Uncertainty Analysis of the Nonideal Competitive Adsorption-Donnan Model: Effects of Dissolved Organic Matter Variability on Predicted Metal Speciation in Soil Solution

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Ion binding models such as the nonideal competitive adsorption–Donnan model (NICA–Donnan) and model VI successfully describe laboratory data of proton and metal binding to purified humic substances (HS). In this study model performance was tested in more complex natural systems. The speciation predicted with the NICA–Donnan model and the associated uncertainty were compared with independent measurements in soil solution extracts, including the free metal ion activity and fulvic (FA) and humic acid (HA) fractions of dissolved organic matter (DOM). Potentially important sources of uncertainty are the DOM composition and the variation in binding properties of HS. HS fractions of DOM in soil solution extracts varied between 14 and 63% and consisted mainly of FA. Moreover, binding parameters optimized for individual FA samples show substantial variation. Monte Carlo simulations show that uncertainties in predicted metal speciation, for metals with a high affinity for FA (Cu, Pb), are largely due to the natural variation in binding properties (i.e., the *affinity*) of FA. Predictions for metals with a lower affinity (Cd) are more prone to uncertainties in the fraction FA in DOM and the maximum site density (i.e., the *capacity*) of the FA. Based on these findings, suggestions are provided to reduce uncertainties in model predictions.

Introduction

Speciation of metals is highly important for their bioavailability and mobility in soils and waters. Chemical speciation models are being used within ecotoxicological effect models such as the biotic ligand model (*1*) and in reactive transport models to calculate metal leaching from soils to ground and surface waters (*2*). In such models ion binding to organic matter is a key process, and model VI (*3*) and the nonideal competitive adsorption–Donnan (NICA–Donnan) model (*4*) are at present the most advanced models for ion binding to humic substances (HS).

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These models have been shown to successfully describe laboratory data of proton and metal binding to HS in binary and ternary systems with either purified humic (HA) or fulvic acid (FA), data which have also been used to derive generic model parameters (*3, 5, 6*). However, when applying these models to natural soil and surface water, predictions are likely to become more uncertain, because natural systems are more complex: there will be an increasing number of competing cations and a more heterogeneous composition of dissolved organic matter (DOM) being a mixture of FA, HA, and other organic substances.

Such uncertainties can be categorized according to their origin: (i) conceptual uncertainty, (ii) uncertainty in model parameters, and (iii) uncertainty in input variables. Conceptual uncertainty has, e.g., become apparent from differences between predictions of model VI and NICA–Donnan for natural systems (*7, 8*) despite the fact that both models are about equally successful in fitting the common data from which they are parametrized (*9*). A possible important source of parameter uncertainty is the use of generic parameters (*3, 5, 6*) while ignoring the variability in ion binding that may exist for HS of different origin (*5*). Uncertainties in input variables may be due to the incomplete characterization of the solution being modeled. In particular, the characterization of DOM is nearly always missing. Consequently estimates of the percentage of FA and HA in DOM are required, which vary between 40 and 100% (*7, 8, 10–13*), resulting in an associated uncertainty in model predictions that is not quantified to date. Insight into the uncertainties of model predictions and their causes provides a reference to interpret deviations between models and measurements and may help to find directions for model improvement, including the parametrization and required input.

Our aim in this paper is to (i) validate NICA–Donnan predictions of metal speciation in soil solutions, taking into account the uncertainties in input variables and model parameters; (ii) quantify the variation in binding properties of HS; (iii) quantify the variation in the composition of DOM; and (iv) quantify the uncertainty in model predictions due to the variations in binding properties and DOM composition both separately and together.

To validate the NICA–Donnan model, speciation measurements are presented, obtained with the Donnan membrane technique (DMT) (*14*) in solutions extracted from eight soils with a broad range in metal contents and soil properties. To be able to distinguish between model parameter uncertainty and uncertainty in input variables, we also measured the FA and HA concentrations with the rapid batch technique of van Zomeren and Comans (*15*). The variability of the model parameters for proton and metal binding to FA, which appeared to be the dominant metal binding fraction of DOM in the studied soil extracts, was assessed by optimizing the model parameters for individual samples of FA followed by determination of their variation among FA samples. Uncertainties were quantified by Monte Carlo (MC) simulations for each sample. Additionally, we evaluated the dependence of the uncertainty on pH and FA and metal concentrations using model scenarios with a broad range in pH and FA and metal concentrations for systems with a (i) fixed total dissolved metal concentration and (ii) fixed free metal ion (FMI) activity in solution. The first system is representative for cases where FMI activities are to be calculated, e.g., to assess metal bioavailability. The second system represents cases where the total concentration in solution is to be calculated from the FMI activity for example in (reactive transport) models assuming equilibrium of the FMI with the

solid phase or when calculating critical loads for metals which are related to a critical FMI activity in solution (*16*).

