbury (northern Ontario), Canada. Both surface (Ah, FH and H horizons) and subsurface (Bhf, Bf1 and Bm horizons) samples were collected at different distances from the smelters and thus reflect a wide range of soil properties and metal contamination.

Soils were air-dried and aggregates were broken up and passed through a 2-mm sieve for subsequent analyses.

Soil Analysis

Soil pH was measured with a soil:water ratio of 1:2 for mineral soils and 1:10 for organic soils (Hendershot *et al.*, 1993a). Cation exchange capacity (CEC) and exchangeable cations were determined using a 0.1 M $BaCl_2$ extraction method (Hendershot *et al.*, 1993b). Particle size analysis was carried out with the procedure in Sheldrick and Wang (1993). A wet oxidation method was used to measure soil organic carbon (Org. C) (Tiessen and Moir, 1993). Soils were extracted by the acid ammonium oxalate solution to analyze Fe and Al oxides (Ross and Wang, 1993). Ethylene glycol monoetheyl ether (EGME) adsorption technique was used to determine specific surface area (SSA) of soils (Heilman *et al.*, 1965).

Total metals (Cd, Hg and Pb) in soils were determined following a HNO_3-HCl digestion protocol with a microwave digestion system (USEPA Method 3051A; USEPA, 1998). The digests were analyzed on a flame atomic absorption spectrometer (AAS) for total Cd and Pb. Mercury was determined by a Hg analyzer (Varian M6000A) using 10% $SnCl_2$ to reduce Hg to the elemental state (Hg^0). A quality-control soil sample (NIST 2710) was analyzed using this method and the average recoveries for the duplicate samples were 108%, 95% and 104% for Cd, Hg and Pb, respectively. All measurements were above the detection limits, which were 0.01 mg L^{-1} for Cd, 0.5 mg L^{-1} for Pb and 1 ng L^{-1} for Hg.

Batch Adsorption Experiment

Binding isotherms of Cd, Hg and Pb were determined by the batch adsorption method described below. Six metal solutions were prepared by adding Cd, Hg and Pb to the unbuffered 0.01 M $NaClO_4$ (supporting electrolyte). The concentrations were 0, 1, 2, 4, 10, 20 mg L^{-1} for Cd and Pb and 0, 1, 2, 4, 10, 20 μg L^{-1} for Hg. These metal levels were chosen because they are environmentally relevant concentrations in soils. Mixed metal solutions were used rather than single metal solutions in order to simulate the competition between metals for available adsorption sites. Metal adsorption experiments were performed in duplicate for each soil.

In the batch adsorption procedure, approximately 0.5 g air-dried organic soil or 2 g mineral soil was weighed into a 50 ml polyethylene centrifuge tube, and 10 ml 0.01 M $NaClO_4$ solution containing different levels of Cd, Hg and Pb was added. The pH of the soil suspension was adjusted to 6 using 0.1 M NaOH or 0.1 M HNO_3 before the solution was brought to a volume of 25 ml with the 0.01 M $NaClO_4$ solution. The soil suspension was shaken end-over-end at room temperature ($25 \pm 2°C$) for 24 h, which was found to be enough for the soil solutions to reach equilibrium. The suspension was then centrifuged at 3000 rpm for 20 min. The supernatant was removed and passed through a 0.45 μm Millipore polycarbonate filter. We ran the quality controls in the process of the metal adsorption experiment and found that the metal recovery was satisfactory (85% ± 10%). The metal adsorption on the containers (i.e., tubes and filters) was not significant. An aliquot of unfiltered supernatant was used to record its pH and electrical conductivity (EC). Dissolved organic carbon (DOC) was also measured using a total carbon analyzer (Shimadzu TOC-5000). The filtered solution was then acidified to $pH < 2$ with HNO_3 and stored for metal analysis.

The concentrations of Cd and Pb in the final solutions were measured by flame or graphite furnace AAS. Mercury was analyzed by Hg analyzer (Varian M6000A) after the sample was digested using a bromide/bromate oxidation protocol provided by Cetac Technologies Inc. (Omaha, NE). Briefly, 20 ml of sample, 2.5 ml 1:1 trace metal grade HCl and 0.5 ml 0.1 N $KBr/KBrO_3$ reagent were added to an acid-cleaned bottle. The yellow bromine color should persist in the sample to fully oxidize Hg. Then the sample was brought to a volume of 25 ml and capped until analysis. The samples were equilibrated overnight prior to analysis. A blank was also prepared to correct for the Hg in the reagents. This method was calibrated with a linear range of 5–1000 ng L^{-1} and a regression coefficient, R^2, of 0.99 or above. The difference between the metal that was added initially and that in the final solution was considered as the amount of metals adsorbed to soils.

Estimation of the NICA-Donnan Model Parameters

We fit the experimental metal binding data to the NICA-Donnan model in order to obtain estimates of the characteristic metal binding parameters for the thirty-one soils. The model parameters to be determined included maximum available binding sites ($Q_{\max}$), median binding constant (K), non-ideality of the ion (n) and intrinsic heterogeneity of the sorbent (p) (Benedetti *et al.*, 1996a). At the pH (6 ± 0.5) of the experiment, metal sorption by Type 2 sites is less important than by Type 1 sites. Therefore, we fixed the parameters related to the 2nd site, except for $Q_{\max2}$, at the published values for generic humic acid (Milne *et al.*, 2003; Table 1), assuming that the particle surfaces behave similarly to organic matter. The value of $Q_{\max2}$ for each soil was calculated using the formula:

$$Q_{\max2} = Q_{\max2-\mathrm{HA}} \times \mathrm{Org.\ C}(\%)$$

where $Q_{\max2-\mathrm{HA}}$ is 2.55 mol/kg (Milne *et al.*, 2003) and Org. C is the percentage of soil organic carbon.

