Are we able to predict trace metal binding to DOM? Validation and uncertainty analysis of the NICA-Donnan model

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Abstract
The use of metal speciation in risk assessment requires accurate speciation measurement techniques and sound model concepts to predict metal speciation in natural waters. Combination of the Donnan Membrane Technique (DMT) to measure free metal ion (FMI) activities for several metals simultaneously and a rapid batch technique to measure Humic (HA) and Fulvic (FA) acid concentrations provides a good opportunity to test and validate ion binding models for organic matter such as NICA-Donnan. Here we test this model on data from soil extracts obtained by extracting eight soils with 2 mM $Ca(NO_3)_2$. Free metal activities were calculated with NICA-Donnan from measured pH, total concentrations of trace metals and major cations, and HA and FA concentrations in the soil extracts. Uncertainties in predicted FMI activities due to uncertainties in model parameters were accounted for by Monte Carlo simulation. Predicted FMI activities compare rather well with measurements. The largest deviations and uncertainties were found for Cu and Pb which strongly bind to humic substances. Results indicate a consistent underestimation of Cu binding and an overestimation of Pb binding.

Introduction
Speciation of metals in soil solution is highly important for the bioavailability and mobility of trace metals in soils. The use of mechanistic models, like the Biotic Ligand Model, in risk assessment requires the validation of such model concepts including their parameterization.
Ion binding to humic substances in speciation models such as NICA-Donnan (Kinniburgh et al., 1999) and WHAM (Tipping, 1998) is parameterized based on data of ion binding to purified humic substances. To use these models to predict metal binding to natural dissolved organic matter (DOM), information is needed on the nature and reactivity of DOM. So far, most studies use estimates for the fractions of fulvic acid (FA) and humic acid (HA) in DOM, which vary between 40 and 100%. For example, Bryan et al. (2002) optimized WHAM to fit measured Cu^{2+} ion activities by adjusting the fraction of FA in DOM. Optimal fits varied between 40 and 90% FA with an average of 65%. Weng et al. (2001) used an estimate of 30% FA and 30% HA whereas others used estimates of 100% FA (e.g., Christensen and Christensen, 2000). In this study, we have used a newly developed batch technique to measure FA and HA concentrations in soil solution (van Zomeren and Comans, 2007). Now these FA and HA concentrations can be measured and no assumptions have to be made on model input as was needed before we can test these models more thoroughly. Model predictions were compared with free metal ion (FMI) concentrations measured with the Donnan Membrane Technique (DMT) (Temminghoff *et al.*, 2000). An uncertainty analysis was done to interpret the comparison of model predictions with measurements.

Methods
Batch solution extractions and measurements
For the batch solution extractions and DMT measurements, we used the setup described in Koopmans et al. (2008). Eight soils with a broad range of metal contents and soil properties such as pH (4-7.2) clay content (2-28%) and soil organic matter (2-13%) were extracted with 2 mM $Ca(NO_3)_2$ at a soil solution ratio of 1:10 (w/v). The extracts were centrifuged and the supernatants were decanted. The supernatants were used to measure the FMI activities with the DMT. Donor and acceptor solutions were sampled after 4 and 8 d. Donor samples were filtered through 0.45-µm DOC-free filters and analyzed for pH, total concentrations of metals, major cations, and DOC. Acceptor samples were used for measurement of pH and total metal concentrations. For some soils, donor solution was used for analysis of low molecular weight organic (LMWO) acids and anions with HPLC. The remaining part of the donor solution was used for fractionation of DOM into HA, FA, and a hydrophilic fraction (HY) (van Zomeren and Comans, 2007).

Speciation modeling and uncertainty analysis
We calculated the FMI activities in the donor solution with the NICA-Donnan model using the generic parameters from Milne et al. (2003) except for the binding of Fe^{3+} to FA for which we used the parameters from Hiemstra and van Riemsdijk (2006). Measured pH and total concentrations of trace metals (Cd, Cu, Ni, Zn, and Pb) and major cations and, if measured, anions together with measured concentrations of FA and HA, were used as input to the model.
For each data point, we calculated the uncertainty in the predicted FMI concentration due to variation in NICA parameters of FA (i.e., the dominant reactive component of DOC in our $Ca(NO_3)_2$ extracts), using Monte Carlo simulations. Variation in the site density of the two distinguished binding sites was set equal to the variation in optimized site density for various FAs by Milne et al. (2001). Variation in binding strength was set to 20% of the log K value for all cations based on the variation in proton binding strength in the optimized values of Milne et al. (2001). Variation in parameters for heterogeneity and adsorption in the Donnan layer was neglected.

Results and discussion

Measured fractions of FA and HA, expressed as a percentage of total DOC, range from 0-5% for HA and 20-53% for FA for the eight different soils. These numbers are (much) lower than the percentages assumed in model calculations reported in literature so far. Concentrations of LMWO acids were a negligible fraction of DOC.

The average difference between predictions of FMI activities of Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} with the NICA-Donnan model and measured FMI activities is less than 0.5 log units for all metal ions.

Differences between model predictions and measurements, as shown in Figure 1, can be due to (i) measurement errors, (ii) conceptual errors in the NICA-Donnan model, or (iii) deviations from the generic parameterization. Here we evaluate the effect on model predictions, due to possible deviations of metal binding parameters of the humic substances from the generic NICA-Donnan parameters.

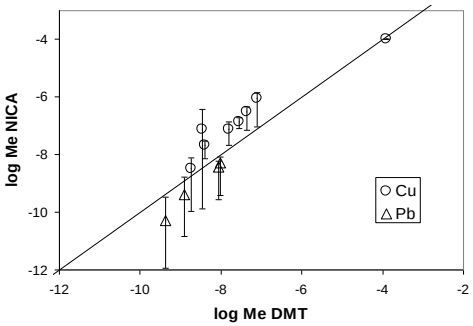

Figure 1 Uncertainty of model predictions for Cu and Pb (log M). Whiskers indicate 5 and 95 percentiles of the Monte Carlo simulations

The uncertainty in model predictions is low for Cd, Ni and Zn, which is in line with the small deviations between predictions and measurements for these metals (data not shown). The largest variation in model results was simulated for Cu and Pb, which are known to bind strongly to humic substances (Figure 1). The range of model predictions between the 5 and 95 percentile covers most of the measured data points. However, the largest part of the predictions are too high for Cu, but at the same time too low for Pb for all measured data points and this needs further investigation.

Analysis of the individual contribution of parameter uncertainty to the overall uncertainty in model predictions shows important contributions from both the maximum site density as well as binding constants for metal and proton binding to FA.

Because concentrations of FA and HA were measured, no assumptions had to be made on the nature of DOM in contrast to the model studies done so far, which allows for a more thorough testing of the model. Deviations between model predictions and measurements in this study are, therefore, likely due to uncertainty in the parameterization of the NICA Donnan model. This parameter uncertainty possibly results from variation in metal binding properties of individual FAs. Our present research aims at (i) the quantification of the variation in binding parameters of FAs and (ii) to quantify the effects of this variation on the uncertainty of predicted FMI activities by the NICA-Donnan model in case generic parameters are used.

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