Modeling of the Solid–Solution Partitioning of Heavy Metals and Arsenic in Embanked Flood Plain Soils of the Rivers Rhine and Meuse

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The aim of this study is to predict the solid–solution partitioning of heavy metals in river flood plain soils. We compared mechanistic geochemical modeling with a statistical approach. To characterize the heavy metal contamination of embanked river flood plain soils in The Netherlands, we collected 194 soil samples at 133 sites distributed in the Dutch part of the Rhine and Meuse river systems. We measured the total amounts of As, Cd, Cr, Cu, Ni, Pb, and Zn in the soil samples and the metal fraction extractable by 2.5 mM $CaCl_2$. We found a strong correlation between heavy metal contamination and organic matter content, which was almost identical for both river systems. Speciation calculations by a fully parametrized model showed the strengths and weaknesses of the mechanistic approach. Cu and Cd concentrations were predicted within one log scale, whereas modeling of Zn and Pb needs adjustment of some model parameters. The statistical fitting approach produced better results but is limited with regard to the understanding it provides. The log RMSE for this approach varied between 0.2 and 0.32 for the different metals. The careful modeling of speciation and adsorption processes is a useful tool for the investigation and understanding of metal availability in river flood plain soils.

Introduction

In the last century, large amounts of heavy metals have accumulated in the embanked river flood plain areas of the Dutch part of the Rhine and Meuse river systems. About 500 km^2 of flood plain soils are affected by the deposition of contaminated sediments. To enable decision making with regard to river flood plain areas, it is necessary to be able to predict adverse effects due to the heavy metal pollution of these flood plain soils.

Relating metal contamination in soils with uptake in plants and biota is one of the key problems in the risk evaluation of heavy metal contamination. Often denoted as *availability* or *bioavailability*, the link between metal contamination and uptake consists of a sequence of several processes (*1–3*). The combination of metal speciation modeling with approaches such as the free ion activity model (FIAM) or the biotic ligand model (BLM), which combines metal speciation with uptake by or toxic effects to biota, can give useful insight in mechanisms and uptake behavior in well-defined aquatic systems or nutrient solutions (*4–7*). However, modeling of metal speciation and uptake in complex soil systems still presents a major challenge in ecotoxicology.

The first step to work out the relation between heavy metal contamination of soils and uptake by biota is to derive the solid–solution partitioning of metals. In the past, geochemical speciation modeling of soil systems has not been satisfactory because of the complexity of sorption processes to the soil matrix (*8*). To be able to use the many experimental data on metal sorption published in the literature, understanding and accurate modeling of the effects of competition by the cations and anions present in pore water on the sorption of metals is essential. Recent improvements of sorption modeling make it possible to describe the complexation of metals by dissolved or soil organic matter (*9–11*) or iron oxides (*12, 13*) in detail. These sorption models describe metal sorption on a molecular scale, taking into account the effects of pH, competition, ionic strength, and background electrolyte on metal binding. Although in practice these models cannot be integrated easily in speciation calculation programs, they are fully parametrized, and therefore they can be applied directly to predict metal behavior under a large range of conditions. Several studies combined many models to a "multisurface" approach (*14–16*).

A more straightforward way to calculate solid–solution partitioning is the use of statistical regression formulas (*17–19*). If many data are available and the statistical approach is applied to soils from similar origin or with comparable properties, this method is expected to result in relations with a fair precision. Whereas this approach might not add much to the understanding of soil processes, it will circumvent the efforts needed to build up a speciation model and determine the numerous parameters necessary for the model. However, different from geochemical modeling, the statistical approach is unlikely to apply over a wide range of redox conditions, in view of the different processes that control metal speciation in oxic and anoxic conditions.

In this paper, we study the heavy metal contamination in the flood plain sediments of the Dutch part of the Rhine and Meuse river systems and assess the possibility of predicting the solid–solution partitioning of heavy metals and arsenic. We compare two different approaches to calculate solid–solution partitioning: a geochemical model fully parametrized by data available in the literature, and a regression model based on the extensive data set presented in this work.

To characterize the properties and heavy metal contamination patterns typical for river flood plain soils, we collected 194 soil samples from locations distributed over the entire Netherlands. To estimate the soluble fraction of metals, we extracted all soil samples with $CaCl_2$, a widely used and efficient extraction method, which was shown to correlate well with the plant uptake of many metals and nutrients (*20–22*).

For the geochemical model, we used a multisurface approach similar to Weng et al. and Dijkstra et al. (*14, 23*) and extended it by also accounting for mineral phases. We

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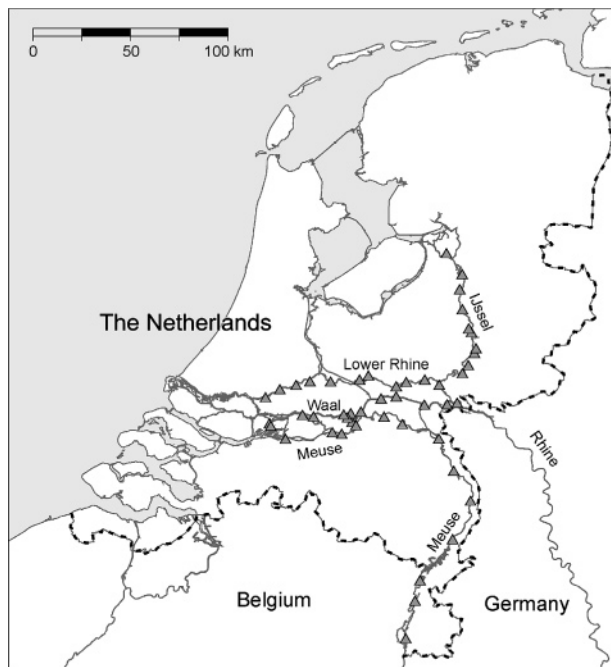‡ Institute for Inland Water Management and Wastewater Treatment.