In the previous paper (Ge and Hendershot, 2004), we studied the acid-base properties of the same soils and estimated the $Q_{\max}$, K_{H} and m_{H} (a term for the H^+ affinity distribution) for Type 1 and 2 surface binding groups. Assuming that metal adsorption takes place on the same sorbent as the proton binding, we took the $Q_{\max}$ and K_{H} values for Type 1 sites in that paper. We used the approach outlined in Benedetti *et al.* (1995) to determine the non-ideality of metal ions (n). Briefly, at low pH and low free metal concentration, it is assumed that the adsorption on the 2nd type site is negligible and the proton term in Eq. 4 is constant and much larger than the metal term: $K_{\mathrm{H}}\ \mathrm{c_{DH}} \approx$ constant and $(K_{\mathrm{H}}\mathrm{c_{DH}})^{n\mathrm{H}} \gg (K_{\mathrm{i}}\ \mathrm{c_{Di}})^{ni}$. Then Eq. 4 may be simplified to a Freundlich isotherm:

$$Q_i = Q_{\max}\xi(\mathrm{c_{Di}})^{ni}, \quad \text{or} \quad \log Q_i = \log(Q_{\max}\xi) + n_i \log(\mathrm{c_{Di}}) \qquad (8)$$

where ξ is a constant. From Eq. 8 we are able to obtain n_i, which describes the non-ideal behavior of the sorbent with respect to the bound metal. Thus in a plot of log bound metal vs. log free metal, the limiting slope of the isotherm at a constant pH corresponds to n_i.

Table 1
NICA-Donnan model parameters of generic HA for Cd and Pb

	b	log K_1	n_1	p_1	log K_2	n_2	p_2
Cd	0.49	−0.2	0.73	0.62	2.37	0.54	0.41
Pb	0.49	1.25	0.6	0.62	4.84	0.69	0.41

In the presence of metal ions, m_{H} is separated into the ion-specific non-ideality of H^{+} (n_{H}) and generic heterogeneity of sorbent (p) (Kinniburgh *et al.*, 1996):

$$m_{\mathrm{H}} = n_{\mathrm{H}} \times p \tag{9}$$

The n_{H} and p describe the binding sites of each soil; they can be obtained from the sorption data of one metal and kept constant for the other metals. Hence, for Cd and Pb, the parameters to be derived include $\log K_{Cd1}$, $\log K_{Pb1}$, n_{Cd1}, n_{Pb1} and p_1. The adjustable parameters for Hg are the $\log K_{Hg}$ and n_{Hg} for both sites.

Furthermore, the estimated $\log K_M$ values need to be corrected for the electrostatic effects associated with the ionic strength in the solutions. This can be achieved by incorporating the proton and metal concentrations close to the sites (Donnan phase) into the NICA model. The concentration ratio between the Donnan phase and bulk solution is defined by the Boltzmann factor, which can be solved using Eqs. 4–7 and the Goal Seek function in Microsoft Excel. We used the Excel program to carry out the optimization. The best data fit was found when the maximum coefficient of determination (R^2) between the measured and predicted sorbed metals was obtained.

Estimation of Free Metal Concentrations

According to our previous experience, the Windermere Humic Aqueous Model (WHAM) Model V can be used to estimate the amount of free metals with reasonable accuracy. Therefore, free metal concentrations in the supernatant, which were a part of input data for the NICA-Donnan model, were estimated using the WinHumicV (Gustafsson, 1999), which was developed from WHAM Model V (Tipping, 1994). The input data for this model included solution pH, total dissolved metal, inorganic ligands and DOC. The anions considered in the model were OH^-, Cl^-, HCO_3^-, CO_3^{2-} and NO_3^- ions. The Cl^- concentration in the field-collected soil solutions from Sudbury and Rouyn-Noranda sites ranged from 1×10^{-6} M to 1×10^{-4} M (data not published). Thus, we used an average $[Cl^-]$ at 1×10^{-5} M in the WinHumicV. The concentrations HCO_3^- and CO_3^{2-} ions were calculated assuming an atmospheric partial pressure for CO_2 of 3.5×10^{-4} atm. In this study we assumed that the fulvic acid was a good analogue of the DOC since when $pH < 6.5$ humic acid does not dissolve into soil solution (Schnitzer, 1986; Benedetti *et al.*, 1996a).

Results and Discussion

Soil Properties

Table 2 shows the chemical properties of the soils in this study. The pH of the 31 soils varied from 3.5 to 7.5, while Org. C ranged from 0.86% to 44%. Values of 0.44 to 28.5 $cmol_c/kg$ were obtained for the CEC. Percentages of Al and Fe oxides were in the following ranges: 0.05% to 0.74% and 0.10 to 9.6%, respectively. The majority of the soils had coarse or medium texture except that a few soils from Rouyn-Noranda and Valleyfield contained around 42% clay. The surface area was from 4.3 to 299 m^2/g (Table 2). High values of surface area were observed when a soil contained a large amount of either organic matter or clay minerals. The Al and Fe oxides were higher in sandy soils, which had more Al and Fe accumulation than in clay soils. Total metal concentrations (Cd, Hg and Pb) of these samples are also summarized in Table 2. It was found that soils with high content of organic matter accumulated large amounts of metals. One organic soil from Rouyn-Noranda

