Monitoring and modelling of the solid-solution partitioning of metals and As in a river floodplain redox sequence

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ABSTRACT

For a period of 2 a, pore water composition in a heavily contaminated river floodplain soil was monitored *in situ*. Pore water samples were collected 12 times over all seasons in a profile ranging from aerobic to sulphidic redox conditions, and As, Cd, Cr, Cu, Pb, Zn, Mn, Fe, Ca, Cl, SO_4, DOC, IOC and pH were determined. The variability of pH, IOC, DOC and Ca was found to be rather small during the year and within the profile (rsd < 0.04, 0.16, 0.24 and 0.22, respectively). The temporal variability of the metal and As concentrations was small, too, whereas changes with depth were distinct. Under sulphidic conditions, concentrations were below 1 $\mu g\,L^{-1}$ (Cd, Cu, Pb) or 10 $\mu g\,L^{-1}$ (Zn, As). The data set was compared with results from a geochemical model that was fully parameterised from literature data and included equilibrium speciation, sorption and mineral dissolution. The general pattern of the solid–solution partitioning of Cd, Cu, Zn and As in the profile was predicted well by mechanistic geochemical modelling on the basis of solid phase composition. Metals strongly bound to organic matter such as Cd and Cu were predicted better than metals mainly present within a mineral. Detailed information regarding the presence of colloidal Fe and Mn in pore water might improve the prediction of the solid–solution partitioning of a number of metals. The study also indicates that the chemical behaviour of Pb is still not understood sufficiently.

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1. Introduction

Large quantities of contaminant metals have accumulated over the last century in the embanked river flood-plain areas of the Rhine and Meuse river system. To enable decision-making with regard to policies for river flood plains, the Dutch government needs to be able to account for complications due to the metal contamination of these floodplain soils. For the risk assessment of contaminated soils, information on the solid–solution partitioning and speciation of contaminant metals is necessary as they both affect metal mobility and bioavailability. Geochemical speciation modelling is a potentially useful tool to quantify metal partitioning and speciation and can be integrated in a GIS environment to conduct scenario studies on a regional scale. Unlike in aquatic chemistry, the application of speciation modelling to soil systems faces additional pitfalls because of the presence of mineral phases and the importance of sorption processes to the soil matrix (Hesterberg et al., 1993). Problems can be circumvented by fitting several parameters to a dataset (Gustafsson et al., 2003; Römkens and Dolfing, 1998), but in this case the extrapolating capabilities to other soils and conditions, which might be important for scenario studies, becomes questionable. Recent advances in sorption modelling enables description of the complexation of metals by dissolved or soil organic matter (Tipping, 1993; Kinniburgh

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et al., 1999; Milne et al., 2003) or Fe oxides (Hiemstra and Van Riemsdijk, 1996; Venema et al., 1996) in detail. These models can be combined to a "multisurface" approach (Weng et al., 2001; Dijkstra et al., 2004; Lofts and Tipping, 1998). The multisurface approach, combined with mineral precipitation reactions, may be well suited to improving geochemical modelling as underlying models are well parameterised (Schröder et al., 2005). On the other hand, the modelling of mineral dissolution by an equilibrium approach encounters a number of known limitations, like kinetic limitation of mineral dissolution, the presence of mixed phases in natural systems or the presence of more soluble (intermediate) mineral forms after precipitation (Stumm and Morgan, 1996). However, mineral fractions may not be decisive for the partitioning of contaminant metals, and given the advances in sorption modelling, the question remains whether geochemical modelling is a useful tool in risk assessment of natural soil systems.

In a previous paper, the authors presented a geochemical model to predict the solid–solution partitioning of contaminant metals in a large number of top soil samples from river floodplains in The Netherlands (Schröder et al., 2005). For the soluble fraction, the metals extractable by 2.5 mM $CaCl_2$ were focused on. Besides giving a measure of bioavailability, the extraction was easy to apply and reflected time independent soil properties. However, a typical feature of floodplain soils is the rapid decrease of the redox potential in the profile under waterlogged conditions, therefore the approach could only be applied to aerobic top soil layers.