FIGURE 1. Sampling locations in the Rhine−Meuse flood plain system.

measured by ICP-AES (Spectros, Spectro Flame) and ICP-MS (Perkin-Elmer, ELAN 6000). The content of soil organic carbon (SOC) was analyzed by wet oxidation with $K_2Cr_2O_7$ (26). Clay content was measured by sedimentation according to Houba et al. (27).

CaCl$_2$ extractions were made according to a modified scheme of Houba et al. (28). We used 2.5 mM of CaCl$_2$ rather than 10 mM CaCl$_2$ in view of the better agreement with the major ionic composition of pore water sampled in the flood plain soils (data not shown).

The pH was measured in the suspension of the 2.5 mM CaCl$_2$ extraction (27). Dissolved organic carbon (DOC) concentration was measured in the extract by a TOC analyzer (Skalar, SK12) after the sample was diluted five times and was acidified to a pH of 3.0−3.5 by the addition of 0.28 M HNO$_3$. Concentrations of As, Cd, Cr, Cu, Ni, Pb, and Zn in the extract were measured by ICP-MS after filtration by 0.45 μm and 1:1 dilution with 0.28 M HNO$_3$ (Merck, suprapur).

Geochemical Modeling. Speciation calculations were performed with the object-oriented modeling framework ORCHESTRA, a new geochemical program that gives the user the flexibility to extend the chemical model with appropriate sorption models (29).

Equilibrium constants for soluble species and mineral phases were used from the MINTEQA2 (30) recent database version 4.0. Equilibrium constants (K_{sp}) for mineral and soluble species from other sources are summarized in Table 1. Unlike in other studies (14, 23), we included in our model all minerals that are likely to occur under the prevailing conditions, and we allowed them to coprecipitate with metals and to control the metal activity in solution. The activity correction was done with the Davis equation (29). All calculations were performed without temperature correction, at the standard state (25 °C).

As input for the geochemical model, we used the total amounts of Al, As, Cd, Cu, Fe, Mn, P, Pb, and Zn measured in aqua regia. The activity of Fe^{3+} is controlled by the presence of goethite, and the activity of Al^{3+} is controlled by the presence of gibbsite. Since the concentrations of phosphate were too low to be measurable, we calculated the activity of PO_4^{3-} by assuming equilibrium with hydroxyapatite. Calcite reaches equilibrium with the soil solution very slowly at neutral pH and is therefore not defined as mineral phase in the model (34). Instead, we defined a fixed background electrolyte of 2.5 mM CaCl$_2$ as input for the model calculations. The redox potential of the model system was defined by a constant $pO_2 = 0.20$ atm, assuming all samples to be in equilibrium with the atmosphere.

A multisurface approach is used to calculate adsorption to the solid phase and dissolved organic matter (DOM). To calculate the adsorption of metals to organic matter, we used the consistent nonideal competitive adsorption model (NICA) that includes a Donnan approach to describe the electrostatic interactions (10). All model parameters necessary to describe adsorption on fulvic and humic acid were taken from the generic NICA parameter set (11). Organic matter consists of variable fractions of nonreactive matter, humic acid (HA),

parametrized the model by data given in the literature rather than by fitting parameters to the data set as done in other studies (8, 15, 24). The predictions of the geochemical model were compared with the measured metal fraction in 2.5 mM CaCl$_2$. We discuss the strength and limitations of this approach and suggest some modifications to overcome the lack of thermodynamic data.

To increase cost efficiency in practice, we explore several simplifications of the models that decrease the laboratory efforts and that limit the necessary model input to parameters that are included in existing databases.

Materials and Methods

Field Sampling. For field sampling, we selected 48 flood plain sites along the Dutch part of the river Meuse and the three major branches of the river Rhine: the IJssel, the Lower Rhine/Lek branch, and the Waal/Nieuwe Merwede branch (Figure 1).

Using prior information, sampling locations were selected to fulfill two requirements, that is, to obtain a representative distribution of contamination levels over the entire contamination range and to distribute the sampling locations well over the river systems. Furthermore, we included a variety of different land use forms and ecosystem types. Within each selected flood plain system, we sampled two or three cores at different points, dependent on the size and heterogeneity of the flood plain. The cores were generally collected on a transect perpendicular to the river, but the sampling scheme was adapted to local conditions if necessary.

We sampled columns with lengths ranging from 60 to 180 cm by a gouche auger sampler (2.5-cm diameter), avoiding the upper 5 cm of the profile. The columns were separated into segments of 20 cm. In case a well-defined interface between layers was apparent in the segment, we adapted the segment length to avoid mixing of different layers. In total, we collected approximately 560 segments, from which we selected 194 samples from the upper 60 cm (137 samples from 5 to 35 cm and 57 samples from 35 to 60 cm) for analysis.

Chemical Analyses. Samples were dried at 40 °C and were sieved (<2 mm) before analysis. As, Cd, Cr, Cu, Ni, Pb, Zn, Mn, Fe, P, and Al concentrations in aqua regia (25) were

and fulvic acid (FA). Reliable data on the HA and FA fractions of organic matter are lacking in the literature, therefore, we made the assumption that 50% of the soil organic matter (SOM) is present as HA and 40% of DOM is present as FA. The remaining fractions of SOM and DOM were assumed to be nonreactive. To recalculate the measured carbon contents to organic matter content, we assume for simplicity a carbon content of organic matter of 50% (*31*).

Adsorption of metals and anions by iron oxide is calculated by the charge distribution multisite complexation model (CD-MUSIC; *12*). For the specific surface area of goethite, values are given from 20 to 200 m^2 g^{-1} (*32*). We assumed a specific surface area of 50 m^2 g^{-1} for iron oxide. The parameters used are given in Tables 1 and 2, Supporting Information. Sorption to manganese oxide is described by a surface complexation model of Tonkin et al. (*33*). For the specific surface area of manganese oxide, a large range of values is given in the literature (*33*). For the model calculations, we used a specific surface area of 50 m^2 g^{-1}. The amounts of Fe and Mn oxides, used for the sorption modeling, were calculated directly by the model.

