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Modeling of metal binding in tropical Fluvisols and Acrisols treated with biosolids and wastewater

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Abstract

There is growing concern about the accumulation of metals in tropical agricultural soils. Experimental results from batch studies were combined with results from the multi-surface models to test whether the multi-surface models (DSG and DNG model) could describe metal binding. The multi-surface models were included soil sorption surfaces, i.e. iron hydroxides (Diffuse Layer Model), organic matter (Stockholm Humic Model and NICA-Donnan Model), and phyllosilicate clay (Gaines-Thomas). The dissolution of Cd, Cr(III), Cu,

Mn, Pb and Zn was investigated. We found that for total dissolved Cd, Cu and Zn the two multi-surface models being tested provided very good model fits for all soils, as evidenced by low root-mean square errors between model predictions and observations. The results suggest that organic matter is an important sorbent for many metals in these soils. However, poor fits were obtained for Cr(III), Mn and Pb for all soils. The study also suggests that the pH is the main factor that controls the solubility of metals in tropical Fluvisols and Acrisols subjected to application of biosolids and wastewater, and that advanced multi-surface models can be used to simulate the binding and release of many trace metals.

Keywords: Adsorption; Cadmium; Copper; Heavy metal; Trace metal; Zinc

Introduction

Use of wastewater and biosolids in food production systems is a subject of increasing concern. Due to high contents of plant nutrients and organic matter, wastewater and biosolids are beneficial as fertilizer as well as for irrigation and soil amendment. However, as these wastes are products of human society, increased concentrations of potential toxic substances including trace metals are found in wastewater or biosolids, which may accumulate in the soil environment (e.g. Bergkvist et al., 2005). Chemical speciation governs the bioavailability, toxicity and transport of trace metals in natural systems (Stumm and Morgan, 1996).

Adsorption is a major process responsible for accumulation of trace metals. The most important interfaces involved in trace metal adsorption in soils are colloidal particles of organic matter and inorganic colloids such as clays and metal (hydr)oxides (Ross, 1996).

Humic substances bind trace metals strongly and therefore they determine the behaviour and the fate of these metals in natural systems especially in the surface horizon of soils (Gustafsson et al., 2003). Several advanced modeling approaches have been developed to describe the speciation of cations in the presence of humic organic matter. Currently, the

most advanced models for organic complexation are Model VI, NICA-Donnan and the Stockholm Humic Model (SHM) (Tipping, 1998; Kinniburgh et al., 1999; Gustafsson, 2001). By combining organic complexation models with models for oxide adsorption and ion exchange it is possible to construct so-called multi-surface models, which may give a comprehensive description of metal binding to soils. Weng et al. (2001) used a multi-surface model to describe metal binding of Dutch sandy soils; they found that organic matter is the most important sorbent that controls the activity of most metals (e.g. Cu, Cd, Ni, Zn), but for Pb, Fe oxide was more important. Similar results were obtained by Dijkstra et al. (2004) for contaminated soils.

The overall objective of this study was to examine whether multi-surface models could be used to describe trace metal binding in some tropical soils amended with biosolids and wastewater. Organic complexation models were combined with a surface complexation model for Fe and Al (hydr)oxides and with ion exchange to phyllosilicate clays. The resulting models were applied to predict dissolved Cd, Cr, Cu, Pb, Mn and Zn in soil solutions from batch experiments; the model results were compared with these measurements.

Materials and methods

Soil sampling site

Samples from eight agricultural soils were collected from peri-urban areas in 4 provinces of northern Vietnam including Hanoi, Nam Dinh, Ha Tay and Vinh Phuc (Table 1). The sampled areas are located in the Red River delta and lowland areas where the parent material is alluvial deposits. These are derived mainly from sedimentary (sandstone, shale, schist) and metamorphic (clay, slate, phyllite, mica, gneiss) material, together with some acid igneous sources (rhyolite, granite and liparite). The annual rainfall is between 1500 and 2000 mm, and more than 50% of the rainfall is concentrated during June to August. The mean

monthly temperature varies between 17 and 29°C, with the warmest period from June to August and the coldest during December and January.

Hanoi site: The soil sample (TTBB) was collected in a rice field in Bang B village, belonging to Hoang Liet commune, Thanh Tri district, a peri-urban area located downstream from Hanoi City. The farmers in this area started to use municipal wastewater from Hanoi City for irrigation in the 1960s. The soil is a Eutric Fluvisol according to WRB (FAO-ISRIC-ISSS, 1998).