Materials and Methods

Measurement of Metal and DOM Speciation in Soil Extracts. Eight soils from contaminated sites were used in this study (Table 1). Samples were oven-dried at 40 °C and sieved (<2 mm) before further use. Metal contents (Aqua Regia and 0.43 M HNO_3-extractable metal) and soil properties were determined using standard analytical procedures. Soil solution extracts were obtained by extraction of soil with 0.002 M $Ca(NO_3)_2$ and 0.001 M NaN_3 (to inhibit microbial activity) at a 1:10 (w/v) solid to liquid ratio (*17*). FMI activities in the supernatants of the batch extracts were determined with the DMT (*14, 17*). DOM composition in the donor solutions sampled at $t = 8$ days of the DMT experiment was determined by measurement of the HA, FA, and hydrophilic acid (Hy) concentrations using a rapid batch technique (*15*). For four soil samples concentrations of low molecular weight organic acids (LMWOA) (i.e., citric and oxalalic acid), Cl, NO_3, and ortho-P were measured in the donor solutions, using a Dionex ICS-2500 high-performance liquid chromatography system (*18*).

NICA−Donnan Model. The NICA−Donnan model (*4*) is a combination of the NICA, which describes competitive binding of protons and metal cations to FA and HA taking into account ion specific nonideality, and a Donnan equilibrium model that describes nonspecific electrostatic adsorption. The model accounts for binding site heterogeneity by distinguishing two different groups of binding sites each with their own continuous affinity distribution: type 1 and type 2 binding sites, the first with a relatively low and the second with a relatively high affinity to bind cations. The amount bound Q_i (mol·kg^{-1}) of a component i at solution concentration c_i (mol·L^{-1}) is given by

$$Q_i = \frac{n_{i1}}{n_{H1}} Q_{max1,H} \frac{(\tilde{K}_{i1}c_i)^{n_{1i}}}{\sum_i (\tilde{K}_{i1}c_i)^{n_{i1}}} \frac{\left[\sum_i (\tilde{K}_{i1}c_i)^{n_{i1}}\right]^{p_1}}{1 + \left[\sum_i (\tilde{K}_{i1}c_i)^{n_{i1}}\right]^{p_1}} + \frac{n_{i2}}{n_{H2}} Q_{max2,H} \frac{(\tilde{K}_{i2}c_i)^{n_{i2}}}{\sum_i (\tilde{K}_{i2}c_i)^{n_{i2}}} \frac{\left[\sum_i (\tilde{K}_{i2}c_i)^{n_{i2}}\right]^{p_2}}{1 + \left[\sum_i (\tilde{K}_{i2}c_i)^{n_{i2}}\right]^{p_2}} \quad (1)$$

Four parameters are characteristic for the FA or HA: $Q_{max1,H}$ and $Q_{max2,H}$ give the proton site density for the two considered groups of binding sites; p_1 and p_2 are a measure for the widths of the affinity distributions and describe the intrinsic heterogeneity of the humic material. Four ion specific parameters for each considered component describe the median affinities ($\tilde{K}_{i1}$, $\tilde{K}_{i2}$) and nonidealities (n_1 and n_2) of the ion binding to both distributions. The charge of the humic particle is counteracted by the attraction of counterions and the exclusion of co-ions within the Donnan volume V_D (L·kg^{-1}), which is calculated according to

$$\log V_D = b(1 - \log I) - 1 \quad (2)$$

with b being an empirical constant and I the ionic strength (mol·L^{-1}).

Speciation Modeling. Metal speciation in solution was calculated using ORCHESTRA (*19*) including the NICA−Donnan model. For the uncertainty analysis, we used the sampled NICA parameters for H, Cd, Cu, and Pb. Generic parameters (*6*) were used for all other elements except for the binding of Fe^{3+} to FA for which we used the parameters from Hiemstra and van Riemsdijk (*20*). Inorganic speciation and binding to LMWOA was calculated on the basis of the MINTEQ database (*21*), the parametric uncertainties of which were not included in this study.

Measured values of either the total concentrations or ion activities of Cd, Cu, and Pb were used to calculate the speciation in the soil extracts together with measured pH, concentrations of major cations (Al, Ca, Fe, K, Mg, Mn, and Na), additional trace metals (Cr, Ni, and Zn), and FA and HA. When available, we used measured concentrations of anions (Cl, NO_3, and PO_4); otherwise the NO_3 concentration was set to that of the background electrolyte.