To be able to study the effect of the changing water levels of floodplain soil on metal partitioning, the geochemical model has to be extended with all necessary redox processes and species. Whereas the theory of redox processes is well established, predictive geochemical modelling of metals, accounting for both mineral equilibrium and multisurface sorption under changing redox conditions is still relatively new. Redox processes influence the metal speciation by precipitation and dissolution of metal containing minerals (Lindsay, 1979; Stumm and Morgan, 1996) or minerals which sorb metals (Dixit and Hering, 2003). Furthermore, elevated Fe concentrations can influence metal speciation by competition and elevated pCO_2 can lead to the formation of soluble and insoluble metal complexes. To the authors' knowledge, the many chemical reactions that need to be accounted for in redox affected systems have not been integrated into a complete model study before.

To compare the results of a geochemical model that includes redox processes with the extraction of samples by $CaCl_2$ or by other extractants is not appropriate, since those do not preserve the redox conditions of a sample adequately. In contrast, the extraction of pore water *in situ* is a good way to obtain an undisturbed sample that reflects the redox conditions of the sampled soil layer. However, since the composition of pore water may vary during the year, a single sample of pore water gives only limited information about the availability of metals at a location. Parameters that strongly control the metal partitioning, such as the pH or the concentration of dissolved organic C (DOC), are known to be influenced by seasonal variations and biotic soil processes (Farley and Fitter, 1999; Linehan

et al., 1989). Thus, for the risk assessment of river floodplains, besides easily extractable metal quantities in aerobic soil layers, also knowledge of the time and depth dependent composition of relevant pore water constituents is needed.

In this paper, the solid–solution partitioning of metals in a soil profile of a floodplain situated along the Dutch Nieuwe Merwede river is studied as a function of time. There are two scopes of this study: first, to obtain experimental data on the composition of pore water and the temporal variability for metals and As and other important variables in a soil profile ranging from oxic to sulphidic. For this, the pore water composition was monitored *in situ* over a period of 2 a. Second, it was of interest to study the processes influencing metal partitioning under different redox conditions. For this purpose, a multisurface geochemical model is developed that predicts the solid–solution partitioning and computes the speciation of metals in pore water and the solid phase. The model is fully parameterised from literature data and uses the solid phase composition to calculate pore water concentration profiles. The metal partitioning calculated by this generic model is compared with the measured pore water profiles and the strengths and limitations of the extended geochemical model are presented.

2. Materials and methods

2.1. Field sampling

Pore water composition was monitored on a heavily contaminated river floodplain location ("Lage Hof"). This location is situated along the Nieuwe Merwede, a channel which connects the largest branch of the Dutch part of the Rhine, the river Waal, with the North Sea (Fig. 1). Due to the proximity to the North Sea, the flooding pattern on the Lage Hof location is strongly influenced by the tide. The Lage Hof site is therefore subject to flooding in all seasons (Fig. 2).

For pore water sampling, a Rhizon soil moisture sampler was used (SMS MOM, Rhizosphere Research Products, Wageningen, The Netherlands). The Rhizon samplers were placed permanently in the floodplain sediment, which enabled repeated sampling of pore water *in situ* at the same position with a minimum interference to the soil system.

The Rhizon soil moisture sampler consists of a polyethersulfone (PES) membrane with a pore diameter <0.2 μm. The membrane has a diameter of 2.5 mm and a length of 10 cm and is connected to the soil surface by a PVC/PE tube. Before use, Rhizon samplers were cleaned by forcing 30 mL of 0.28 M HNO_3 through the membrane. The Rhizons remained for 2 h in 0.28 M HNO_3, before they were rinsed with 20 mL ultra pure water. Finally, the Rhizons were rinsed with 30 mL 1 mM $Ca(NO_3)_2$ and stored overnight in 1 mM $Ca(NO_3)_2$.