Nam Dinh site: The soil sample (HL) was collected in the Hong Long cooperative, a peri-urban area of Nam Dinh City, Nam Dinh province, 100 km south-east of Hanoi. This area has been using municipal wastewater for irrigation since the 1980s and rice is the main cultivated crop. The soil is a Humi-Endogleyic Fluvisol (Eutric) (FAO-ISRIC-ISSS, 1998).

Vinh Phuc site: Soil samples (BoM11, BoM14 and BoM16) were collected from a field experiment with biosolids (chicken manure). Three soil samples were taken representing three different application rates (Table 1). Vegetables were grown at this site, predominantly cabbage (*Brassica oleacea* L.) and squash (*Benicasa hispida* L.). The site is located in the Vinh Phuc province, 25 km north of Hanoi. The soil is a Haplic Acrisol (FAO-ISRIC-ISSS, 1998).

Ha Tay site: Three soil samples (BoDp1, BoDp4 and BoDp6) were collected from another experimental site with biosolids representing three different application rates of composted manure (Table 1). The main crop was rice. The studied site is located in the Ha Tay province, 20 km north-west of Hanoi. The soil is a Cambic Fluvisol (FAO-ISRIC-ISSS, 1998).

Soil sampling and preparation

Soil sampling was conducted in June 2004 with a stainless steel corer. Five subsamples of topsoil (0-20 cm) were collected within a circle of 2 m diameter for the Ha Tay and Vinh Phuc sites and within the plot (approximately 250 m²) for the Nam Dinh and Hanoi sites. The subsamples were bulked into one sample in the field. After air drying at room temperature, the soil samples were sieved to remove particles > 2 mm, and then stored in plastic bags. The < 2 mm fraction was used for analyses.

Soil analysis

Soil texture was determined using standard methods (wet sieving and pipette method), following dissolution of carbonate by 1 M NaOAc (pH 5) and removal of organic matter by H₂O₂ (Gee and Bauder, 1986). After treatment by 4 M HCl (1:1 soil:solution ratio) for the dissolution of carbonates, finely ground samples were analyzed for total organic carbon (TOC) (Leco CHN[®]CHN 932 analyzer). The soil pH was measured in deionized H₂O (1:5). Soil samples were extracted with 1 M NH₄NO₃ (1:2.5) for 2 h to quantify initial concentrations of sorbed Ca, Mg, K and Na (AAS, Perkin Elmer 300). Amorphous Fe oxide was extracted with 2.5% ascorbate (1:60) for 4 h (Kostka and Luther, 1994). Crystalline and non-crystalline forms of Fe were extracted by 1.7% sodium dithionite (1:60) for 16 h (van Reeuwijk, 1993). Amorphous Al-(hydr)oxides were extracted by 0.2 M ammonium oxalate (1:100) for 4 h (van Reeuwijk, 1993). The analyses of Al and Fe were carried out by plasma emission spectroscopy (ICP-OES, Jobin-Yvon JY24) or by mass spectrometry (ICP-MS, Perkin Elmer ELAN 6100). Humic (HA) and fulvic acids (FA) were extracted twice with 0.1 M NaOH (2 h). The centrifuged supernatants were pooled into one sample, which was analyzed for TOC with a Shimadzu TOC-5000 analyzer. After acidification to pH 2 with HCl, the rest of the sample was centrifuged, and the supernatant was analyzed for TOC (Shimadzu TOC-5000 analyzer). The latter fraction was assumed to represent the soil content of FA, whereas HA was calculated by difference. Extraction in 0.025 M Na₂H₂EDTA (1:10) for 1.5 h

(Streck and Richter, 1997) was used for potentially bioavailable metals (Cd, Cr, Cu, Mn, Pb and Zn) fraction. After centrifugation and filtration, metal concentrations were determined by mass spectrometry (ICP-MS).

Mineralogical analysis of bulk soil and clay fraction

Three grams of the bulk samples (< 2 mm) were ground in an agate McCrone mill for 12 min, with 15 g of water and spray dried as per Hillier (1999). The resulting powders were quantified by full-pattern fitting as described in detail by Omotoso et al., (2006). Uncertainty at 95% confidence is given by $X^{0.35}$ (Hillier, 2003). X-ray powder diffraction (XRPD) patterns were recorded on a Siemens D5000 instrument from 2-75°2 θ using Cobalt K α radiation, in 0.02° steps counting for 2 s per step. Clay fractions of < 2 μ m were obtained by timed sedimentation, prepared as oriented mounts using the filter peel transfer technique and scanned from 2-45°2 θ counting for 1 second per 0.02° step, in the air-dried state, after glycolation, and after heating to 300°C for 1 h. Clay minerals identified were quantified using a mineral intensity factor approach based on calculated XRPD patterns as described by Hillier (2003).