Clay adsorption of Ca, Zn, and Mn is calculated by a simple ion exchange model with a constant CEC (*34*). We assumed clay to be present as illite, the predominant clay mineral in these soils, with a CEC of 0.35 mol$_c$ kg^{-1} (*31*), and we used an exchange coefficient $K_{Zn/Ca}$ and $K_{Mn/Ca}$ of 1 (*35*).

Statistical Model. For the statistical approach, we fitted a linear regression equation that relates the extractable metal concentrations to the sum of all adsorbing phases, pH, and total amount (*17*, *18*):

$$\log Me_{CaCl_2} = \sum_i a_i \log X_i + const. \tag{1}$$

where for the different i, X_i represents, respectively, the H$^+$ activity, total amount of the heavy metal, SOC, DOC, total amount of Fe and Mn, and the amount of clay. All variables and constants not significant at $p < 0.05$ (t-test) were removed stepwise.

Results and Discussion

Figure 2 presents the total amount of heavy metal as a function of the soil organic carbon content for the Rhine and Meuse river systems. The similarity of the contamination pattern within and between the two river systems is remarkable. Zn, Cd, Cu, Cr, Pb, and As correlate strongly with the organic matter content, Ni to a little lesser extent. The regression equations differ only slightly between the Rhine and Meuse river branches except for Cr and As, where the regression equations are significantly different. For heavy metals preferentially bound to organic matter, the solid−solution partitioning is strongly dependent on the solid−solution partitioning of organic matter. With the organic carbon content positively correlated to the contamination degree, the solution concentration of the metals preferentially bound to organic matter will therefore depend to a large extent on the DOC concentration in soil solution.

Whereas the contamination patterns were quite comparable for the two rivers, the flood plain sediments of the Meuse and Rhine differed significantly in Ca content. In the Rhine branches, an average concentration of 31 g kg^{-1} of Ca (±11.2 g kg^{-1}) was measured, whereas in the Meuse flood plain the Ca concentrations were significantly smaller and more variable (9.2 g kg^{-1} ± 8.8 g kg^{-1}). Although the Ca content is not expected to influence metal behavior directly, it will influence the pH of the soils when it is present as calcite. Figure 3 shows that indeed a relation between Ca content and sediment pH is observed. Because of sufficient amounts of Ca in the Rhine sediments, the pH is high (7.47 ± 0.16). In comparison, the pH values of the Meuse flood plain
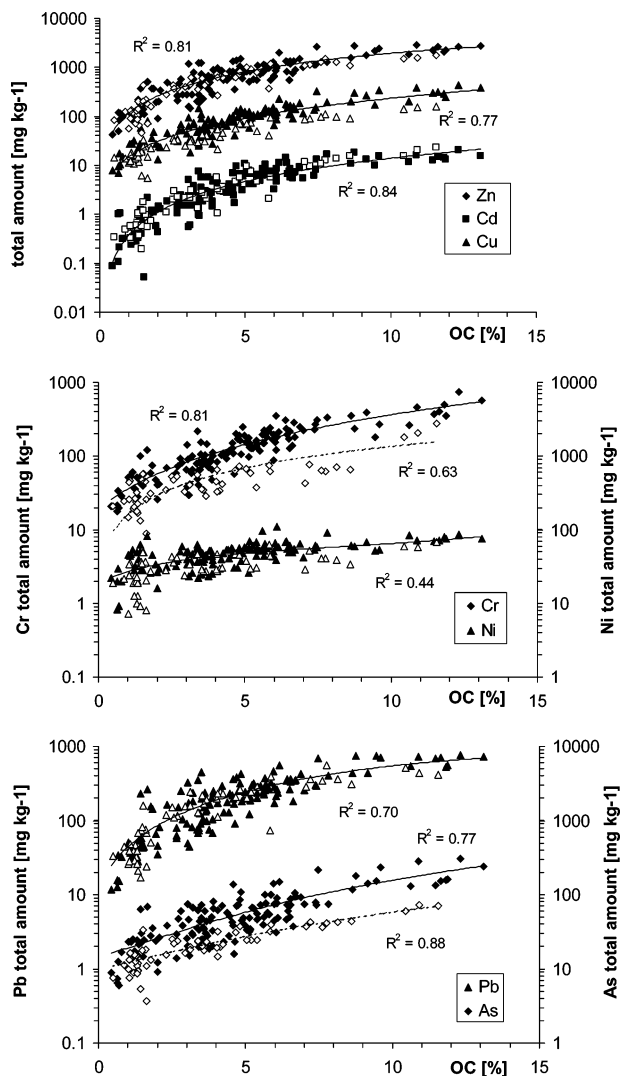

FIGURE 2. Heavy metal content of top soil layers (5−60 cm) as a function of the organic carbon content. (a) Zn, Cd, and Cu; (b) Cr and Ni; and (c) Pb and As. Open symbols: Meuse river. Solid symbols: Rhine river system. Fitted trendline functions and R^2 values are shown for all samples from both rivers. In the case of Cr and As, fitted trendline functions are shown for each river.