The Rhizon samplers were inserted horizontally in the floodplain sediment from 10 to 65 cm depths with a 5 cm distance increment. From 45 to 65 cm depth, the Rhizons were used in duplicate with a horizontal distance of 10 cm. To extract pore water, a vacuum was built up inside
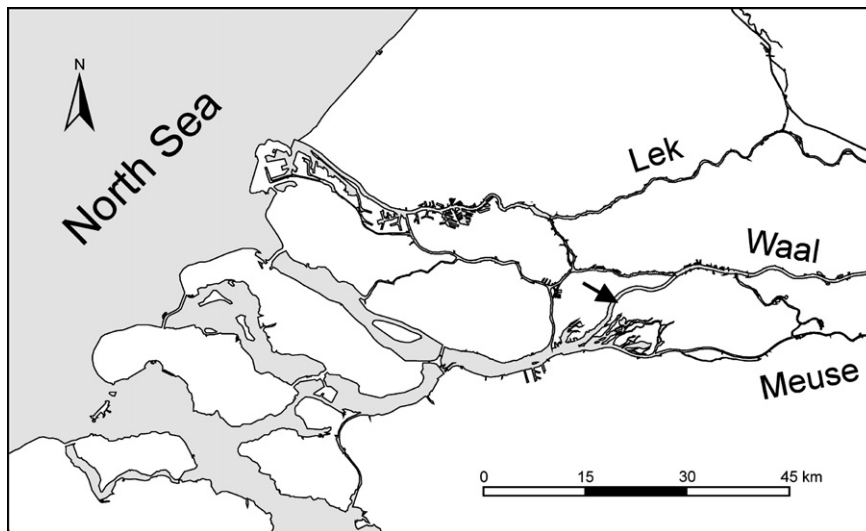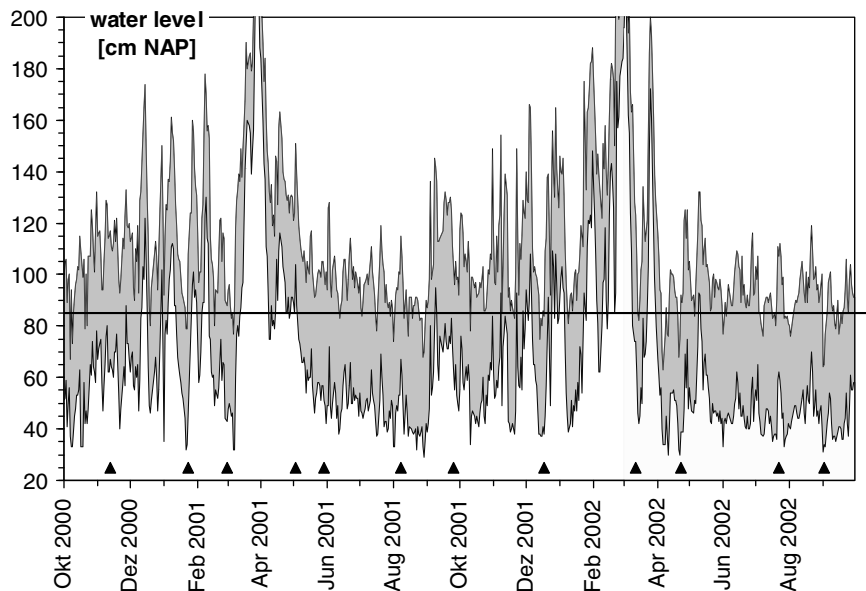
Fig. 1. Monitoring location Lage Hof.

Fig. 2. Daily minimum and maximum water level measured at Werkendam Buiten, The Netherlands. The water level is relative to the Dutch reference sea level (NAP). Triangles represent sampling dates, horizontal black line indicates the height of the sampling location. Source: Rijkswaterstaat, The Netherlands.

the Rhizon sampler by a 10 mL syringe (Becton Dickinson, 10 mL LL). Depending on moisture conditions, the extraction of 12 mL of pore water took between 15 and 120 min. Prior to sampling, the Rhizon samplers including the connecting tube systems were rinsed with the first 2 mL of sample solution (i.e., exceeding 3 ∗ dead volumes). Pore water was sampled 12 times over a period of 2 a (Fig. 2).

2.2. Chemical analysis

The pH of the pore water samples was measured immediately on location before oxidation affected the pH. Inor-

ganic C (IOC) and DOC were measured on a TOC analyser (Skalar, SK12) within 24 h of sampling. For the analysis of DOC, samples were acidified to a pH of 3.0–3.5 by addition of 0.28 M HNO_3. Arsenic, Cd, Cu, Pb, Zn, Mn, Fe and Ca concentrations of pore water were measured by ICP-MS (Perkin Elmer, ELAN 6000). Sulphate and Cl concentrations were measured by ion chromatography (Dionex, DX-600 with Ionpac AG 9-HC and Ionpac AS 9-HC column) (ISO, 1992). Due to the time delay between sampling and measurement it was not possible to preserve the reduced S species in the pore water samples. Therefore, it was assumed that the concentration of SO_4 measured in the oxidised samples represents the total amount of S in pore water.