Batch equilibrations

In batch experiments, 2 g soil was transferred to a 50 mL polypropylene centrifuge tube. Various amounts of acid (HNO₃) or base (NaOH) were added to the systems, so that each system was studied at eleven different pH values, each analyzed in duplicate. Additional NaNO₃ was added to produce an ionic strength of approximately 0.02 M in the suspensions. The final volume of solution in the centrifuge tubes was 30 mL. The centrifuge tubes were capped and shaken for 7 d in an end-over-end shaker at 20°C. After equilibration, the samples were centrifuged for 20 min at 3000 rpm. 2 mL of the supernatant was taken for pH measurement. The remaining supernatant was filtered through a 0.2 μ m filter (Pall Acrodisc®

PF syringe filter) and the filtrate was divided between two vessels, one was analyzed for TOC and for anions (Cl^- , SO_4^{2-} , PO_4^{3-}) by ion chromatography (Dionex ICS-90), whereas the other one was acidified (0.5% HNO_3) for measurement of dissolved metals using ICP-MS.

The multi-surface models, DSG and DNG model

We assumed that three reactive surfaces could account for the adsorption behaviour of the soil. These three surfaces were iron/aluminum (hydr)oxide, organic matter and phyllosilicate clay.

Binding to iron/aluminum (hydr)oxide: To take surface complexation to iron (hydr)oxide surfaces into account, we used the Diffuse Layer Model (DLM) (Dzombak and Morel, 1990) for specific binding of metal cations and (oxy)anions to hydrous ferric oxide (HFO). The recommended specific surface area of $600 \text{ m}^2 \text{ g}^{-1}$ for HFO was used to calculate site concentrations for the amorphous iron and aluminum (hydr)oxides (Dijkstra et al., 2004). The total amount of amorphous iron (hydr)oxides was calculated from Fe extracted with ascorbate and represented by HFO in the model. The amount of crystalline iron (hydr)oxides was calculated from the difference between Fe-dithionite and Fe-ascorbate. However, site concentrations of crystalline iron (hydr)oxides were calculated using a specific surface area of $100 \text{ m}^2 \text{ g}^{-1}$ (Dijkstra et al., 2004), therefore, to include crystalline iron (hydr)oxides in the model, we converted the suspension density of crystalline Fe (hydr)oxides to HFO equivalents by dividing it with 6. In addition, amorphous aluminum (hydr)oxides were considered, for which HFO was taken as a surrogate sorbent in the model (Dijkstra et al., 2004). This contribution was calculated from Al extracted with ammonium oxalate.

Binding to soil organic matter (SOM): The SHM and the Non Ideal Competitive Adsorption Donnan model (NICA-Donnan) were used. Both are available in Visual MINTEQ (Gustafsson, 2007). The SHM is a discrete-site / electrostatic model in which the HA or FA is

assumed to have eight proton-binding sites with different acid-base characteristics (for details see Gustafsson, 2001; Gustafsson et al., 2007). The principles of the NICA-Donnan model have been discussed in detail elsewhere (Kinniburgh et al., 1999; Milne et al., 2003). For parameters and parameter values of the SHM and NICA-Donnan models see the Supplementary material; the metal-binding parameters were those used by Linde et al. (2007) for the SHM and by Milne et al. (2003) for the NICA-Donnan model.

Binding to phyllosilicate clay minerals: The Gaines-Thomas equation was used to simulate ion exchange to phyllosilicate clays. For all cations, the selectivity coefficient was set to unity. To estimate the cation exchange capacity of the latter (CEC_{clay}), soil samples from the C horizon of the Acrisols (60-70 cm depth, where the TOC was low) were analyzed for the total cation exchange capacity (CEC_{soil}) and TOC (%). The CEC_{clay} for these C horizons were calculated from the equation below given by van Reeuwijk (1993), and the resulting CEC_{clay} was assumed to be valid also for the A horizon since XRD analyses had shown that the composition of clay minerals was similar in the A and C horizons.

$$CEC_{clay} = \frac{100}{\%clay} (CEC_{soil} - 3.5 \times TOC)$$

For the Fluvisols, CEC_{clay} was taken from literature data as $0.1 \text{ mol}_c \text{ kg}^{-1}$ (Nguyen et al., 2001).