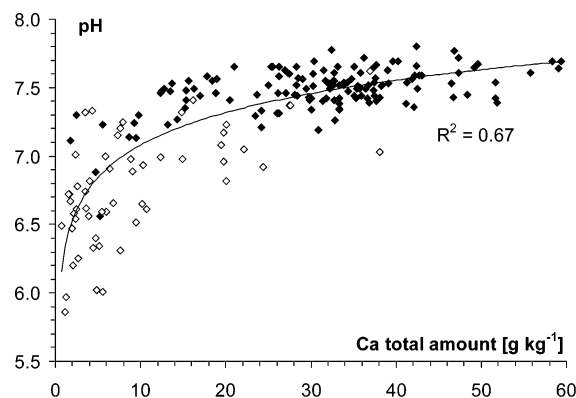FIGURE 3. Soil pH as a function of Ca content of top soil layers (5−60 cm). Open squares: Meuse river, solid squares: Rhine river system.

samples were much smaller and more variable (6.76 ± 0.40) and ranged from 5.86 to 7.62 dependent on the amount of Ca present. Since the effect of pH on metal partitioning is well documented, one should expect that, despite the comparable contamination patterns in both river systems,
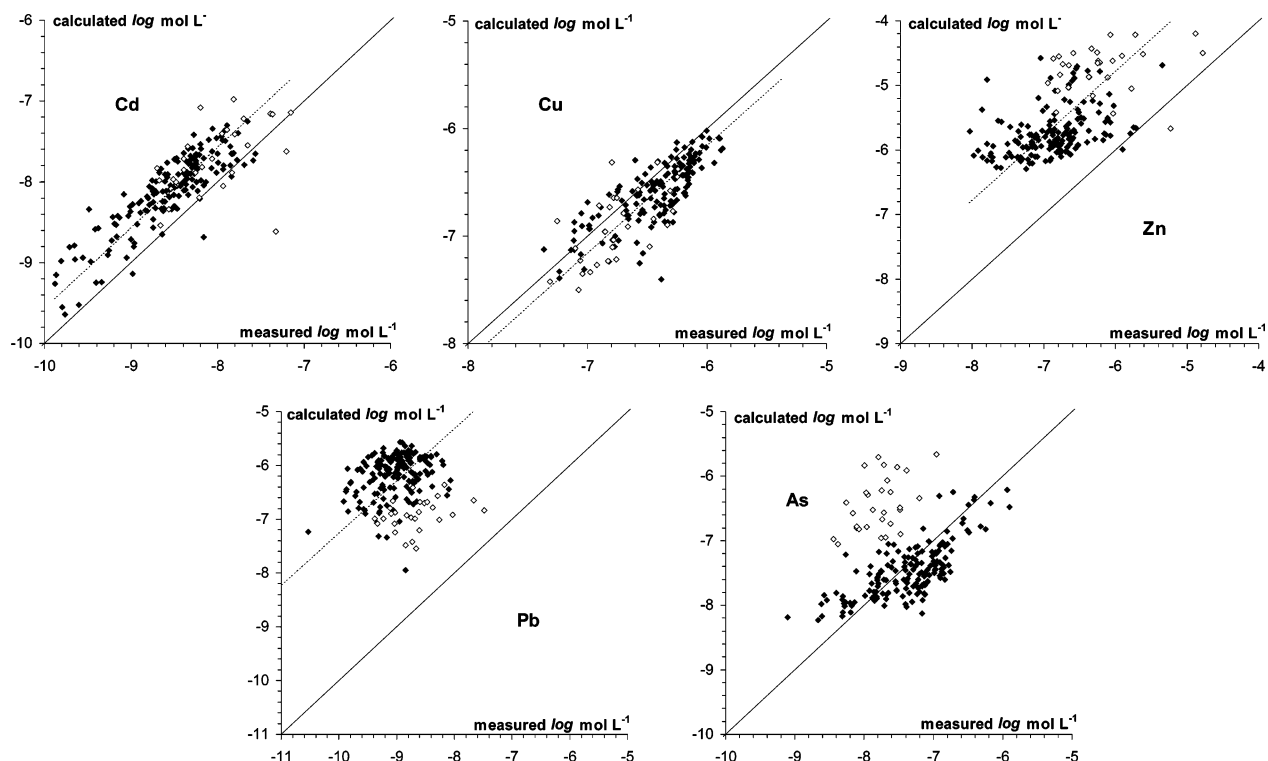
FIGURE 4. Concentrations of Cd, Cu, Zn, Pb, and As extracted by 2.5mM CaCl₂ and calculated by the geochemical model. Open symbols correspond to samples with a pH < 6.8. The dashed line represents a trendline through the average values; the full line represents the 1:1 line.

the extractable metal fractions in the Meuse samples will be higher.

Figure 4 shows the measured concentrations in the 2.5 mM CaCl₂ extractions compared to the predictions of the fully parametrized geochemical model. We did not present geochemical calculations for Ni, because the thermodynamic data were of poor quality (*40*), the data support for the NICA parameter was weak (*11*), and no parameters for the binding to goethite were available. Since in 90% of all samples the extractable concentrations of Cr were below the limit of determination (<3 μg L⁻¹), we also omitted further calculations for Cr.

Without any calibration or fitting, the general trend for the extractable metal fraction of Cd and Cu is predicted well by the speciation model. The predicted values for Cd were on average approximately 0.45 log units too large, whereas the results for Cu were 0.15 log units too small. In the case of Cu, the speciation model calculates that more than 98% of soluble Cu was bound to DOM. By calibrating the HA and FA fractions, the prediction of Cu can therefore easily be improved. However, this affects the prediction of Cd, which is mainly bound to organic matter, too. We tested different combinations of HA and FA content in DOM and SOM, but there was no reasonable way to improve the predictions for Cd without worsening the prediction of Cu. No known mineral phases influenced the speciation of Cd under the prevailing conditions, and because of the low activity of Cd²⁺, binding in diffuse double layers of organic matter, oxides, and clay was negligible (<1%). Manganese oxide can potentially bind large amounts of Cd (*41*). However, despite the use of four surface binding sites, the model of Tonkin et al. (*33*) fails to describe the available literature data on Cd binding to manganese oxides. The binding of Cd was largely underestimated in several cases. It is difficult to improve the manganese sorption model in such a way that it would fit both our data and literature data consistently. Therefore, we did not attempt to change model parameters to improve our model.