To characterise the soil properties, a soil column was sampled and divided into segments. The segmented soil samples were dried at 40 °C and sieved (<2 mm) before analysis. Arsenic, Cd, Cr, Cu, Pb, Zn, Mn, Fe, P, S, Ca and Al concentrations in aqua regia extracts (NEN, 1992) were measured by ICP-AES (Spectros, Spectro Flame) and ICP-MS (Perkin Elmer, ELAN 6000). The soil organic C (SOC) content was determined by wet oxidation with $K_2Cr_2O_7$ (Wallinga et al., 1992). Clay content was measured by sedimentation according to Houba et al. (1997).

The redox potential was measured *in situ* by a Pt electrode (Radiometer, MC3051Pt) after the pore water sampling was completed. Values were recorded 20–30 min after insertion into the soil (rate of change <1 mV/2 min).

Table 1
Soluble and mineral species and $\log K_{sp}$ values used for calculation from sources other than Allison et al. (1991)

Species or mineral	$\log K_{sp}$	Ref.
$Ca^{2+} + Cl^- = CaCl^+$	−1.00	Lindsay (1979)
$Ca^{2+} + 2Cl^- = CaCl_2(aq)$	0.00	Lindsay (1979)
$Fe^{2+} + CO_3^{2-} = Fe^{(II)}CO_3(aq)$	4.38	Stumm and Morgan (1996)
$Fe^{3+} + H_2O + CO_3^{2-} = Fe(OH)CO_{3(aq)} + H^+$	−3.83	Bruno et al. (1992a)
$Fe^{2+} + 2CO_3^{2-} = Fe^{(II)}(CO_3)_2^{2-}$	7.10	Bruno et al. (1992b)
$Mn^{2+} + CO_3^{2-} = MnCO_{3(aq)}$	4.90	Stumm and Morgan (1996)
$Zn^{2+} + 2CO_3^{2-} = Zn(CO_3)_2^{2-}$	9.63	Parkhurst and Appelo (1999)
$Zn_3(PO_4)_2 \cdot 4H_2O + 4H^+ = 3Zn^{2+} + 2H_2PO_4^- + 4H_2O$	3.80	Lindsay (1979)
$ZnFe_2O_4 + 8H^+ = Zn^{2+} + 2Fe^{3+} + 4H_2O$	9.85	Lindsay (1979)
$Zn_5(OH)_6(CO_3)_2 + 10H^+ = 5Zn^{2+} + 2CO_2(g) + 8H_2O$	45.00	Preis and Gamsjäger (2001)
$Zn_2SiO_4 + 4H^+ = 2Zn^{2+} + H_4SiO_4$	15.33	Parkhurst and Appelo (1999)
$Zn_2Al(OH)_6Cl + 6H^+ = 2Zn^{2+} + Al^{3+} + Cl^- + 6H_2O$	23.50	Ford and Sparks (2000)

2.3. Geochemical modelling

Speciation calculations were done with the object-oriented modelling framework ORCHESTRA (Meeussen, 2003). The model set-up and parameterisation is based on Schröder et al. (2005). The previous model was already fully parameterised from the literature data, but the model definition was extended to the species present at more reducing conditions. All minerals that are likely to occur under the prevailing conditions were included in the model and were allowed to coprecipitate with metals and to control the metal activity in solution. For the speciation calculation the most recent database of MINTEQA2 (Allison et al., 1991), from September 1999 was used. Additional equilibrium constants for minerals and soluble species from other sources are summarised in Table 1.

To calculate the adsorption of metals to solid phases and DOC, the consistent NICA model was used (Kinniburgh et al., 1999). Sorption parameters were used from the generic NICA parameter set of Milne et al. (2003). Organic matter consists of variable fractions of non-reactive matter, humic acid (HA), and fulvic acid (FA). It was assumed that 30% of soil organic C (SOC) was present as HA and 50% of DOC as FA. The remaining fractions of SOC and DOC were assumed to be non-reactive (Schröder et al., 2005; Tipping, 2002; Weng et al., 2001). To recalculate the measured C contents to organic matter content, for simplicity an organic matter C content of 50% was assumed (Schachtschabel et al., 1992).