The difference between the DSG and DNG models was that the former used the SHM to describe metal binding onto SOM, whereas the DNG used the NICA-Donnan model. Both models used the DLM for oxide adsorption and the Gaines-Thomas equation for ion exchange. To apply the models, we used the chemical equilibrium program Visual MINTEQ (Gustafsson, 2007), which also contains relevant solution complexation constants.

Model application

Important input parameters to the models include the geochemically active concentrations of metals and competing cations. In this study the geochemically active concentrations were estimated mainly from extractions: The NH_4NO_3 extraction results were used for base cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}), metals (Cd^{2+} , Cr^{3+} , Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+}) were estimated from EDTA extraction. It was assumed that Cr(III) and Mn(II) were the dominating redox forms of Cr and Mn. To account for the effect of Cl^- , SO_4^{2-} and PO_4^{3-} , measured concentrations were used as input in the model. The adsorption of SO_4^{2-} and PO_4^{3-} to HFO was considered using the parameters of Dzombak and Morel (1990). Added NO_3^- ions were assumed to behave conservatively. In addition, precipitation of Al hydroxide (non-crystalline soil $\text{Al}(\text{OH})_3$) and ferrihydrite was permitted with $\log^*K_s$ of 8.6 and 3.0, respectively, at the experimental temperature (20°C).

Measured dissolved organic carbon (DOC) concentrations were used as input in the model, and it was assumed that 87% of DOM is active (Linde et al., 2007) and 50% of it is FA (Weng et al., 2002) for both multi-surface models.

Model-fit evaluation

Measured and simulated metal concentrations were compared through calculation of root-mean square errors (RMSEs) for the logarithms of the total dissolved concentration (Gustafsson and van Schaik, 2003). Because the metal determinations at low equilibrium concentrations were uncertain due to analytical limitations, data points with observed concentrations of $< 3.6 \times 10^{-10}$ M Cd, $< 3.9 \times 10^{-9}$ M Cr, $< 6.3 \times 10^{-9}$ M Cu, $< 3.6 \times 10^{-8}$ M Mn, $< 1.9 \times 10^{-9}$ M Pb and $< 3.1 \times 10^{-8}$ M Zn were not included in the calculation of RMSEs.

3. Results and discussion

Soil properties

Some chemical and physical properties of the studied soils are shown in Table 1. In the Vinh Phuc soils (Haplic Acrisols), the organic carbon and clay contents were lower than in the other soils. The soil pH was slightly acid (between 6.0 and 6.6) except for the soil from the plot in Vinh Phuc that had received the highest biosolid treatment (BoM16) in which pH was 7.6. The clay fractions were dominated by expandable clays followed by illite (Table 1), the illite being higher in the Fluvisols (30-40%) and expandable clays relatively more abundant (> 70%) in the Acrisol. The expandable clays were all highly illitic mixed-layer illite-smectite and/or illite-vermiculite types, such as may be produced by the weathering of mica. Muscovite mica was an important component of the bulk samples which further suggests that the expandable clays may be weathering products of mica. For bulk mineralogy, ammonium oxalate Al and Fe, ascorbate-extractable Fe, dithionite-extractable Al and Fe, and the EDTA-extractable metal concentrations, see the Supplementary material.

Dissolved metals

Figures 1-2 show the pH dependence of dissolved Cu, Zn, Cd, Pb, Mn and Cr(III) of all experimental soils. The concentration of dissolved metals was low at high pH values. The dissolved concentration increased with decreasing pH, particularly at pH lower than 5. Most total dissolved metal concentrations were lowest in the pH range of 5-7. When pH is higher than 7, metal solubility in soil solution (e.g. Cu and Zn) tends to be increased because of increased dissolution of metal-complexing organic ligands (Gustafsson et al., 2003).

Modeling metal solubility in soils

Optimized value of humic and fulvic acid

Before simulation of dissolved metal concentrations, it is important to consider the proportion of the total organic matter that can be considered as 'active' HA and FA

(Gustafsson and van Schaik, 2003; MacDonald and Hendershot, 2006). The ratio of active HA to FA was assumed to equal that determined by NaOH extraction. In this work we adjusted the sum of ‘active’ HA and FA using the procedure of Weng et al. (2001): ‘active’ HA and FA was changed until organically bound Ca^{2+} , Mg^{2+} , Na^{+} , and K^{+} as calculated by the model equalled the CEC_{OM} , which was calculated as the difference between the effective CEC determined by NH_4NO_3 extraction and the estimated value of CEC_{clay} . For each soil, this calculation was made for the data points where no acid or base was added.