The extractable Zn concentrations were overestimated by more than one log scale. For the speciation of Zn, organic matter binding is less important than in the case of Cd and Cu. The minerals williamite, franklinite, and hemimorphite are possible sinks for Zn. Although they have been shown to be present in contaminated soils (*42*, *43*), reliable solubility data are lacking. Moreover, the dissolution of franklinite depends on the form in which iron oxides are assumed to be present in soil. Our model assumes iron oxide to be present as goethite, however, Lindsay (*36*) found that in soil the activity of Fe³⁺ can be larger than calculated in equilibrium with goethite. He recommends the use of an empirical "soil"-Fe(OH)₃ with a solubility between amorphous iron oxide and goethite. In the case of hemimorphite, no solubility constant is available at present. We can improve therefore our model by either calibrating the solubility constants of iron oxide, franklinite, or williamite or by proposing a solubility constant for hemimorphite. We cannot prove which of the minerals is present in soil. However, since all of them have the same pH-dependency (log Zn²⁺ + 2pH = const.), the mineral actually present does not affect the outcome of the calculation much. We chose to decrease the log K_{sp} value of franklinite by one unit to 8.85. Figure 5a shows the result of the calculation with the modified log K_{sp} of franklinite. The modification improved the prediction of Zn, except for samples with a pH smaller than 6.5, which is due to the strong pH dependency of the dissolution reaction of the mineral phase.

Lead concentrations were profoundly overestimated too, a problem already discussed by Weng et al. (*14*). In view of our model predictions for the extractable Pb fractions, which were more than 2 orders of magnitude too large, we estimated that only 1% of all Pb in soil can be bound to organic matter. Because of the high affinity of Pb to organic matter at high pH, the Pb²⁺ activity is too low to make it likely that mineral phases such as chloropyromorphite or PbHPO₄ (*44*) can be formed under these conditions. Several studies imply that Pb can be sorbed to goethite not solely as a Pb²⁺ cation but
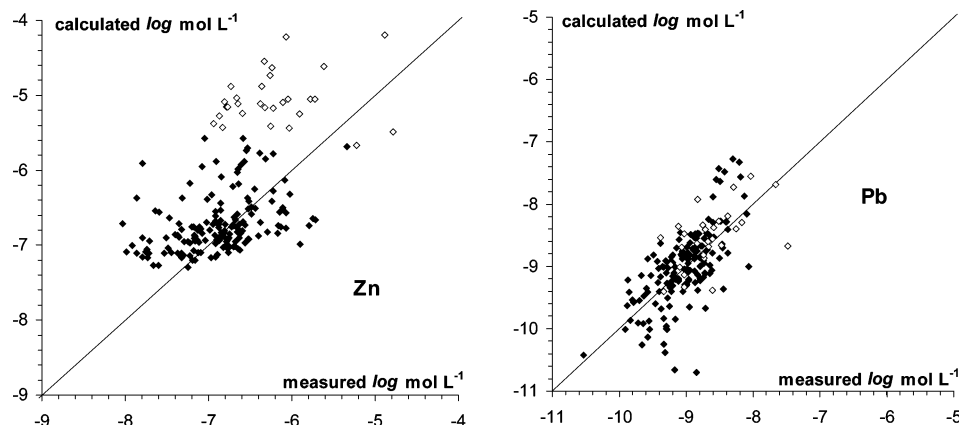
FIGURE 5. Concentrations of Zn (a) and Pb (b) extracted by 2.5mM CaCl$_2$ and calculated by the modified model. Open symbols correspond to samples with a pH < 6.8. The line represents the 1:1 line.

TABLE 2. Regression Parameter for Cd, Cu, Zn, Pb, Ni, and As Extractable by 2.5 mM CaCl$_2$[a]

	const	pH [−]	log Me$_{tot}$ [mol kg^1]	log SOC [kg kg^{-1}]	log DOC [kg L^{-1}]	log Fe$_{tot}$ [mol kg^{-1}]	log Mn$_{tot}$ [mol kg^{-1}]	log clay [kg kg^{-1}]
log Cd [mol L^{-1}]	n.s.	−0.668	0.604	0.484	0.184	−0.589	−0.308	n.s.
log Cu [mol L^{-1}]	−3.692	0.108	0.414	0.374	0.404	−0.368	n.s.	n.s.
log Zn [mol L^{-1}]	1.056	−0.824	0.580	0.637	n.s.	−1.087	n.s.	n.s.
log Pb [mol L^{-1}]	−3.795	−0.414	0.719	n.s.	0.335	n.s.	−0.751	−0.414
log Ni [mol L^{-1}]	−1.157	−0.380	0.467	0.382	0.568	n.s.	−0.700	n.s.
log As [mol L^{-1}]	−−4.654	0.114	0.794	1.051	n.s.	−0.951	n.s.	−0.411

[a] Me$_{tot}$ is the total amount of the metal in question. n.s. = not significant.

also as PbCO$_3$ (45, 46), PbSO$_4$ (47), PbCl$^+$ (48, 49), and PbPO$_4^-$ species (50, 51). We used the data available in the literature to fit the presence of a PbCO$_3$, PbSO$_4$, and PbCl surface species on goethite, but none of this species improved our model outcome much. Literature data on phosphate and Pb sorption are not consistent: when we calculate a PbPO$_4$ species sorbed to goethite that fits to our data, we derive a value that is too large to explain the data of Ler et al. (50) but too small to describe the data of Weesner et al. (51). However, despite the contradictory data, we hypothesize the formation of a PbPO$_4$ complex on goethite, recognizing that we cannot support this by independent literature data. Figure 5b shows that the proposed PbPO$_4$ surface species can explain the measured Pb concentrations substantially (see also Table 6).