Table 2
Selected chemical properties of the soils

Soil	Horizon	pH	CEC $\mathrm{cmol_c/kg}$	Sand	Silt	Clay	Org. C %	Al oxides	Fe oxides	Surface area $\mathrm{m^2/g}$	Cd mg/kg	Pb mg/kg	Hg μg/kg
sud1	Ah	5.83	7.22	65.0	25.5	9.5	2.20	0.126	0.282	31.6	0.165	10.8	20.7
sud2	Ah	7.03	11.2	49.6	41.9	8.5	1.60	0.061	0.278	20.6	0.196	11.2	17.4
sud3	Ah	6.01	2.12	47.0	49.7	3.3	0.96	0.740	0.631	11.9	0.082	7.95	40.3
sud4	Ah	4.03	5.33	51.5	44.0	4.5	3.63	0.233	2.98	54.1	0.526	96.7	34.5
sud5	Ah	5.82	3.28	59.8	30.7	9.5	2.59	0.434	1.26	33.3	0.417	142	39.1
sud6	Ah	6.52	4.87	67.0	25.9	7.1	1.03	0.127	0.666	14.0	0.278	28.6	16.5
sud7	Ah	6.27	18.1	24.2	59.0	16.8	2.59	0.074	0.453	68.0	0.231	33.7	40.8
sud8	Ah	7.53	9.55	45.2	42.8	12.0	1.08	0.111	0.358	20.8	0.154	11.9	24.3
sud9	Ah	6.19	15.1	26.0	56.0	18.0	2.34	0.107	0.593	55.9	0.247	22.9	23.8
sud10	Ah	6.11	10.7	42.0	38.6	19.4	1.54	0.145	0.335	56.7	0.108	11.2	15.2
sud11	Ah	5.36	6.35	43.5	42.1	14.4	2.30	0.160	0.506	50.1	0.064	11.4	19.8
sud12	H	4.7	8.45	n.d.	n.d.	n.d.	16.5	0.155	1.31	85.4	4.04	194	65.7
sud13	H	4.35	25.8	n.d.	n.d.	n.d.	28.6	0.127	0.253	91.0	3.61	63.3	140
sud14	Bhf	4.74	1.70	74.5	17.5	8.0	9.57	0.492	9.56	26.1	3.99	18.0	33.5
sud15	Bhf	5.03	2.61	63.0	24.5	12.5	7.83	0.737	1.67	25.5	0	5.37	48.8
rn1	Ah	7.25	11.3	62.0	13.6	24.4	0.977	0.157	0.434	33.6	0.170	31.0	50.9
rn2	Ah	7.44	14.6	50.9	24.4	24.7	2.57	0.233	0.584	55.8	0.967	118	31.8
rn3	Ah	5.65	10.2	41.2	25.3	33.5	5.58	0.574	0.997	127	0.955	79.4	38.8
rn4	Ah	6.16	14.0	29.8	28.4	41.8	1.46	0.237	0.466	92.2	0.577	28.5	19.3
rn5	Ah	5.8	25.3	64.3	20.6	15.1	11.0	0.234	0.998	136	4.0	243	52.9
rn6	Ah	6.96	15.5	70.5	21.2	8.3	2.31	0.186	0.519	29.8	1.82	117	37.5
rn7	FH	3.54	12.5	n.d.	n.d.	n.d.	42.3	0.070	0.277	299	12.4	1095	281
rn8	Bhf	4.87	0.71	76.5	15.5	8.0	1.52	0.404	0.916	8.17	2.70	1.35	27.2
rn9	FH	3.91	15.9	n.d.	n.d.	n.d.	44.0	0.050	0.103	237	3.72	311	323

(Continued on next page)

Table 2

Selected chemical properties of the soils (*Continued*)

Soil	Horizon	pH	CEC cmol_c/kg	Sand	Silt	Clay	Org. C %	Al oxides	Fe oxides	Surface area m^2/g	Cd mg/kg	Pb mg/kg	Hg μg/kg
rn10	Bf1	5.69	0.44	74.0	17.0	9.0	0.86	0.690	0.367	4.33	1.79	8.05	34.7
val1	Ah	6.04	28.5	21.6	43.0	35.4	4.61	0.381	0.483	170	1.46	21.3	105
val2	Ah	6.68	21.6	30.8	36.8	32.4	2.65	0.216	0.429	135	0.178	10.3	23.2
val3	Ah	5.92	12.5	58.1	29.8	12.1	3.61	0.303	0.549	58.3	0.249	18.1	40.6
val4	Ah	6.19	18.1	52.0	32.0	16.0	5.72	0.255	0.574	63.4	8.82	62.5	239
val5	Bm	5.38	5.77	58.0	31.0	10.0	1.46	0.305	0.583	32.1	0.972	18.0	95.5
val6	Bm	6.54	4.34	59.0	31.0	10.0	0.87	0.250	0.569	21.8	0.488	17.2	91.2

sud: Sudbury, rn: Rouyn-Noranda, val: Valleyfield.
n.d.: not determined.

contained 12.4 mg kg^{-1} Cd, 281 $\mu g\ kg^{-1}$ Hg and 1095 mg kg^{-1} Pb. Elevated Cd and Hg concentrations (8.82 mg kg^{-1} and 239 $\mu g\ kg^{-1}$, respectively) were found in a Valleyfield surface soil. Compared to typical values for Cd and Pb in unpolluted soils (0.06–1.1 mg/kg and 50–100 mg/kg, respectively; Adriano, 1986), these soils seem to be contaminated by the two metals. According to Schlüter (1997), common Hg concentration in uncontaminated soils ranges from 100–300 $\mu g\ kg^{-1}$ for organic horizons of forest soils and 20–100 $\mu g\ kg^{-1}$ in mineral soils. Therefore, our soils do not appear to have been contaminated with Hg. We included blank $NaClO_4$ solutions in the sorption study but the metals in the blank solution were below the detection limit of atomic absorption spectrophotometer.