Uncertainty Analysis. Parameter sampling and statistical analysis of the Monte Carlo (MC) simulations were done using the software package UNCSAM (*22*). For each simulation, 1000 random parameter sets were sampled from the derived distributions in NICA parameters and FA fractions using the latin hypercube sampling method assuming a normal distribution. Correlations between parameter values were imposed in the sampling procedure to avoid unrealistic parameter value combinations that might lead to overestimations of uncertainty. From the output of the MC runs, the individual contribution of each parameter to the uncertainty in model outputs was then derived by the linear correlation coefficient (LCC) of the least-squares linear regression of model outputs as a function of the varied parameters.

Modeling Scenarios. The uncertainty in the predicted metal speciation at various levels of pH and concentrations of FA, Cd, Cu, and Pb was evaluated using MC simulations for model scenarios in the range of pH 3−8. Realistic levels (low, medium, and high) of total metal concentrations or FMI activities and DOM concentrations were chosen on the basis of measured data of 118 samples with a large range in soil properties and metal concentrations (*23*) (Table S-1, Supporting Information). For Al and Fe we used Al^{3+} and Fe^{3+} activities calculated with solubility products of $Al(OH)_3$ (p$K_{so,25}$ = 8.5) and $Fe(OH)_3$ (p$K_{so,25}$ = 2.5) representative for soil solutions (*24*). We evaluated model scenarios to obtain the uncertainty in predicted metal speciation due to (i) the uncertainty in NICA parameters by MC simulations with sampled NICA parameters for H, Cd, Cu, and Pb, (ii) the

TABLE 1. Soil Properties and Metal Contents

	SOM (%)	clay (%)	total soil metal content Aqua Regia (μmol·kg^{-1})			0.43 M HNO_3-extractable metal content (μmol·kg^{-1})		
			Cd	Cu	Pb	Cd	Cu	Pb
Zlatitza	4.8	13	16.4	22448	687	4.0	14806	653
Wildekamp	3.4	2	1.5	1435	114	0.56	1282	94.9
Hygum	7.1	10	4.6	12142	144	2.9	10344	95.6
Zhejiang	6.9	13	71.2	11627	7042	69.8	13215	8059
Noorderbos 1	12.9		15.7	1158	763	12.7	705	517
Noorderbos 1 A	12.5		7.30	943	637	5.9	625	533
Noorderbos 2	5.2		2.4	167	162	3.1	139	144
Noorderbos 2A	5.7		0.80	181	195	0.91	105	141

TABLE 2. Fitted NICA-Donnan Parameters

element	$Q_{max1,H}$ (equiv·kg^{-1})	$Q_{max2,H}$ (equiv·kg^{-1})	mean ± SD log K_1	log K_2	n_1	n_2	RMSE
H	5.66 ± 1.24	2.37 ± 1.67	2.65 ± 0.432	8.60 ± 0.781	—[a]	—	0.08
Cd	—	—	−1.12 ± 0.638	—	0.689 ± 0.0527	—	0.13
Cu	—	—	−0.139 ± 0.647	8.03 ± 2.41	0.525 ± .145	0.597 ± 0.387	0.07
Pb	—	—	−0.308 ± 0.679	6.46 ± 1.27	—	—	0.11

[a] — = parameter was not optimized.

TABLE 3. Composition of the Solution Extracts

sample	pH (mg·L^{-1})	DOC	%HA	%FA	%Hy	total metal[a] MI (log mol.L^{-1}) Cd	Cu	Pb
Zlatitza	4.67	9.4	1.7	24.4	73.8	**−7.05** −7.03	**−4.09** −4.15	nm[b]
Wildekamp	5.22	15.2	2.0	27.3	70.7	**−7.77** −8.51	**−6.10** −7.61	nm
Hygum	5.86	31.2	1.0	30.7	68.3	**−8.40** −8.64	**−5.50** −7.32	nm
Zhejang	7.23	9.1	3.8	27.7	68.4	**−7.21** −7.41	**−5.59** −8.74	**−6.77** −8.27
Noorderbos 1	5.23	36.1	0.9	41.8	54.1	**−7.45** −7.63	**−6.43** −8.05	**−7.93** −8.65
Noorderbos 1z	4.58	22.9	0.5	41.5	54.7	**−7.32** −7.50	**−6.63** −7.79	**−7.59** −7.74
Noorderbos 3	5.69	32.7	1.2	48.3	45.2	**−8.01** −8.28	**−6.97** −8.97	**−8.22** −9.11
Noorderbos 3z	4.71	17.5	1.3	35.7	59.2	**−7.99** −8.15	**−7.28** −8.65c	**−7.75** −7.80

[a] Total concentrations in bold; FMI in italics. [b] nm = not measured.

uncertainty in the fraction FA by MC simulations with sampled fractions of FA, and (iii) the combined uncertainty due to uncertainty in NICA binding parameters and FA fractions.