At pH > 6.8, the extractable amounts of As were well predicted and 90% of all samples were within one log unit. However, larger deviations appeared at pH values below 6.8. Since no As-containing mineral phase precipitates under the given conditions and our model defines a specific binding of As only to iron oxides, the distribution relies predominantly on the assumed surface amount of iron oxide. Changes of the assumed specific surface area of goethite will only affect the overall sorption amount but will not improve the As prediction at low pH values. It is unclear whether specific binding to other surfaces or binding of other arsenic species to goethite is responsible for the solid−solution partitioning at lower pH. Smedley et al. (52) suggest that at the given pH range, binding to Al hydroxides, which are present in flood plain soils at approximately 20 g kg^{-1} on average, might affect the solid−solution partitioning of As.

Table 2 and Figure 6 show the results of the regression calculations of the statistical model. The statistical model shows better results than the fully parametrized geochemical model with a root-mean-square error (RSME) of the log-transformed data varying between 0.11 and 0.33 (Table 3). The statistical approach also resulted in a smaller standard error of prediction than in other studies that aimed at developing a more general statistical model (17, 18). This

TABLE 3. Root-Mean-Square Error (RMSE) of the Statistical Model for Cd, Cu, Zn, Pb, Ni, and As in 2.5 mM CaCl$_2$[a]

log RMSE	Cd	Cu	Zn	Pb	As	Ni
full model	0.201	0.113	0.324	0.311	0.255	0.194
Me$_{tot}$, SOC, clay, pH	0.223	0.141	0.339	0.330	0.269	0.244
Me$_{tot}$, SOC, clay	0.327	0.149	0.448	0.361	0.276	0.274
Me$_{tot}$, SOC, clay, Ca$_{tot}$	0.198	0.144	0.339	0.318	0.271	0.224

[a] The RMSE is calculated from log-transformed concentrations. Me$_{tot}$ is the total amount of the metal in question

can be attributed partly to the large size of the used data set and partly to the limited and well-defined area of this study, with soils of a comparable origin.

Reduction of Input Variables. Both statistical and geochemical models required an extensive input. Several options were explored to reduce the number of input parameters of the models.

Table 3 summarizes the effect of these simplifications on the RMSE of the statistical model. Table 4 summarizes the regression parameters for the simplified models.

A statistical approach using the total amount, SOC, clay, and pH performed only slightly less than the full statistical model (Table 2). The RMSE-values differ less than 0.03 log units for all metals except Ni. In The Netherlands, the pH is often not measured for risk assessment of soils. Therefore, we tested the effect of disregarding the pH on model agreement. Without pH, the RMSE increases for Cd, Zn, and Ni by 0.08−0.13 log units. Measuring the pH requires an extra analytical procedure, whereas the total amount of Ca can be easily measured simultaneously with other metals on ICP-AES at negligible extra costs. Hence, we assessed whether the correlation between Ca and the pH (Figure 3) can be used to replace the pH by Ca in the statistical model, where

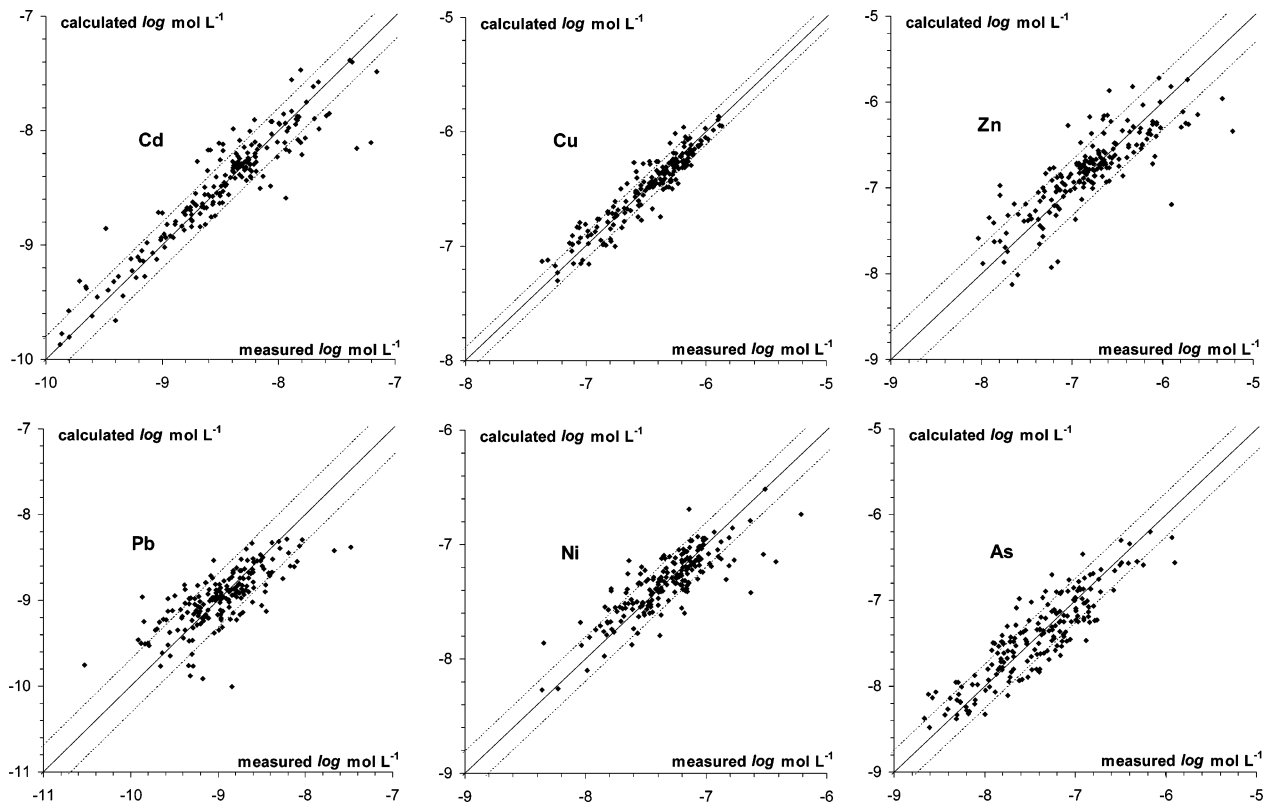$$pH = 0.787 \log Ca_{tot} + 7.588 \qquad (2)$$

FIGURE 6. Concentrations of Cd, Cu, Zn, Pb, Ni, and As extracted by 2.5mM CaCl$_2$ and concentrations calculated by a regression model (Table 2). The full line represents the 1:1 line and the dashed lines represent the standard error of estimation.