The optimized value of $f_{\text{HS-tot}}$ (the mass fraction of active humic matter ($\text{HS}=\text{HA}+\text{FA}$) compared to the total organic matter content) ranged from 0.28 to 0.50 for the DSG model, and from 0.27 to 0.48 for the DNG model (Table 2). The optimized value of HS was of the same magnitude as the content determined from base extraction. This indicated that the base extraction may provide a reasonable estimate of the ‘active’ HS in these Vietnamese soils.

Simulation of dissolved metal concentrations

The fits with the DSG and DNG models are shown in Fig. 3. These fits are predictions based on the optimized HS values for individual soils.

The model simulations for Zn in most cases agreed rather well with the observations. The overall RMSE value was 0.44 for DSG model and 0.53 for DNG model (Table 3). Also for Cu, the simulations in most cases corresponded rather well with measured data for all soils. The overall RMSE values were 0.30 and 0.34 for DSG and DNG model, respectively. The model results showed that the proportion of Cu bound to SOM accounted for the highest proportion of sorbed Cu (92-98%, Table 3 and Supplementary material). The predominance of SOM as a Cu sorbent across the pH range investigated is in agreement both with earlier observations and modeling results (McGrath et al., 1988; Weng et al., 2001; Dijkstra et al.,

2004). For Zn, SOM is a significant sorbent, but at high pH the model results suggest that adsorption of Zn on HFO should also be considered.

The model fits for Cd were very good for all soils. The overall RMSE for Cd was 0.44 for DNG model. The RMSE was slightly improved to 0.31 when simulated by DSG model. The results indicated that the Cd binding was determined mainly by complexation to organic matter. Models gave good fit for Mn when the pH lower than 6 (Fig. 2). However, dissolved Mn was not satisfactorily simulated when the pH higher than 6, neither with DSG nor with DNG model (the overall RMSE = 1.40 and 1.07, respectively). In most cases, the DSG as well as DNG model prediction overestimated dissolved Mn possibly due to Mn oxidation and formation of MnO₂ under these conditions.

Soil organic matter is important sorbent since models predicted that in most cases SOM is dominant affinity for metal binding e.g. Cu, Zn and Cd. In addition, the adsorption of Cd and Zn on phyllosilicate clays become more important at pH values below 3.5, while at pH above 7 the adsorption of those metals on HFO should be considered (Figure S1, supplemental data).

The model-predicted value of total dissolved Cr(III) in most cases agreed poorly with the observed total dissolved concentration of Cr (Fig. 3), both the DSG and DNG model underestimated the dissolved Cr(III) concentration. One possible reason may be uncertain complexation constants; for example the surface complexation constant for HFO suggested by Dzombak and Morel (1990) is only an estimate based on a linear free-energy relationship. Alternatively, the poor model fit can be explained by poor efficiency of the EDTA solution in removing Cr(III) from oxides and organic matter.

For Pb, the models often overestimated dissolved Pb. The RMSE value for the DSG fit was 0.69. The RMSE was slightly improved to 0.56 when simulated by DNG. The models

showed that Pb is relatively strongly bound to Fe oxides at pH > 4. One reason for the poor fit could be due to the fact that Pb is even more strongly bound to Fe and Mn oxides than the models suggest. The importance of Mn oxides has been stressed earlier (McKenzie, 1980). In our case, we did not include Mn oxide in the model and XRPD data indicate that a variety of different crystalline iron oxides are present in the samples so that they may require a more complex parameterization. Another possibility is that the models underestimate Pb binding to organic matter. The finding that Pb binding to soil is underestimated with generic model parameters for metal-humic complexation is in agreement with previous studies (Weng et al., 2002; MacDonald and Hendershot, 2006; Linde et al., 2007).