Estimation of Metal Speciation

WinHumicV was used to estimate the speciation of Cd, Hg and Pb in the filtered soil solutions after shaking and centrifugation. Generally, more than 60% of dissolved Cd existed as free ions. This contrasted with the Pb speciation where, in some solutions, almost all Pb was bound to DOC. This is not surprising because the affinity of Pb to DOC is usually higher than that of Cd (Harter and Naidu, 1995). However, Hg was the metal most strongly bound to DOC and uncomplexed Hg^{2+} was very low ($<10^{-17}$ M). The Hg speciation reported here is in agreement with others' findings that the concentration of Hg^{2+} was many orders of magnitudes less than Hg complexed with soluble organic matter (Yin *et al.*, 1996; Skyllberg *et al.*, 2000).

Metal Adsorption Isotherms

The adsorption of Cd, Hg and Pb in two soils from the Sudbury site was chosen for illustration (Figure 1). These two soils differed in properties such as pH, CEC, Org. C and oxides. Figure 1 shows that the adsorption of the three metals increased with increasing metal addition to the soils. However, the amount of bound metals was quite different between the two types of soils. Generally, it was found that in the soil with higher content of Org. C, the retention of metals was higher (Figure 1). Further, to identify which soil properties were responsible for the variation in metal sorption, multiple linear regression analysis for all 31 soils was conducted using sorbed Cd, Hg and Pb concentrations and soil properties. Significant ($p < 0.01$) positive correlation was found between the metal sorption and log Org. C, especially when the added metal concentrations were low (e.g., 1 mg L^{-1} Cd, Pb and 1 $\mu g\ L^{-1}$ Hg). The R^2 was 0.58 for Cd, 0.47 for Hg and 0.55 for Pb.

The regression analysis demonstrated the importance of organic matter for Cd, Hg and Pb adsorption in the soils of this study. Since many of these soils were taken from podzolic profiles, where a majority of adsorption sites were originated from organic matter, it is not surprising to observe a significant relationship between this soil component and metal retention. Furthermore, it has been well documented that Cd, Hg and Pb, which are classified as moderately soft metals according to "the hard and soft acid base (HSAB) theory" (Harter and Naidu, 1995), have a strong affinity for soil organic matter (Bolton and Evans, 1996; Yin *et al.*, 1996; Phillips, 1999; Skyllberg *et al.*, 2000).

The shape of the metal adsorption isotherms was similar for the soils in this study. In a soil taken from Rouyn-Noranda (RN 5; Figure 2a,b,c), the isotherms for Cd, Hg and Pb were similar to the L-type isotherm (McBride, 1994), which is characterized by a curve that has an initially large slope and then gradually reaches a plateau (Figure 2a,b,c). This type of isotherm may be related to the adsorption capacity of a soil. The *fractional* adsorption

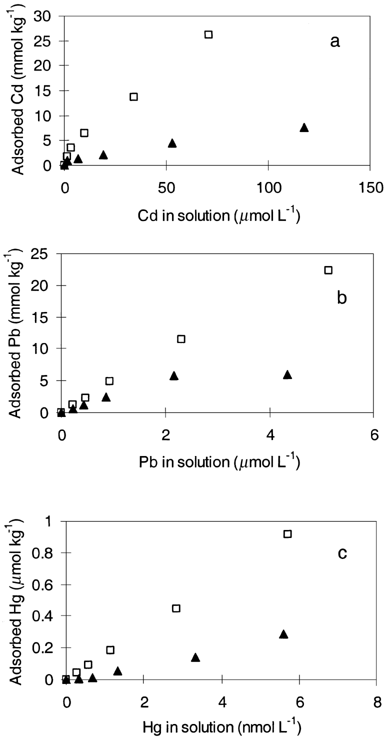

Figure 1. Adsorption of Cd (a), Hg (b) and Pb (c) in two soil horizons from Sudbury, Ontario with different content of organic matter (open squares: organic soil horizon; filled triangles: mineral soil horizon).

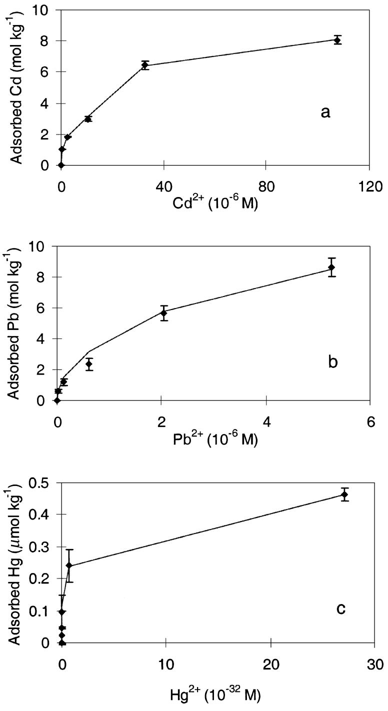

Figure 2. Adsorption isotherms of Cd (a), Hg (b) and Pb (c) for a soil from Rouyn-Noranda, Quebec (filled diamonds: measured metal adsorption; solid line: NICA-Donnan model prediction. Error bars are calculated from duplicate experiments and represent the standard error of adsorbed metals at each level of metal additions.)

increases until the adsorption capacity is exceeded. Further additions of metals may cause a decrease of the *fractional* adsorption.

Estimation of the NICA-Donnan Model Parameters

An adsorption isotherm equation such as the NICA-Donnan model (Eq. 4) contains several parameters describing the site characteristics (i.e., median binding constants, ion-specific non-ideality and site heterogeneity factors). Although in this study we were unable to conclude the exact nature of metal adsorption mechanism, fitting the NICA-Donnan model to the experimental data provides a useful means to estimate the metal affinity and distribution of each site (Kinniburgh, 1986).