TABLE 4. Simplified Statistical Model for Cd, Cu, Zn, Pb, Ni, and As Extractable by 2.5 mM CaCl$_2$[a]

	const	log Me$_{tot}$ [mol kg^1]	log Ca$_{tot}$ [mol kg^1]	log SOC [kg kg^{-1}]	log clay [kg kg^{-1}]
log Cd [mol L^{-1}]	−5.260	0.620	−0.700	0.548	−0.287
log Cu [mol L^{-1}]	−4.920	0.170	0.120	0.682	n.s.
log Zn [mol L^{-1}]	−5.141	0.621	−0.822	0.600	−0.375
log Pb [mol L^{-1}]	−7.425	0.445	−0.472	0.480	−0.554
log Ni [mol L^{-1}]	−5.663	0.274	−0.459	0.656	n.s.
log As [mol L^{-1}]	−4.395	0.654	0.159	0.928	−0.792

[a] Me$_{tot}$ is the total amount of the metal in question. n.s. = not significant.

TABLE 5. Generalized Input Parameters for Simplified Speciation Model[a]

DOC [mg L^{-1}]	pH [−]	Al$_{tot}$ [mg kg^{-1}]	P$_{tot}$ [mg kg^{-1}]	Mn$_{tot}$ [mg kg^{-1}]	Fe$_{tot}$ [mg kg^{-1}]
eq 3	eq 2	20 000	1000	900	30 000

[a] DOC values and pH are calculated according to eq 3 and 2, respectively.

The RMSE values of the model that uses eq 2 were comparable to the values of both the full model and the simplified model using the individual pH values, that is, they vary less than ±0.03 log units from both models.

In Table 5, we provide several generic input parameters on the basis of averaged values measured in both river systems. These values were used to reduce the number of input variables for the modified version of the geochemical model. Table 6 summarizes the RMSE of the simplified geochemical models and the fully parametrized model. Using average values for the total amount of P, Mn, and Al hardly changed the RMSE values for the metals. Use of an average value for Fe also increases the RMSE of Pb and As by 0.13 and 0.04 log units, respectively. Unlike Pb and As, which are mainly bound to iron oxides, for the other metals the agreement is not affected by using an average value for Fe.

TABLE 6. RMSE of the Geochemical Model for Cd, Cu, Zn, Pb, and As in 2.5 mM CaCl$_2$ with a Reduced Number of Input Variables[a]

log RMSE	Cd	Cu	Zn	Pb	As
fully parametrized model	0.523	0.268	1.298 (1.245)[b]	2.765	0.656 (0.395)[b]
modified model (Figure 5)	0.513	0.272	0.697 (0.517)[b]	0.450	0.740 (0.508)[b]
average P$_{tot}$, Mn$_{tot}$, and Al$_{tot}$	0.513	0.272	0.697 (0.517)[b]	0.452	0.740 (0.507)[b]
average Fe$_{tot}$, P$_{tot}$, Mn$_{tot}$, and Al$_{tot}$	0.513	0.273	0.697 (0.517)[b]	0.577	0.775 (0.594)[b]
average P$_{tot}$, Mn$_{tot}$, and Al$_{tot}$, DOC from SOC (eq 3)	0.499	0.269	0.696 (0.517)[b]	0.451	0.740 (0.503)[b]
average P$_{tot}$, Mn$_{tot}$, and Al$_{tot}$, DOC from SOC (eq 3), pH from Ca$_{tot}$ (eq 2)	0.503	0.269	0.692 (0.629)[b]	0.419	0.659 (0.543)[b]

[a] The RMSE is calculated from the log-transformed concentrations. Me$_{tot}$ is the total amount of the metal in question. [b] Values in parentheses are for samples with pH > 6.8.
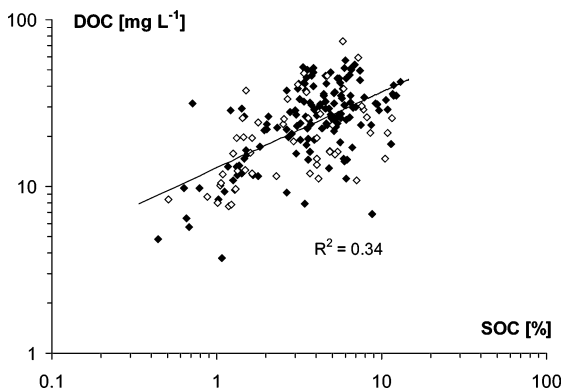
FIGURE 7. DOC concentration as a function of the organic carbon content. Open symbols: Meuse river. Solid symbols: Rhine river system.

Since the HA and FA fraction of DOC can be variable, we tested whether DOC is a good estimator for the HA and FA concentration of pore water. When we replaced the measured values of DOC by an average value, the geochemical model did not perform well (data not shown). In view of a significant, but not very strong correlation between SOC and DOC (Figure 7) for the soils in this study, DOC may be derived from SOC according to

$$DOC = 1.0488 \times 10^{-4} \times SOC^{0.4545} \tag{3}$$

Calculating DOC concentrations with eq 3, the RMSE decreased for Cd and Cu, which are both mainly bound to organic matter. Since the correlation between SOC and DOC is not very strong, the better agreement of a DOC value calculated by eq 3 indicates that DOC is not a reliable estimator for HA and FA in soil solution. However, there is no method available at this moment to measure the fulvic and humic fractions efficiently on a routine basis. A calibration of the HA and FA fractions to the individual soil system is recommended in the literature (*53*), and averaged DOC values are found to perform almost as well as individual measured samples for a single soil with different treatments (*54*). DOC values calculated with eq 3 lead to good or even slightly better agreements as using measured values, which implies that HA and FA fractions of natural DOC can be considerably variable.