Conclusions

Although the organic carbon contents in top soil layer were small, the success of the model approach indicates that the organic matter is the most important soil component that controls the solubility of metals in the studied soils, certainly for some trace metals such as Cd, Cu and Zn. The multi-surface models provided good model fits for the total dissolved concentrations of Cd, Cu and Zn in all studied soils. For Pb, Cr(III) and Mn, however, modeling was not successful with either the DSG nor the DNG model. Nonetheless, the success of the models for Cd, Cu and Zn indicates that the multi models can be used for simulations of metal binding and release in tropical surface soils subjected to additions of biosolids and wastewater, while further refinements are required for Pb, Cr(III), and Mn.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

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Fig. 1. Total dissolved Cu, Zn and Cd (log[M]) against pH for all soils. Titration of soil samples with HNO_3 and NaOH . Ionic strength (I) = 0.02 M (as NaNO_3). The observations are shown as points. The model simulations are shown as lines. The lines in left panes are predicted by DSG model, whereas the lines in right panes are predicted by DNG model.

Fig. 2. Total dissolved Pb, Cr(III) and Mn(II) (log[M]) against pH for all soils. Titration of soil samples with HNO₃ and NaOH. Ionic strength (I) = 0.02 M (as NaNO₃). The observations are shown as points. The model simulations are shown as lines. The lines in left panes are predicted by DSG model, whereas the lines in right panes are predicted by DNG model.

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3 **Fig. 3.** Comparison of the simulated values of $\log[\text{Cu}]_{\text{tot}}$, $\log[\text{Zn}]_{\text{tot}}$, $\log[\text{Cd}]_{\text{tot}}$, $\log[\text{Pb}]_{\text{tot}}$,
4 $\log[\text{Cr}]_{\text{tot}}$, and $\log[\text{Mn}]_{\text{tot}}$ with measurements. The line indicates
5 the perfect 1:1 fit.

1 Table 1. Selected properties of the investigated soil samples

Soil	Treatment	pH _{H2O}	EC ^a	TOC	Clay ^c	Clay ^d	Clay composition ^e			
							(%) ^b			
							Chlorite	Kaolinite	Illite	Expandable ^h
Hanoi										
TTBB	Wastewater	6.6	113	1.6	23	24	6	5	32	57
Nam Dinh										
HL	Wastewater	6.1	182	2.7	45	46	6	7	40	47
Vinh Phuc Biosolid ^f										
BoMl1	0 t ha ⁻¹	6.1	43	0.9	12	6 ^d	5	11	11	73
BoMl4	30 t ha ⁻¹	6.2	35	1.1	12					
BoMl6	90 t ha ⁻¹	7.6	101	1.3	13					
Ha Tay Biosolid ^g										
BoDp1	0 t ha ⁻¹	6.0	71	2.2	35	36	5	9	30	56
BoDp4	21 t ha ⁻¹	6.1	73	2.5	35					
BoDp6	63 t ha ⁻¹	6.1	80	2.8	35					

2 ^aElectrical conductivity (EC) determined with 1:5 soil:deionized water ratio, $\mu\text{S cm}^{-1}$.

3 ^bTotal organic carbon (TOC).

4 ^c% of the particle size fraction $< 2\mu\text{m}$ in soil sieved through 2 mm.

5 ^d% phyllosilicate clay minerals of the bulk soil mineralogy ($< 2\text{mm}$). In BoMl1 there was a lot
6 of quartz in the $< 2\mu\text{m}$ fraction.

7 ^e% of clay mineral in the $< 2\mu\text{m}$ clay size fraction.

8 ^fChicken manure, fresh weight.

9 ^gMuck compost – pig manure mixed with crop residues, fresh weight.

10 ^hExpandable clay is a mixture of highly illitic mixed-layer illite-smectite/illite-vermiculite

1 Table 2. Optimized values for model fitting parameters including $f_{\text{HS-tot}}$, FA, HA and pH

Soil	FA ^a	HA ^a	pH ^b	DSG		DNG	
	(g kg ⁻¹)	(g kg ⁻¹)		$f_{\text{HS-tot}}^{\text{c}}$	Factor ^d	$f_{\text{HS-tot}}^{\text{c}}$	Factor ^d
Hanoi							
TTBB	3.75	4.68	6.30	0.44	1.66	0.42	1.61
Nam Dinh							
HL	5.58	9.84	5.87	0.34	1.19	0.33	1.16
Vinh Phuc							
BoMl1	3.57	2.84	6.05	0.31	0.88	0.30	0.85
BoMl4	3.43	3.13	6.16	0.28	0.89	0.27	0.87
BoMl6	3.66	3.81	7.19	0.50	1.74	0.48	1.67
Ha Tay							
BoDp1	5.16	6.98	5.92	0.39	1.40	0.39	1.38
BoDp4	5.19	7.15	6.07	0.37	1.41	0.36	1.38
BoDp6	5.18	7.03	6.06	0.35	1.51	0.35	1.50

2 ^aConcentration fulvic acid (FA) and humic acid (HA) extracted by NaOH.