The NICA-Donnan model parameters for the soils are listed in Table 3. The values of n_{H1}, which account for the heterogeneity of the 1st site toward the proton, are generally close to 1. This suggests that Type 1 sites in these soils show little non-ideal behavior for H^+. The average p value for the 1st site (p_1) is 0.92, which is more than twice of the p_2 (0.41). Thus, Type 1 sites seemed to be less heterogeneous than Type 2 sites.

The metal complexation parameters (log K_M and n_M) were obtained through fitting the NICA-Donnan equation (Eq. 4) to the metal adsorption data in the Excel program. The agreement between the model description and the measurements for adsorbed Cd and Pb is generally good as the R^2 values are above 0.85 (Table 3) except for one soil in Sudbury ($R^2 = 0.829$ for Pb). The binding of these two metals to the 31 soils was somewhat similar since the standard deviations of log K, n and p for the 1st type of sites were relatively small (Table 3). Cadmium had a smaller log K_1 than Pb, suggesting that Cd was less strongly complexed on the surface of soil particles. This agrees with the general observation that the order of metal selectivity for soils is Pb > Cd (Elliott *et al.*, 1986; Phillips, 1999). For Cd and Pb, log K_1 was slightly lower than log K_2. The heterogeneity of both types of sites was similar for Cd and Pb ($n_{Cd1} = 0.59$, $n_{Cd2} = 0.54$; $n_{Pb1} = 0.61$, $n_{Pb2} = 0.69$).

Good agreement is also found between measured and predicted Hg adsorption (Table 3). Compared with Cd and Pb, the adsorption of Hg on Type 1 surface groups was much more variable, as the standard deviation of log K_{Hg1} was 2.18. Interestingly, Type 2 sites had a much stronger affinity towards Hg than Type 1 sites, as log K_{Hg2} varied within the range of 18.0 ± 3.2 (Table 3). The values of n_{Hg} for the first group of sites were quite small (0.21 ± 0.01), indicating a strong non-ideal behavior for Hg. The non-ideality of Hg for the second group was much less pronounced because the average n_{Hg2} was 0.92 (Table 3). In addition to the phenolic-type groups, Hg adsorption on this site may possibly be associated with the S-containing ligands (−SH, thiol group) in organic matter. This type of Hg complex possesses formation constants many orders of magnitude higher than those of Cd and Pb. It has been suggested that soil organic matter binds Hg^{2+} predominantly via the thiol group (Wallschläger *et al.*, 1998). Therefore, at the low level of Hg^{2+} in this study, this surface functional group may remove Hg from the soil solution even though its complexing capacity is not high.

In comparing the NICA-Donnan model parameters obtained in this study with those for generic HA published by Milne *et al.* (2003) (Table 1), we found that the log K_1 values for Cd (1.8) and Pb (3.55) were several orders of magnitude higher than the constants for the generic HA (−0.20 for Cd, 1.25 for Pb). This implies that the surface of soil particles, which is a mixture of inorganic and organic components, may display an average binding for Cd and Pb stronger than the extracted and purified soil humic acid alone.

Milne *et al.* (2003) presented a set of estimated NICA-Donnan parameters for Hg (log $K_1 = 5.2$; log $K_2 = 14$). Those values are several orders of magnitude different from our

Table 3

Optimized parameters and goodness of fit for the NICA-Donnan model

Soil	Qmax1	Qmax2	log KH1	nH1	p1	log KCd1	nCd1	R^2Cd	log KPb1	nPb1	R^2Pb	log KHg1	log KHg2	nHg1	nHg2	R^2Hg
sud1	8.3	5.60	2.5	0.99	0.99	1.95	0.53	0.936	3.74	0.56	0.939	−2.5	19	0.21	0.92	0.894
sud2	9	4.08	2.4	0.90	0.89	1.3	0.47	0.923	2.28	0.41	0.967	−4.5	18	0.19	0.92	0.895
sud3	2.6	2.46	3.3	0.99	0.99	2.35	0.62	0.888	3.5	0.4	0.976	0.3	18	0.21	0.92	0.993
sud4	14	9.26	2.5	0.99	0.99	2.26	0.71	0.996	4.25	0.75	0.996	3.6	23	0.21	0.92	0.966
sud5	4	6.59	2.9	0.90	0.91	3.5	0.86	0.968	4.85	0.66	0.974	4.5	17	0.21	0.92	0.977
sud6	16	2.62	2	0.94	0.96	2.2	0.72	0.923	4.42	0.78	0.931	−0.2	15	0.21	0.92	0.951
sud7	7.1	6.60	3	0.95	0.95	3.1	0.55	0.913	4.5	0.5	0.862	0.8	15	0.21	0.92	0.978
sud8	2.5	2.76	4.2	0.86	0.86	3.2	0.5	0.991	5.7	0.31	0.882	3.7	18	0.21	0.92	0.934
sud9	18	5.98	2.2	0.81	0.74	1.1	0.57	0.884	3.5	0.7	0.856	−2.7	17	0.21	0.92	0.92
sud10	19	3.92	2.1	0.83	0.72	1.44	0.68	0.974	3.6	0.77	0.96	1.1	20	0.25	0.92	0.97
sud11	13	5.86	2.5	0.99	0.99	2.4	0.69	0.98	4.1	0.65	0.967	2.4	16	0.21	0.92	0.967
sud12	33	42.1	2.55	0.99	0.99	3.5	0.85	0.982	5	0.58	0.977	5	27	0.2	0.92	0.91
sud13	52	73.0	2	0.95	0.95	2.02	0.64	0.98	3.2	0.62	0.995	−2.1	16	0.21	0.92	0.956
sud14	2	24.4	2.5	0.80	0.88	3.5	0.79	0.942	6.2	0.97	0.829	1	17	0.18	0.92	0.868
sud15	16	20.0	2	0.85	0.82	1.4	0.62	0.979	3.85	0.62	0.984	2.6	19	0.22	0.92	0.99
rn1	18	2.49	2	0.95	0.74	2.1	0.85	0.864	1	0.79	0.957	0.1	22	0.24	0.92	0.986
rn2	4.5	6.54	3.9	0.80	0.88	1.63	0.36	0.937	3.8	0.48	0.973	0.9	15	0.2	0.92	0.95
rn3	9	14.2	3	0.99	0.99	1.6	0.49	0.997	3.1	0.55	0.984	1.4	14	0.22	0.92	0.877
rn4	14	3.72	2.4	0.90	0.94	1.1	0.5	0.994	2.6	0.56	0.966	−0.5	18	0.22	0.92	0.967
rn5	21	28.0	2.8	0.92	0.98	0.62	0.42	0.999	2.6	0.51	0.983	0.4	24	0.2	0.92	0.998