The average fraction FA and its variability has been derived from compiled studies (Table S-2, Supporting Information) in which the FA, HA, and Hy fractions were measured in soil extracts with water or 0.002 M Ca(NO$_3$)$_2$. DOM was modeled comprising 41% FA being equal to the average HS content of these extracts.

Variability in NICA Parameters of Fulvic Acids. The variation in the maximum proton site densities $Q_{max1,H}$ and $Q_{max2,H}$ and variation in log $\tilde{K}$ values for proton binding were derived from the individual fits for proton binding to FA (5). The variation in binding properties for metals was derived from the binding properties determined for individual FA samples from the data compiled by Milne et al. (6), using FIT, a nonlinear least-squares optimization code (25). Only for Cd, Cu, and Pb were we able to fit the NICA parameters for three or more FA samples. Because it was not always possible to optimize all parameters independently due to the incomplete definition of model parameters using the available data (6), we selected the parameters for which the model is most sensitive based on a sensitivity analysis taking into account all parameters, except p_1 and p_2, two parameters that cannot be determined independently from n_1 and n_2 for individual samples of FA. The most sensitive parameters for Cu and Pb are the affinity constants $\tilde{K}_1$ and $\tilde{K}_2$ and the distribution coefficients n_1 and n_2, whereas for Cd only $\tilde{K}_{Cd1}$ and n_1 are sensitive. The Donnan constant b was not a sensitive parameter for any of the metals. On the basis of these results, we have limited the parameters to be optimized to $\tilde{K}_{i1}$ and $\tilde{K}_{i2}$ and n_{i1} and n_{i2}. The intrinsic heterogeneity parameters p_1 and p_2 and the constant b to calculate the Donnan volume were kept at their generic values (6). The available data for Cd and Pb did not allow us to fit all four

parameters freely. Therefore, we reduced the number of parameters by fixing the least sensitive parameters to their generic values. For Cd, we fixed the parameters of the type 2 high-affinity sites $\tilde{K}_2$ and n_2 because the model is insensitive to variation in these parameters. For Pb, we fixed the parameters n_1 and n_2 similar to Milne et al. (6), who used the n values derived for HA. Fixing these parameters for Cu showed a limited decrease (≤20%) in the variation of model output.

Because no data sets were available for FA samples with both proton and metal binding data, we had to use the generic values of $Q_{max1,H}$ and $Q_{max2,H}$, $\tilde{K}_{H1}$ and $\tilde{K}_{H2}$ when optimizing the NICA parameters for metals. To be able to derive the correlation between the Qs and other parameters, we also optimized the parameters with preset values of $Q_{max1,H}$ and $Q_{max2,H}$ at their generic values plus or minus their standard deviation (SD).

Results and Discussion

Metal and DOM Speciation in Soil Solution Extracts. The soil extracts show considerable variation in their measured composition (Table 3). Total metal concentrations ranged from a factor 30 for Cd and Pb to a factor of 1000 for Cu between lowest and highest concentrations. There is also considerable variation in the fraction free metal, which varied between 18 and 95% of the total concentration for Cd, between 3 and 87% for Pb, and between 0.1 and 87% for Cu.