Adsorption of metals and anions by Fe oxide was calculated by the CD-MUSIC model (Hiemstra and Van Riemsdijk, 1996). For the specific surface area of goethite, a specific surface area of 50 $m^2\,g^{-1}$ for Fe oxide was assumed (Cornell and Schwertmann, 1996). The used sorption parameters are given in Schröder et al. (2005) and Table 2. Due to lack of data, sorption on magnetite (Fe_3O_4) is modelled similar to goethite (Dixit and Hering, 2003; Cornell and Schwertmann, 1996). Sorption to Mn (hydr)oxides is described by the surface complexation model of Tonkin et al. (2004). For the model calculation a specific surface area of 50 $m^2\,g^{-1}$ was used. Clay adsorption of Ca, Zn and Mn was calculated by a simple ion exchange model with a constant CEC. Clay was assumed to be present as illite, the most abundant clay mineral in Dutch soils (Kuipers, 1984), with a CEC of 0.35 $mol_c\,kg^{-1}$ (Schachtschabel et al. 1992) and an exchange coefficient $K_{Zn/Ca}$ and $K_{Mn/Ca}$ of 1 was used (Bruggenwert and Kamphorst, 1982).
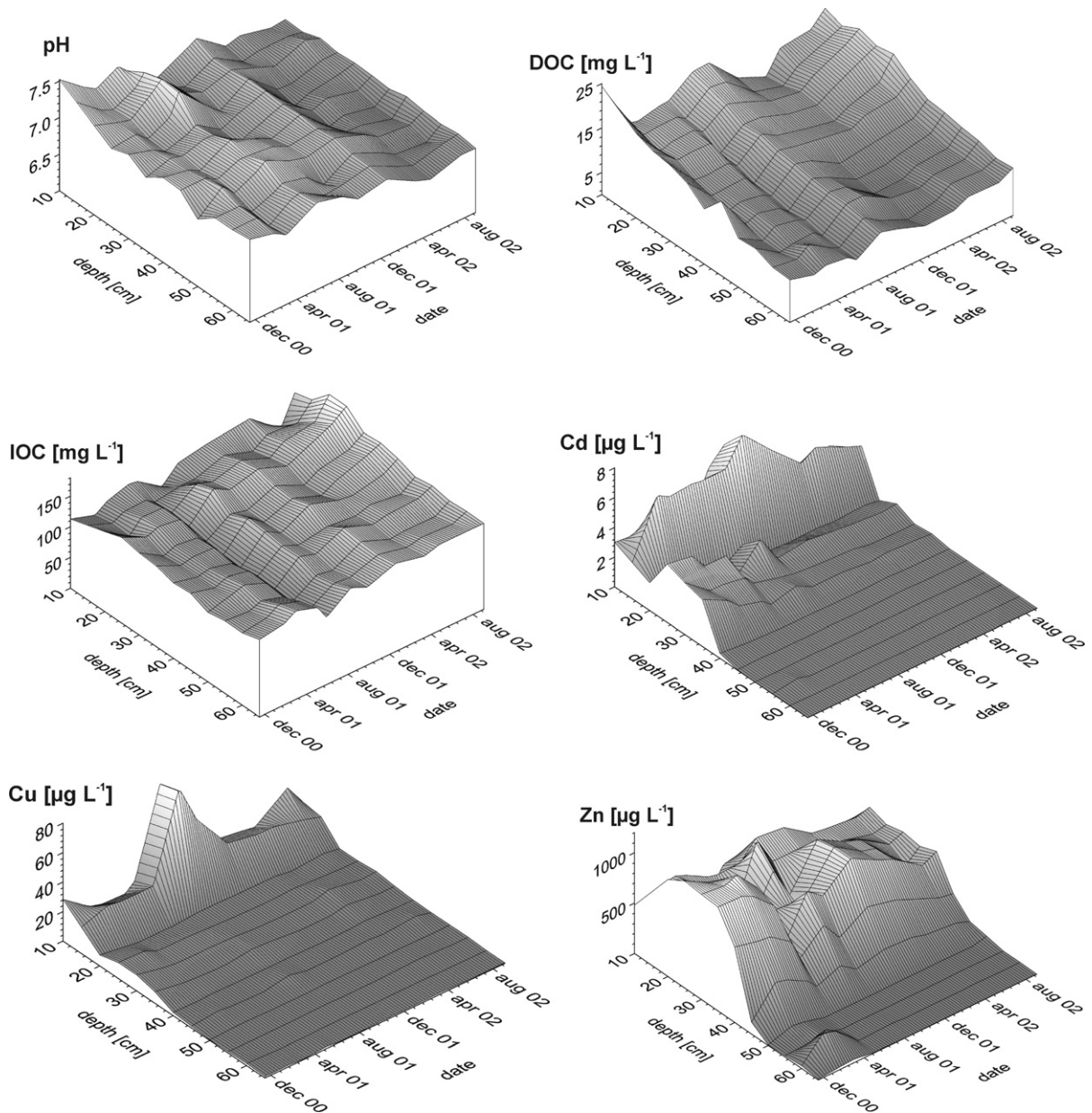
The activity of Fe^{3+} is controlled by the presence of goethite, and the activity of PO_4^{3-} by hydroxyapatite. Silicate activity is calculated in equilibrium to quartz. Calcite reaches equilibrium with soil solution very slowly at neutral pH and is therefore not defined as a mineral phase