rn6	12	5.90	2.4	0.91	0.99	0.5	0.39	0.973	2.5	0.45	0.984	−1.5	15	0.2	0.92	0.897
rn7	30	108	2.9	0.99	0.91	1.75	0.52	0.996	3.4	0.6	0.984	1.8	16	0.22	0.92	0.978
rn8	17	3.88	2	0.99	0.91	1.6	0.66	0.918	3.7	0.64	0.992	−1	21	0.21	0.92	0.988
rn9	55	112	2.5	0.91	0.66	1.6	0.62	0.99	3.75	0.92	0.963	−3	16	0.22	0.92	0.992
rn10	14	2.19	2	0.99	0.99	1.6	0.61	0.964	1.7	0.41	0.986	0	20	0.22	0.92	0.924
val1	26	11.8	2.5	0.71	0.99	0.7	0.44	0.986	2.8	0.59	0.974	−0.1	23	0.21	0.92	0.962
val2	32	6.77	2	0.61	0.98	−1.1	0.36	0.962	1.77	0.49	0.986	−0.7	16	0.23	0.92	0.829
val3	19	9.20	2.4	0.99	0.99	1.6	0.55	0.975	3.42	0.63	0.985	1.4	16	0.22	0.92	0.874
val4	34	14.6	2.2	0.80	0.88	1	0.49	0.977	2.95	0.53	0.985	1.2	15	0.23	0.92	0.881
val5	17	3.72	2	0.99	0.99	2.3	0.66	0.99	3.82	0.65	0.956	0.5	16	0.21	0.92	0.901
val6	16	2.21	2	0.95	0.95	1.87	0.64	0.876	4.4	0.69	0.89	−0.4	15	0.23	0.92	0.923
Min			2	0.3	0.66	−1.1	0.36		1	0.31		−4.5	14	0.18	0.92	
Max			4.2	0.99	0.99	3.5	0.86		6.2	0.97		5	27	0.25	0.92	
Average			2.50	0.91	0.92	1.80	0.59		3.55	0.61		0.44	18	0.21	0.92	
Std			0.55	0.09	0.09	0.98	0.14		1.12	0.15		2.18	3.18	0.01	0.00	

sud: Sudbury, rn: Rouyn-Noranda, val: Valleyfield.

results. We also compared our derived values with those reported from other types of models in the literature. Skyllberg *et al.* (2000) studied binding of Hg^{2+} to reduced sulfur groups in soil organic matter and their log K_{Hg} values were in the range of 31.6–32.2. Yin *et al.* (1997) modeled the adsorption isotherms of inorganic Hg in a group of soils and found that the surface complexation constants for Hg varied from 5.3 to 6.1. These results were again quite different from ours; however, they used different modeling approaches, in which the binding surface was described either as a two-fold coordination with one carboxylic- and one thiol-group (Skyllberg *et al.*, 2000) or one uniform, negatively charged site (Yin *et al.*, 1997). In our study we cannot rule out the possibility that Hg adsorption was taking place on the thiol site, which was not specified in our NICA-Donnan model.

One of our goals is to be able to predict metal adsorption by soils with a range of properties. Since we conducted metal adsorption in a group of soils with different properties, it is interesting to find out whether the derived metal binding parameters are related to soil properties. We performed multiple linear regressions using SYSTAT 8 (Wilkinson, 1998) but were not successful in finding any statistically significant relationships between the parameters and soil properties. Therefore, we calculated the average of each derived parameter and used them in the NICA-Donnan model to predict the metal adsorption across the soils in this study. Figure 3 showed that the average parameters could explain 58.2%, 45.3% and 51.9% of the variability of measured adsorbed Cd, Hg and Pb, respectively. These findings are encouraging given the fact that the variations of some parameters (e.g., log K_{Hg1}) are high. Therefore, although no parameters were statistically related to soil

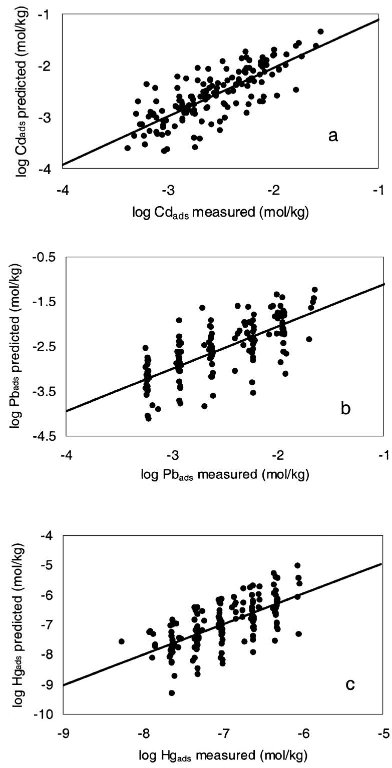

Figure 3. Comparison of the predicted with the measured adsorbed Cd (a), Hg (b) and Pb (c) in all soils of this study.

characteristics in this study, their average values seemed appropriate to simulate the metal sorption in a wide range of soil properties.