DOM mainly consisted of FA (average 38%) and Hy (average 60%), whereas the HA fractions in the extracts were very low (average 2%). This is in agreement with the compilation of DOM fractions in soil extracts, in which FA (average 34%) and Hy (average 61%) are the dominant fractions and the fraction HA (average 5%) is low. The fraction Hy contains LMWOA, sugars, and amino acids (26). Concentrations of citric and acetic acid, two of the prevailing LMWOA in soils (27), were negligible (≤0.11% of DOC).
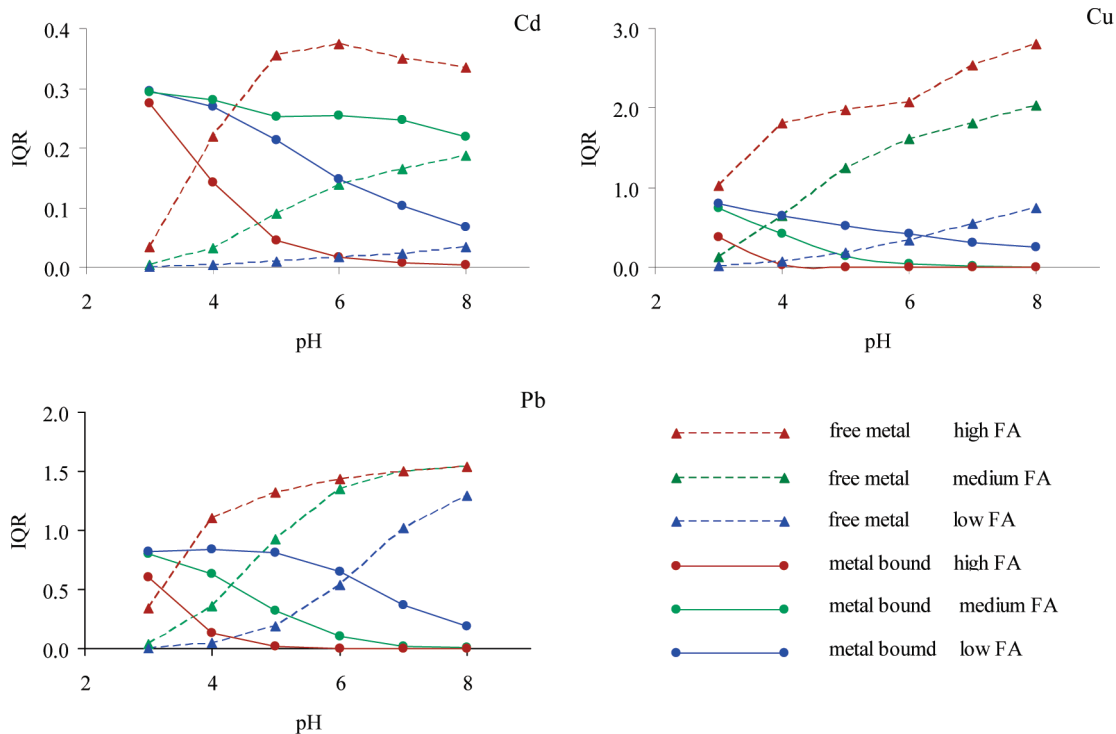
FIGURE 1. Interquantile ranges (IQR) of the model predictions from the Monte Carlo simulations for log concentrations of metal bound to FA (lines) and the free metal ion (dotted line) as a function of pH for various concentrations of FA (high = 200, medium = 20, and low = 2 mg·L^{-1}) for Cd, Cu, and Pb.

Variability in NICA Parameters of Fulvic Acids. Variation in NICA parameters for proton and metal binding to be used in the uncertainty analysis were derived from individual fits of the NICA−Donnan model to proton binding data (5) and the newly derived individual fits for metal binding data for various FA samples from the compilation by Milne et al. (6).

Parameters derived for each FA sample individually (Table S-4, Supporting Information) describe the data more precisely than the generic parameters according to their lower RMSE (Table 2) compared to those based on generic parameters (6). The distributions of the NICA parameters are close to a normal distribution and can, therefore, be described with their mean value and SD. The highest variation was found for the NICA parameters related to the high-affinity sites, i.e., $Q_{max2,H}$ for protons, log $\tilde{K}_2$ for Cu and Pb and n_2 for Cu. The obtained parameter variation appears to be within realistic ranges according to the ratios derived for n_{Me}/n_H, which can be interpreted as the inverse of the stoichiometry of the exchange between the metal cation and proton. The obtained values are almost within the theoretical range between a minimum of 0.5 (maximal 2 protons exchanged) and a maximum of 1 (minimal 1 proton exchanged) for divalent cations (9) (0.6 ≤ n_{Cu1}/n_{H1} ≤ 1.2; 0.9 ≤ n_{Cd1}/n_{H1} ≤ 1.2; 0.4 ≤ n_{Cu2}/n_{H2} ≤ 1.1). Therefore, we have used the obtained ratios as an additional constraint in the sampling of n.

Statistical analysis of the optimized parameters shows medium to strong negative correlation between several parameters, e.g., between $\tilde{K}_1$ and $Q_{max1,H}$ for Cd and Cu. Such correlations can be explained statistically since several parameter value combinations fit the data about equally well. Alternatively, the correlation between n_{Cu2} and $Q_{max2,H}$ can also be interpreted physically: an increase in the site density of the high affinity sites ($Q_{max2,H}$) increases the probability of multidentate binding, resulting in a decrease of n_{Cu2} which is related to the inverse of the stoichiometry (9). The correlations have been imposed on the sampling of parameters for the uncertainty analysis to avoid overestimating uncertainty.