3 ^bMeasured pH in the batch experiment for samples with no acid or alkali added.

4 ^cThe mass fraction of active humic matter (optimized value) compared to the total organic
5 matter content.

6 ^dRatio between the optimized value for the sum of HS and the base-extractable HS
7 (=HA+FA) value.

8

1 Table 3. Goodness-of-fit for the DSG and the DNG models and proportion of metal sorption
2 on different adsorbents

		n ^a	DSG				DNG			
			RMSE ^b	SOM ^c	HFO ^c	Clay ^c	RMSE ^b	SOM ^c	HFO ^c	Clay ^c
Cu	69	0.36	86(45-99)	6(0-19)	8(0-55)	0.29	98(81-100)	1(0-5)	1(0-19)	
Zn	66	0.49	50(10-89)	16(0-70)	33(0-90)	0.55	74(18-98)	7(0-65)	20(0-82)	
Cd	31	0.38	67(15-96)	7(0-43)	26(0-85)	0.20	92(54-100)	<1(0-3)	8(0-46)	
Pb	40	0.75	46(5-93)	51(0-95)	3(0-26)	0.65	54(5-95)	42(0-95)	4(0-41)	
Mn	69	1.34	42(6-80)	11(0-92)	47(2-91)	1.04	70(27-96)	5(0-48)	25(1-73)	
Cr	67	1.28	49(5-99)	29(0-75)	22(0-95)	1.56	100	-	-	

3 ^aNumber of observations above the detection limit.

4 ^bRoot mean square error of simulated and observed logarithms of total dissolved
5 concentrations.

6 ^cFractional (%) metal adsorption on soil organic matter(SOM), iron (hydro)oxide.
7 (HFO) and clay as mean (min-max).

1 SUPPLEMENTARY DATA (4 tables, 1 figure)

2 Table S1. Parameter values for cation complexation to soil organic matter in the SHM and NICA-Donnan models

Cation	SHM ^a					NICA-Donnan ^b							
	Humic acid and fulvic acid					Humic acid				Fulvic acid (solid-phase and dissolved)			
	$\log K_{Mm}$	$\log K_{Mb}$	$\log K_{MbOH}$	$\log K_{MtOH}$	ΔLK_2	$\log \tilde{K}_1$	n_1	$\log \tilde{K}_2$	n_2	$\log \tilde{K}_1$	n_1	$\log \tilde{K}_2$	n_2
Al ³⁺	-	-4.0	-9.0	-	1.0	-1.05	0.40	8.89	0.30	-4.11	0.42	12.16	0.31
Ca ²⁺	-2.2	-	-	-	0.3	-1.37	0.78	-0.43	0.75	-2.13	0.85	-3.0	0.80
Cd ²⁺	-1.6	-9.5	-	-	1.3	-0.20	0.73	0.37	0.54	-0.97	0.68	0.50	0.50
Cr ³⁺	-	-3.75	-7.75	-	1.0	4.3	0.35	12	0.27	2.8	0.35	20	0.27
Cu ²⁺	-0.55	-6.0	-13.6	-	1.4	2.23	0.56	6.85	0.34	0.26	0.53	8.26	0.36
Fe ³⁺	-	-	-	-5.15	1.8	3.5	0.30	17.5	0.25	6.0	0.25	36	0.19
Mg ²⁺	-2.5	-	-		0.3	-0.6	0.77	0.6	0.59	-2.1	0.77	-2.4	0.59
Mn ²⁺	-2.4	-	-		0.3	-0.3	0.72	1.3	0.56	-1.55	0.72	-1.1	0.56
Pb ²⁺	0.15	-	-		1.3	1.25	0.60	4.84	0.69	-1.16	0.60	6.92	0.69
Zn ²⁺	-1.65	-9.8	-		1.0	0.11	0.67	2.39	0.27	-3.84	0.67	-0.73	0.61

3 ^aFrom Gustafsson et al. (2007) and from Linde et al. (2007). ^bFrom Milne et al. (2003).