Table 2
Parameter for the sorption of As$^{(III)}$ on goethite. Surface species, affinity ($\log K$), species and surface sites composition, and charge distribution to 0- and 1-plane according to the CD-MUSIC approach

Surface species	$\log K$	composition		Surface sites			Charge distribution	
				FeOH	Fe$_3$O	FeOHh	0-plane	1-plane
$FeOH_2AsO_3$	9.2	1 AsO$_3$	3 H	1	1		0	0
$FeOH_2AsO_3$	8.7	1 AsO$_3$	3 H	1			0	0

in the model (Appelo and Postma, 1994). Instead, the total concentration of Ca measured in pore water was used as input parameter. The P_{CO_2} is calculated from the amount of IOC measured in pore water.

To address the complex chemistry of S properly, a practical approach was chosen, considering two boundary conditions for S: the amount of soluble S was kept equal to the concentration measured in pore water as long as the calculated total amount of S did not exceed the total amount

Table 3
Soil properties

Depth (cm)	SOC (%)	<2 μm (%)	Cd (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})	Pb (mg kg^{-1})	As (mg kg^{-1})
0–20	12.6	32.5	16.8	316.0	2308	561.0	144
20–40	11.5	33.9	14.5	290.8	2758	633.8	255
40–55	11.5	32.0	15.6	270.7	2722	569.2	223
55–70	8.7	30.4	14.5	274.2	2368	516.4	220

Fig. 3. pH, DOC, IOC, Cd, Cu, Zn, Pb, As, Fe and Mn measured in pore water extracted at Lage Hof site as a function of sampling date and depth.
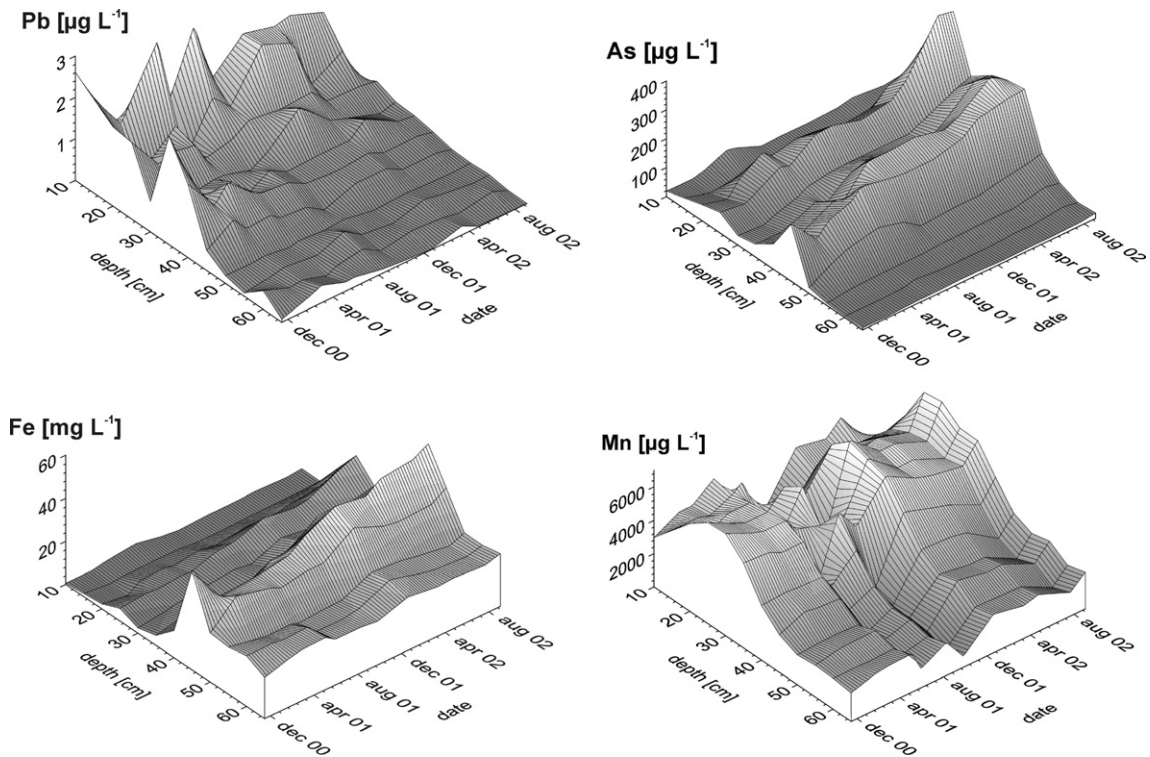
Fig. 3 (*continued*)

measured in soil. When the total amount calculated was larger than the amount measured, the model was run with a constant total amount of S in soil.