Uncertainty in Modeled Speciation Resulting from Variation in NICA Parameters. The variation in predicted concentrations of metal bound to FA decreases with increasing pH for each of the three metals (Figure 1). Because of the skewed distribution of model outputs from the Monte Carlo simulations, with median values of FMI activities being closer to the p5 than to the p95, we used the interquantile range (IQR), the difference between the 75 and 25%-iles of the results, instead of the SD. The simulated variation appears to be within realistic ranges when comparing the average standard deviation ranging from 0.11 to 0.25 (used here only because of its comparability with RMSE) with the RMSE of the generic fits, ranging from 0.16 to 0.28 (6). The trend of decreasing uncertainty with increasing pH is consistent with the decreasing deviation between predicted and observed values with increasing pH for acid/base titration data of a solution with Cu and FA (28) using generic parameters (6). Uncertainty is high when concentrations of metals bound to FA are relatively small, (i) at low pH, (ii) at low concentrations FA (Figure 1), or (iii) when concentrations of metals are high (results not shown), i.e,. at high metal to FA ratios.

Variations in the predicted FMI activities are considerably higher than variations in concentrations of metal bound to FA. Opposite to the trend found for metals bound to FA, the uncertainty in FMI activities increases with increasing pH. At high pH, the largest fraction of the metals is bound to FA. Hence a small change in this concentration results in a large change in the FMI concentration to fulfill the mass balance constraint. This observation also explains the increasing uncertainty with increasing concentrations FA or decreasing total metal concentrations.

Uncertainty in Modeled Speciation Resulting from Uncertainty in DOM Composition. According to the compilation of DOM composition in batch extracts, the percentage HS varies between 14 and 63%, with an average value of 39% and a standard deviation of 13%. Fractions of HS thus vary considerably and the fractions of HS obtained from our measurements are significantly lower than those assumed

TABLE 4. Maximum Values Interquantile Range (IQR)[a]

metal	NICA[b]	FA[c]	NICA + FA[d]
Cd	0.19	0.23	0.29
Cu	2.04	0.56	2.06
Pb	1.54	0.33	1.58

[a] At medium levels of metal and FA concentration in the range of pH 3–8. [b] Scenario varying the NICA parameters. [c] Scenario varying the concentration FA in DOM. [d] Scenario varying the NICA parameters and the concentration of FA together.

in most other studies, which vary between 40 and 100% (7, 8, 10–13).

Because the HS fraction contains mainly FA (average 90%), we evaluated the variation in HS assuming that it consists totally of FA. Uncertainties due to variation in the fraction of FA show trends similar to those observed for the variation in NICA parameters; increasing uncertainties in predicted FMI activities with increasing pH, and FA and decreasing total metal concentrations. For Cd, the uncertainties due to parameter uncertainty and uncertainty in FA concentrations are about equal in magnitude (Table 4). However, uncertainties in Cu and Pb activities of FMI due to variation in the fraction FA are considerably lower than the uncertainty due to model parameter variability.

Because of the large Hy fraction, we evaluated the possible contribution of LMWOA to the binding of trace metals for LMWOA being 10% of DOC, which must be considered a maximum (27). In addition, a scenario was calculated in which the total hydrophilic fraction (50%) was assumed to have binding properties similar to LMWOA. On the basis of the measured concentrations LMWOA in A-horizons of soils (27), we considered LMWOA as 70% mono-, 20% di-, and 10% tricarboxylic acids represented by fumaric-, oxalic-, and citric acids, respectively, the first with a low and the two latter with a relatively high metal binding affinity. Including LMWOA in the speciation calculations for the scenario with medium concentrations of metals, and FA lowered the log activity of free Cu^{2+} with 0.2–0.5 (10% LMWOA) or 0.6–1 units (50% LMWOA) below pH 6 (Table S-6, Supporting Information). LMWOA did not affect metal speciation of Cd and Pb and had no effect on Cu above pH 6.

Combined Uncertainty and Contributions of the Different Sources. The total uncertainty in model output due to the sources of uncertainty investigated in this study, i.e., the uncertainty in NICA parameters and the uncertainty in FA concentrations, is clearly not additive (Table 4). IQRs for the total uncertainty are only slightly higher than those for the source with the highest uncertainty contribution alone. For Cu and Pb, the contribution of parameter uncertainty is most important, whereas for Cd, uncertainty in the FA fraction contributes most to uncertainty.