The substitution of the measured values of pH by the total amount of Ca (eq 2) had a positive effect on the prediction of Pb and As (Figure 8) in the modified geochemical model. This substitution leveled out the variation of pH values and mainly affected the results at low pH values. For the samples with a pH > 6.8, the RMSE for Zn and As were larger

but for pH < 6.8 the RMSE was smaller (Table 6). This result is difficult to explain, but it implies that the Ca content is a better estimator of pH than the measured values itself, at least for pH values below 6.8. The measurement of pH is a rather robust technique for the given pH range, and deviations of the measurements are more likely to happen at high pH. We attribute this effect on the RMSE to the suspension effect during the measurement of the pH.

Reducing the number of input variables of the geochemical model by replacing them with average values or equations, the agreement between model and measurements remained good or even improved for some metals. Comparable to the statistical model, the only modification necessary for using this model for risk assessment is to extend the standard set of parameter measured in aqua regia by Fe and Ca. For the Rhine river system, the pH is rather constant (Figure 3) and it is therefore unnecessary to replace the pH value by Ca. This makes it possible to use the existing governmental databases on contaminated flood plain soils to calculate the solid−solution partitioning with this simplified model.

Geochemical Modeling versus Statistical Approach. We presented two models to predict solid−solution partitioning of heavy metals in oxic river flood plain soils. Both approaches have their specific advantages.

The statistical approach results in very accurate predictions for all metals in a 2.5 mM CaCl$_2$ extract. However, this approach relies on the availability of a sufficiently large number of consistent data. Furthermore, the regression equations can only be applied to soils with the same properties. Nevertheless, with the reduced set of variables, the equations can be easily applied to calculate the availability of heavy metals in river flood plain soils in The Netherlands under oxic conditions.

To study the influence of redox processes on heavy metal speciation, which is important in view of frequent flooding, we need a geochemical model. After two modifications, the model presented here predicts the extractable amount of all metals with an RMSE better than 0.74 log scale. This is comparable to the results of other studies (*14*, *23*).

Whereas the trend is predicted well, a large part of the RMSE is due to a systematic deviation from the 1:1 line. When we are less interested in predicting soluble metal concentrations but using the model to test out the influence of certain parameters on the solid−solution partitioning, this systematic deviation might be less relevant. When the RMSE is calculated relative to the trendline as given in Figure 4 instead of the 1:1 line, the residuals of the geochemical model were smaller for all elements. Thus, for the simplified geochemical model, RMSE-values equal 0.312, 0.211, 0.642, 0.419, and 0.613 for Cd, Cu, Zn, Pb, and As, respectively, with respect to the trendlines.
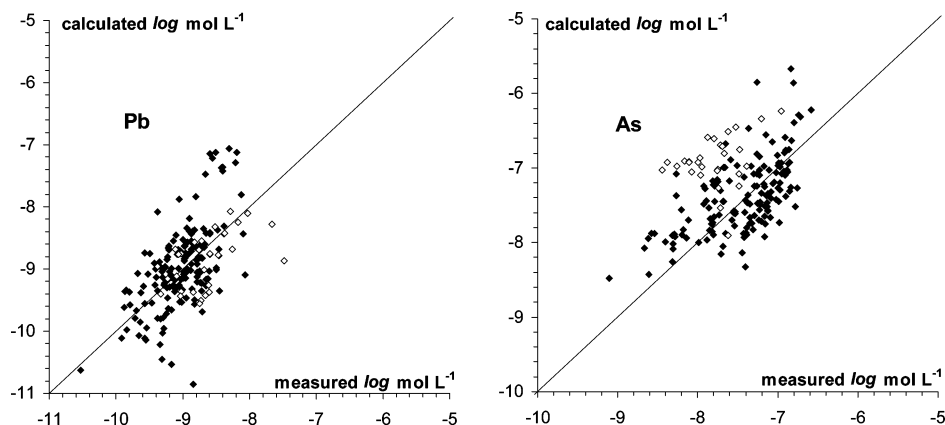

FIGURE 8. Concentrations of Pb and As extracted by 2.5 mM CaCl$_2$ and calculated by the simplified geochemical model with generic values for DOC, Al$_{tot}$, Mn$_{tot}$, Fe$_{tot}$, and P$_{tot}$. The pH is calculated from Ca$_{tot}$. Open symbols correspond to samples with a pH < 6.8.

Still less precise than the statistical model, the geochemical model has several advantages: the quality of a geochemical model is not dependent on the number of samples, which is often limited in risk assessment studies. Instead, the outcome solely depends on the quality of thermodynamic data on speciation and sorption and adequate sorption models. Progress in this field can be incorporated in a mechanistic geochemical model, and the shortcomings of the model prediction can point us to important gaps in the understanding of soil chemical processes, as is here the case for Zn and Pb.

Besides solid−solution partitioning, geochemical models provide detailed information on the speciation of metals in soil solutions. Although we did not measure metal activities, several other studies showed that a realistic modeling of metal speciation in the soil solution is possible if metal complexation by DOC is taken into account (*14*, *16*, *19*). If the heavy metal uptake by biota is linked to the free metal cation activity, as is proposed by FIAM, a geochemical calculation is necessary to provide the activities of specific species.

Acknowledgments

Supporting Information Available

Parameters used for the modeling of cation and anion adsorption to goethite by the CD-MUSIC model. This material is available free of charge via the Internet at http://pubs.acs.org.

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