4 Table S2. Results of bulk mineralogical analysis by full-pattern fitting (% by weight)

Soil type/ Sample, horizon	Quartz	Plagio- clase	K-feld- spar	Hema- tite	Goethite	Anatase	Gibbsite ^d	Musco- vite (2M ₁)	Di- 2:1 ^{a,c}	Kaoli- nite ^c	Chlorite ^c	Tri-2:1 ^{b,c}
Eutric Fluvisol												
TTBB, Ap	61.1	5.1	2.8	0.9	0.6	0.3	0.1	5.5	16.7	3.4	1.4	2.0
Eutric Fluvisol												
HL, Ap	32.4	3.5	2.5	1.4	2.1	0.4	0.9	10.7	30.4	9.4	3.1	3.4
Haplic Acrisol												
BoM11, Ap	90.9	0.3	0.8	0.2	0.2	0.2	0.0	1.5	4.8	0.9	0.2	0.0
BoM11, C	69.9	0.3	0.5	0.7	2.0	0.5	0.0	2.3	16.5	7.1	0.0	0.2
Cambic Fluvisol												
BoDp1	43.6	4.1	2.4	1.1	2.3	0.4	0.4	9.3	25.9	5.5	2.3	2.6

5 ^aD-2:1: dioctahedral 2:1 minerals

6 ^bTri-2:1: trioctahedral 2:1 minerals

7 ^cPhyllosilicate clay minerals (in Table 1)

8 ^dPresence of traces of gibbsite is uncertain, the main peak at 4.85 Å may be due to mica/vermiculite.

Table S3. NH_4NO_3 -extractable Ca, Mg, Na, K and EDTA-extractable trace metals
(Cu, Zn, Mn, Cd, Cr, Pb) in the studied soils (see Table 1)

Soil	NH_4NO_3 -extractable ^a				EDTA-extractable ^b					
	Ca	Mg	Na	K	Cu	Zn	Mn	Cd	Cr	Pb
TTBB	0.92	0.23	0.11	0.17	9.6	2.7	22.4	0.10	0.15	9.2
HL	1.56	0.21	0.18	0.10	13.5	1.7	42.3	0.13	0.07	15.2
BoMl1	0.56	0.04	0.03	0.02	3.7	9.2	12.3	0.03	0.09	3.3
BoMl4	0.57	0.06	0.01	0.01	4.1	10.5	12.5	0.02	0.13	3.8
BoMl6	1.00	0.17	0.05	0.04	6.2	37.5	44.5	0.05	0.44	4.7
BoDp1	1.38	0.20	0.02	0.12	16.1	3.9	149.2	0.19	0.05	21.2
BoDp4	1.41	0.23	0.02	0.10	17.1	4.5	152.9	0.19	0.05	21.6
BoDp6	1.49	0.23	0.02	0.08	19.6	6.7	180.3	0.24	0.05	23.8

^aExtractable with 1 M NH_4NO_3 (1:2.5 soil:solution ratio), g kg^{-1} .

^bExtractable with 0.025 M $\text{Na}_2\text{H}_2\text{EDTA}$ (1:10 soil:solution ratio), mg kg^{-1} .

16 Table S4. Oxalate, dithionite and ascorbate-extractable Al and Fe

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Soil	Al (g kg ⁻¹)		Fe (g kg ⁻¹)		
	Oxalate ^a	Dithionite ^b	Oxalate ^a	Dithionite ^b	Ascorbate ^c
TTBB	0.56	0.46	3.74	8.94	3.12
HL	1.02	0.88	5.35	16.92	4.16
BoMl1	0.23	0.11	1.44	2.25	0.96
BoMl4	0.27	0.13	1.38	1.68	0.92
BoMl6	0.24	0.07	1.26	1.78	0.95
BoDp1	0.89	1.25	6.74	18.94	4.84
BoDp4	0.87	1.30	6.08	20.50	4.88
BoDp6	0.93	1.46	6.67	21.85	5.56

18 ^aExtractable with 0.2 M ammonium oxalate (1:100 soil:solution ratio)

19 ^bExtractable with 1.7% sodium dithionite (1:60 soil:solution ratio)

20 ^cExtractable with 2.5% ascorbate (1:60 soil solution ratio)

21 **Fig. S1.** Adsorption percentages (percent of total sorbed) of Cu, Zn, Cd, Cr, Pb and Mn on soil organic matter (SOM), clay and hydrous ferric
 22 oxide (HFO). Panes a-f are the predictions with the DSG model, whereas panes g-l are the predictions with the DNG model.