Ranking the parameters according to the absolute value of the linear correlation coefficient (LCC; Table 5) shows that variation in the NICA parameters (log $\tilde{K}$ and n) contributes most to the uncertainty of model outputs of Cu and Pb. The parameters with the largest contribution to the uncertainty shift from the parameters related to the type 1 low-affinity sites to those related to the type 2 high-affinity sites with increasing pH. For Cd, the fraction FA is the most important source of uncertainty, followed by log $\tilde{K}_{H1}$ and log $\tilde{K}_{Cu1}$ due to competition with H and Cu. Additionally, the maximum proton site density $Q_{max1,H}$ appeared to be important for Cd. It appears that the number of binding sites, which depends on the maximum site density, and the FA fraction are the most important factors for metals that have a relatively low affinity (log $\tilde{K}$) for binding to FA, such as Cd, whereas for metals with a high affinity $Q_{max1,H}$ and the fraction FA appear to be of lower importance than log $\tilde{K}$ and n.

Comparison of Predicted Speciation and Associated Uncertainty with Speciation Measurements. Figure 2 shows the comparison of modeled FMI activities (left panel) and total concentrations (right panel), including their uncertainty, with measurements. Modeled FMI activities using the average parameter values derived in this study show comparable agreement with measurements, as reported in other studies (7, 13, 29–31), according to their RMSE. Predicted total metal concentrations show a somewhat smaller variation than FMI activities and the distribution is less skewed (Figure 2).

The uncertainty in the predicted FMI activity is highest for Cu and Pb, which bind strongly to FA, and is less pronounced for Cd. Results of the model scenarios (see Figure 1) show considerable uncertainty in predicted FMI activities already at pH values around 4 for Cu and Pb, whereas for Cd uncertainty starts to become important at pH 6 and higher. Because most extracted soil solutions have a pH below 6 the uncertainties for Cd are low, consistent with the observed small deviation between model predictions and the measurements. The larger deviations for Cu and Pb are consistent with the larger uncertainties for both metals. Although the differences between the model predictions and measurements for Cu lie within the error bars, the FMI activities tend to be overestimated since all predictions (using either average or generic parameters) are systematically higher than the measurements. FMI activities of Cu in soil solutions tend to be overestimated in other studies as well (7, 31, 32). Most likely these systematic differences are due to deviations in log$K$ and n, the parameters that contribute most to the uncertainty. Meanwhile, predictions for Pb are systematically too low. Other studies however show both underestimation (7), overestimation (32), or no systematic deviation (29) in predicted Pb^{2+}.

The uncertainty in NICA parameters of competing cations may also affect the uncertainty in predicted trace metal speciation. We evaluated this additional uncertainty for the important competitors Al^{3+} and Fe^{3+} (24) with MC simulations

TABLE 5. LCC of the Three Variables That Contribute Most to the Uncertainty

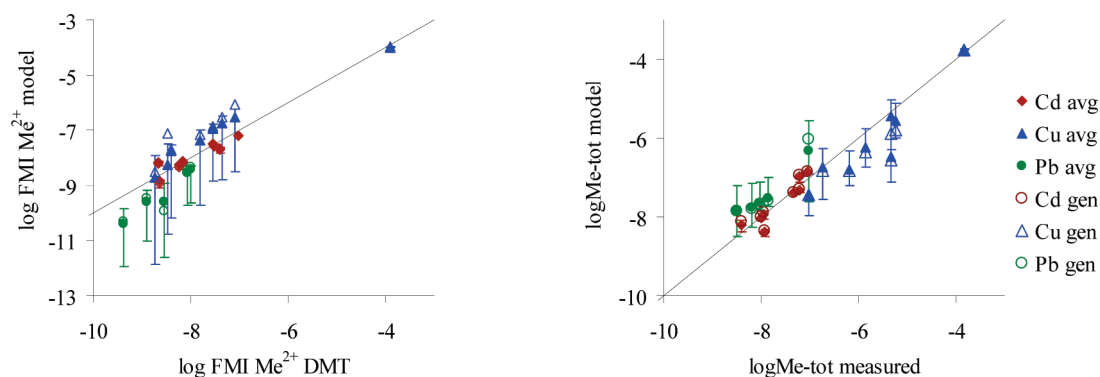|	pH 3			pH 6			pH 8	
Cd	**Cu**	**Pb**	**Cd**	**Cu**	**Pb**	**Cd**	**Cu**	**Pb**
FA[a]	n_{Cu1}	K_{Pb1}	FA[a]	n_{Cu1}	K_{Pb2}	FA[a]	K_{Cu2}	K_{Pb2}
0.62	−0.74	0.75	0.68	−0.37	0.60	0.68	0.26	0.44
K_{H1}	K_{Cu1}	K_{Pb2}	K_{H1}	FA[a]	K_{Pb1}	K_{Cu1}	FA[a]	K_{Pb1}
−0.50	0.36	0.73	−0.30	0.34	0.57	−0.23	0.26	0.39
n_{Cd1}	FA[a]	K_{H2}	K_{Cu1}	K_{Cu1}	K_{H2}	$Q_{max1,H}$	n_{Cu1}	K_{H2}
−0.25	0.32	−0.35	−0.25	0.28	−0.26	0.13	−0.18	−0.15