3. Results

Fig. 2 presents the daily maximum and minimum water level at the station Werkendam Buiten, situated 11 km upstream from the Lage Hof location. The triangles mark the 12 occasions that pore water was sampled *in situ*. The sampling location can get flooded during all seasons, but water retracts usually also twice a day due to the tidal pattern. Longer periods of continuous flooding, lasting several weeks, occur only in the spring.

Table 3 summarises the soil properties of the profile that was monitored. The profile was relatively uniformly contaminated and showed a slight decrease of organic matter content, clay and metal contamination with increasing depth.

Fig. 3 presents the results of monitoring of the pore water composition. Whereas in the upper layers the concentrations of metals and As are comparable to the extractable concentrations reported in Schröder et al. (2005), the metals and As get immobilised in the lower layers. Iron concentrations in pore water reached a maximum at 45 cm depth, with concentrations up to 50 mg L^{-1}. The maximum concentrations of Mn were approximately 5 mg L^{-1} on average and this maximum was situated above the Fe peak.

The temporal variability of the 12 samples taken during the 2-a period was found to be surprisingly small: the standard deviations of the pH and the log-transformed data of DOC, IOC, Zn, Cu, As, Ca, Cl, Fe and Mn at the designated depth were generally within 0.3 log units (Fig. 4). Larger temporal variability is observed only in the upper layers for Fe and Mn and for metals under sulphidic conditions. The time-averaged values of the DOC concentrations decreased from 15 to 9 mg L^{-1} with increasing depth, whereas the IOC concentrations and the pH were almost constant within the profile (125 ± 14 mg L^{-1} and 7.0 ± 0.16, respectively).

Since the properties of the soil layers do not differ much (Table 3), the average value of all soil layers were used for the calculations with the generic geochemical model. Compared to the precision of the predictions feasible with geochemical modelling, the variability of the soluble concentrations of Ca, Cl, DOC, and IOC and the pH were found to be small. Therefore the average concentrations of all samples in time and depth were used as a first estimate. By using the same input for all calculations, it is easier to present and discuss the results since pe is the only variable left. Table 4 gives the values of the input parameters used for the geochemical speciation calculations.