Soils have multiple complexation sites generated from organic and mineral surface components. Clay minerals and metal oxides may interact with organic matter and modify the metal sorption behavior of the surface particles (Naidu *et al.*, 1997). This makes the surfaces of soil particles very heterogeneous and difficult to model. However, the contribution of the inorganic materials is difficult to separate quantitatively in batch adsorption experiments. On the other hand, some major cations in the acidic, organically enriched soils such as Al and Fe are also strongly bound to the soil organic matter and may reduce the number of sites available for metal complexation. The surface heterogeneity and competition of Al and Fe may possibly explain the lack of strong relationships between soil properties and model parameters. Nevertheless, the average of derived parameters reasonably predicted the binding of Cd, Hg and Pb in the soils with a range of soil properties. This suggests that in the soils of this study, organic substances may be the major reactive component for metal binding. The NICA-Donnan model is a useful tool to evaluate the affinities of the surface of soil particles to trace metals.

Conclusions

The mobility and bioavailability of toxic metals may be related to their sorption to the surface components of soils. In this paper, the binding of Cd, Hg and Pb in a group of soils with different characteristics was studied using the batch adsorption method. The experimental results showed that metal adsorption was strongly affected by the amount of soil organic matter. It is reasonable to assume that the surfaces of soil particles have chemical behavior similar to organic matter. We therefore applied the NICA-Donnan model to fit the metal complexation data and derived the model parameters to describe the metal adsorption. The metal binding constants (K) and the non-ideality of metal ions (n) and sorption phase (p) differed among the metals. The soils had higher affinities for Pb and Hg than Cd. From the data fitting we found that Pb had highest affinity for Type 1 sites while Hg appeared to be most strongly bound to the Type 2 groups. Although no soil properties could predict the derived parameters, their average values made reasonable predictions of the adsorption of Cd, Hg and Pb in the soils. This indicates that the optimized NICA-Donnan model parameters may be useful to predict the metal binding provided that organic matter is the highly reactive component in soils.

References

Adriano, D.C. 1986. *Trace Elements in the Terrestrial Environment*. Springer-Verlag, New York, NY.

Benedetti, M.F., Milne, C.J., Kinniburgh, D.G., Van Riemsdijk, W.H., and Koopal, L.K. 1995. Metal ion binding to humic substances: Application of the non-ideal competitive adsorption model. *Environ. Sci. Technol.* **29**, 446–457.

Benedetti, M.F., Van Riemsdijk, W.H., Koopal, L.K., Kinniburgh, D.G., Gooddy, D.C., and Milne, C.J. 1996a. Metal ion binding by natural organic matter: From the model to the field. *Geochim. Cosmochim. Acta* **60**, 2503–2513.

Benedetti, M.F., Van Riemsdijk, W.H., and Koopal, L.K. 1996b. Humic substances considered as a heterogeneous Donnan gel phase. *Environ. Sci. Technol.* **30**, 1805–1813.

Bolton, K.A. and Evans, L.J. 1996. Cadmium adsorption capacity of selected Ontario soils. *Can. J. Soil Sci.* **76**, 183–189.

Derome, J. and Lindroos, A. 1998. Effects of heavy metal contamination on macronutrient availability and acidification parameters in forest soil in the vicinity of the Harjavalta Cu-Ni smelter, SW Finland. *Environ. Pollut.* **99**, 225–232.

Duquette, M. and Hendershot, W.H. 1990. Copper and zinc sorption on some B horizons of Quebec soils. *Commun. in Soil Sci. Plant Anal.* **21**, 377–394.

Elliott, H.A., Liberati, M.R., and Huang, C.P. 1986. Competitive adsorption of heavy metals by soils. *J. Environ. Qual.* **15**, 214–219.

Evans, L.J. 1989. Chemistry of metal retention by soils. *Environ. Sci. Tech.* **23**, 1046–1056.

Freedman, B. and Hutchinson, T.C. 1979. Pollutant inputs from the atmosphere and accumulations in soils and vegetation near a nickel-copper smelter at Sudbury Ontario, Canada. *Can. J. Botany.* **58**, 108–132.

Ge, Y. and Hendershot, W. 2004. Evaluation of soil surface charge using back-titration technique. *Soil Sci. Soc. Am. J.* **68**, 82–88.

Gustafsson, J.P. 1999. WinHumicV For Win95/98/NT. http://amov.ce.kth.se/people/gustafjp/winhumicv.htm.

Harter, R.D. and Naidu, R. 1995. Role of metal-organic complexation in metal sorption by soils. *Adv. Agron.* **55**, 219–263.

Heilman, M.D., Carter, D.L., and Gonzales, C.L. 1965. The ethylene glycol monoetheyl ether technique for determining soil-surface area. *Soil Sci.* **100**, 409–413.

Hendershot, W.H., Lalande, H., and Duquette, M. 1993a. Soil reaction and exchangeable acidity. In: *Soil Sampling and Methods of Analysis for Canadian Society of Soil Science*, pp. 141–145. (Carter, M. R., ed.) Lewis Publishers, Boca Raton, FL.

Hendershot, W.H., Lalande, H. and Duquette, M. 1993b. Ion exchange and exchangeable cations. In: *Soil Sampling and Methods of Analysis for Canadian Society of Soil Science*, pp. 167–176. (Carter, M. R., ed.) Lewis Publishers, Boca Raton, FL.