[a] FA = the fraction FA in DOM.

FIGURE 2. Comparison between calculated and measured log free metal ion concentrations (left) and total concentrations (right) for Cd, Cu, and Pb. Error bars indicate p5 and p95 of the Monte Carlo simulations, closed symbols represent calculations with average values of the parameters (avg), and open symbols represent calculations with the generic parameters of Milne et al. (gen).

of the FMI predictions for the soil extracts. The measured dissolved Fe and Al concentrations in these extracts (Table S-3, Supporting Information) enable an explicit analysis of the additional effect of uncertainty in the parameters for Al and Fe binding to FA. Binding parameters were varied according to the SD reported for Fe (20), assuming a similar variation for Al, for which no data were available. Differences between the uncertainties (Table S-9, Supporting Information) of the MC calculations with and without variation in the Al and Fe parameters were insignificant, implying that, with the present parameter uncertainty for Cd, Cu, and Pb, the parameter uncertainty of Al and Fe does not lead to additional uncertainty in the predicted speciation.

Implications for Model Use and Improvement. HS fractions extracted from different soils vary between 14 and 63% of total DOM. Considerable variation is shown to exist in NICA-model parameters for various samples of FA. This natural variation in binding properties and DOM composition creates considerable uncertainty in the predictions of metal speciation when using ion binding models such as NICA−Donnan. The variability in model parameters is the most important source of the uncertainty in predicted speciation of metals with a relatively high affinity to bind to organic matter (Cu and Pb), whereas the variation in the composition of DOM is most important for metals with a relatively low affinity (Cd). It is, therefore, worthwhile to investigate the extent to which uncertainties can be reduced by restricting the variability of the (dissolved) organic matter composition and model parameters by determining their ranges for certain groups of soils, soil and surface waters, and other materials in which metal binding to HS is important. However, due to the heterogeneous nature of (dissolved) organic matter a certain level of variability is to be accepted. For example the observed 5-fold temporal variation in Cu-binding affinity of DOM in leachates from a single soil (33). The large uncertainties at low FMI activities (e.g., at high pH and/or low total metal concentration and/or high FA concentration) are unlikely to be substantially improved because these uncertainties are mainly the result of the difference between two relatively large numbers: the total metal concentration and the concentrations of metal bound to FA. However, the practical need for further precision at these very low FMI activities may be questioned.

It is also important to note that the contribution of LMWOA should be considered when modeling Cu speciation in acid soils, while the effect was found to be insignificant for Cd and Pb and higher pH.

When new model parameters are derived, their uncertainty can be reduced when proton and metal binding data are determined for the same HS sample. At present there are

almost no samples for which both data are available. Our results show a clear difference (Figure 2) between the predicted speciation using either the average values from this study or the generic values of the NICA parameters as derived by Milne et al. (6). Their method employed to derive the generic parameters weighs the data points according to their quality, possibly leading to a strong bias for HS samples with many data points, although the particular HS may show far from average behavior. Because of the existing variability in binding properties, we advocate a method in which the separate HS samples are weighed equally.

Acknowledgments

Supporting Information Available
Information on the soils used, details of the DMT measurements, concentrations used in the MC calculations (Table S-1), a compilation of DOM fractionation (Table S-2), additional information on composition of the soil extracts (Table S-3), individually optimized NICA parameters (Table S-4), correlations between NICA parameters (Tables S-5), predicted Cu speciation MC analysis (Figure S-1), effects of LMWOA on predicted metal speciation (Table S-6), model performance in other studies (Table S-7), NICA−Donnan parameters for Al and Fe used in the MC Simulations (Table S-8), and uncertainties in predicted FMI activities (Table S-9). This material is available free of charge via the Internet at http://pubs.acs.org.

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