Huang, P.M., Senesi, N., and Buffle, J. 1998. Structure and surface reactions of soil particles. John Wiley & Sons, New York, NY.

Hutchinson, T.C. and Whitby, L.M. 1977. The effects of acid rainfall and heavy metal particulates on a boreal forest ecosystem near the Sudbury smelting region of Canada. *Water, Air Soil Pollut.* **7**, 421–438.

Kinniburgh, D.G. 1986. General purpose adsorption isotherms. *Environ. Sci. Technol.* **20**, 895–904.

Kinniburgh, D.G., Milne, C.J., Benedetti, M.F., Pinheiro, J.P., Filius, J., Koopal, L.K., and Van Riemsdijk, W.H. 1996. Metal ion binding by humic acid: Application of the NICA-Donnan model. *Environ. Sci. Technol.* **30**, 1687–1698.

Kinniburgh, D.G., Van Riemsdijk, W.H., Koopal, L.K., Borkovec, M., Benedetti, M.F., and Avena, M.J. 1999. Ion binding to natural organic matter: Competition, heterogeneity, stoichiometry and thermodynamic consistency. *Colloids Surf. A* **151**, 147–166.

Matínez, C.E. and McBride, M.B. 1999. Dissolved and labile concentrations of Cd, Cu, Pb and Zn in aged ferrihydrite-organic matter systems. *Environ. Sci. Technol.* **33**, 745–750.

McBride, M. B. 1994. *Environmental Chemistry of Soils*. Oxford University Press, NY.

McKeague, J.A., Cheshire, M.V., Andreux, F., and Berthelin, J. 1986. Organo-mineral complexes in relation to pedogenesis. In: *Interactions of Soil Minerals with Natural Organics and Microbes*, pp. 549–592. (Huang, P.M. and Schnitzer, M. eds.) Soil Science Society of America Special Publication Number 17. Madison, WI.

Milne, C.J., Kinniburgh, D.G., Van Riemsdijk, W.H., and Tipping, E. 2003. Generic NICA-Donnan model parameters for metal-ion binding by humic substances. *Environ. Sci. Technol.* **37**, 958–971.

Naidu, R., Kookana, R.S., Sumner, M.E., Harter, R.D., and Tiller, K.G. 1997. Cadmium sorption and transport in variable charge soils: A review. *J. Environ. Qual.* **26**, 602–617.

Phillips, I.R. 1999. Copper, lead, cadmium and zinc sorption by waterlogged and air-dry soil. *J. Soil Contam.* **8**, 343–364.

Ross, G.J. and Wang, C. 1993. Extractable Al, Fe, Mn and Si. In: *Soil Sampling and Methods of Analysis for Canadian Society of Soil Science*, pp. 239–246. (Carter, M.R., ed.) Lewis Publishers, Boca Raton, FL.

Schlüter, K. 1997. Sorption of inorganic mercury and monomethyl mercury in an iron-humus podzol soil of southern Norway studied by batch experiments. *Environ. Geol.* **30**, 266–279.

Schnitzer, M. 1986. Binding of humic substances by soil mineral colloids. In: *Interactions of Soil Minerals with Natural Organics and Microbes*, pp. 77–102. (Huang, P.M. and Schnitzer, M., eds.), Soil Science Society of America Special Publication Number 17. Madison, WI.

Sheldrick, B.H. and Wang, C. 1993. Particle size distribution. In: *Soil Sampling and Methods of Analysis for Canadian Society of Soil Science*, pp. 499–511. (Carter, M.R., ed.) Lewis Publishers, Boca Raton, FL.

Skyllberg, U., Xia, K., Bloom, P.R., Nater, E.A., and Bleam, W.F. 2000. Binding of mercury (II) to reduced sulfur in soil organic matter along upland-peat soil transects. *J. Environ. Qual.* **29**, 855–865.

Temminghoff, E.J.M., Van der Zee, S.E.A.T.M., and De Haan, F.A.M. 1997. Copper mobility in a copper-contaminated sandy soil as affected by pH and solid and dissolved organic matter. *Environ. Sci. Technol.* **31**, 1109–1115.

Tiessen, H. and Moir, J.O. 1993. Total and organic carbon. In: *Soil Sampling and Methods of Analysis for Canadian Society of Soil Science*, pp. 187–199. (Carter, M.R., ed.) Lewis Publishers, Boca Raton, FL.

Tipping, E. 1994. WHAM-A chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. *Comput. Geosci.* **20**, 973–1023.

USEPA (U.S. Environmental Protection Agency). 1998. Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils and oils. In: Draft update IVA of SW-846 on-line (http://www.epa.gov/epaoswer/hazwaste/test/up4a.htm); Washington, DC.

Vermeer, A.W.P., McCulloch, J.K., Van Riemsdijk, W.H., and Koopal, L.K. 1999. Metal ion adsorption to complexes of humic acid and metal oxides: Deviation from the additivity rule. *Environ. Sci. Technol.* **33**, 3892–3897.

Wallschläger, D., Desai, M.V.M., Spengler, M., and Wilken, R.D. 1998. Mercury speciation in floodplain soils and sediments along a contaminated river transect. *J. Environ. Qual.* **27**, 1034–1044.

Wilkinson, L. 1998. SYSTAT 8.0. SPSS Inc., Chicago, IL.

Yin, Y., Allen, H.E., Li, Y., Huang, C.P., and Sanders, P.F. 1996. Adsorption of mercury(II) by soil: Effect of pH, chloride, and organic matter. *J. Environ. Qual.* **25**, 837–844.

Yin, Y., Allen, H.E., Huang, C.P., and Sanders, P.F. 1997. Adsorption/desorption isotherms of Hg(II) by soil. *Soil Sci.* **162**, 35–45.