Fig. 5 shows the calculated and measured concentrations of the contaminant metals, As, Mn and Fe as a function of the pe. The calculated distributions of the metals over all relevant species in the solid and aqueous phase are shown in Figs. 6 and 7, respectively. They indicate which species controls the partitioning of these metals and can be useful to understand and discuss the deviations found between the model predictions and measurements
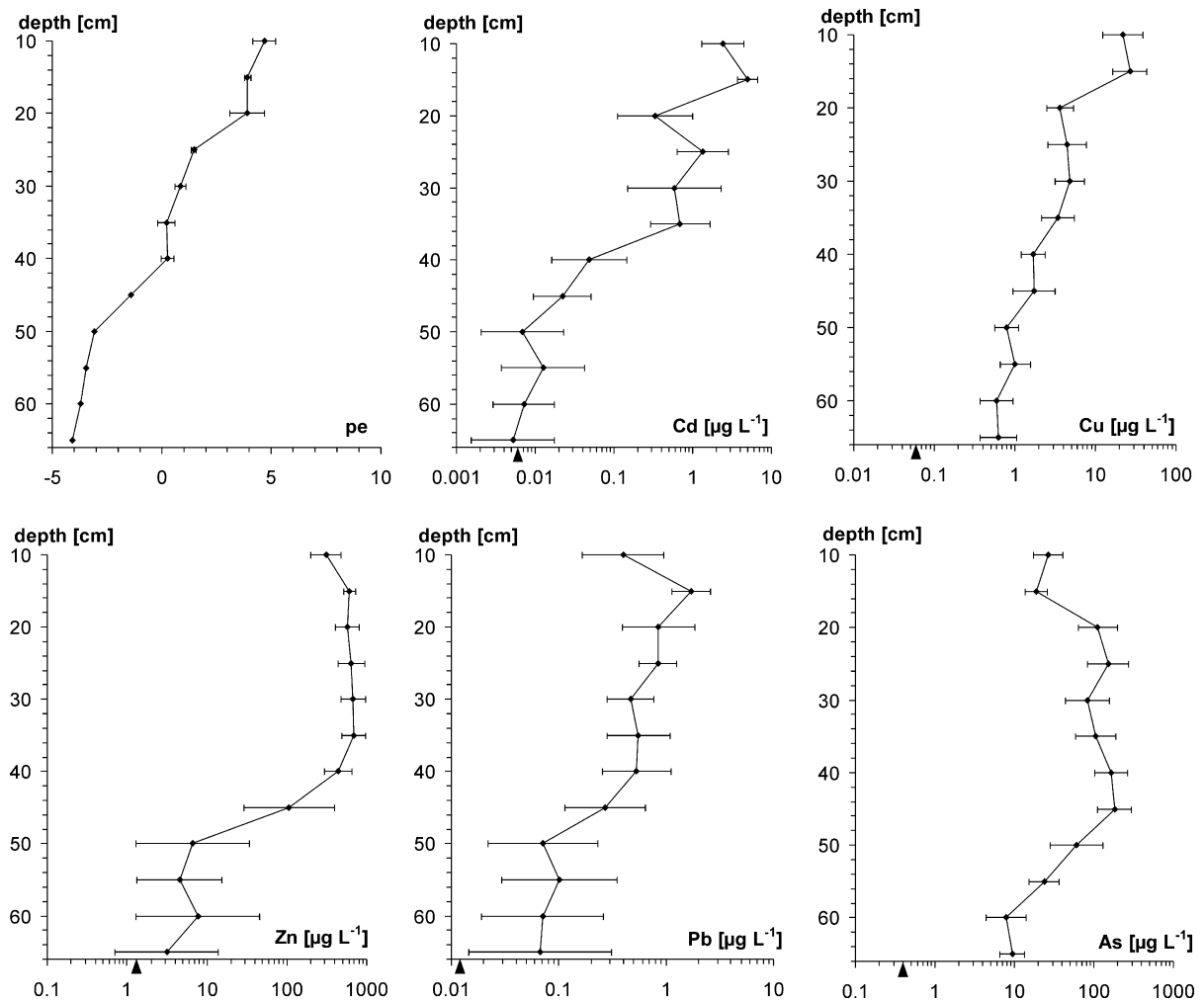
Fig. 4. Soil pe and geometric average concentration of 12 sample times of Cd, Cu, Zn, Pb, As, Fe, Mn, DOC, IOC, sulphate, and the pH in pore water extracted at the Lage Hof site. Horizontal bars represent the standard deviation. The triangles mark the detection limit.

and to propose a way to improve the model as will be discussed in the next sections.

4. Discussion

The small variability found for the measured parameter made it difficult to extract a clear temporal pattern. No significant correlation was found between any of these parameters and the water level (1-, 3-, or 7-day average). Also, the position of several distinct peaks in the profile does not change much, e.g. Cu, As or Fe (Fig. 3). This implies that the varying water level during the year did not have a large influence on the redox condition in the soil profile. However, since metal partitioning can react sensitively to small changes in pH or DOC concentrations, whether there is any correlation that links the variations of metal concentrations with the variations of these parameters was tested. Weak correlations were found between Cu, Zn and Pb in the upper layer and the concentrations of DOC, significant at $p < 0.142$, 0.054 and 0.051, respectively, and

a stronger correlation was found between Pb and the pH ($p < 0.008$). The temporal variability of pH and DOC can therefore influence the metal speciation to a small but significant extent.

The geochemical model generally predicts the pattern of Cd, Cu and Zn in the profile well considering that these results were obtained without any fitting. The sequence of immobilisation in the sulphidic zone is found to be in agreement with the sequence calculated by the model (Cd > Zn > Pb), but happens at higher pe values than in the calculations. Since the measurement of redox potentials by Pt-electrodes does not perform well over the whole redox range, a comparison of the calculated and the measured concentration profiles should be done with care. Small concentrations of O_2 and the $NO_3^- - NO_2^- - NH_4^+$ redoxcouples are known to deliver no reversible electrode potentials in natural groundwater systems (Stumm and Morgan, 1996; Lindberg and Runnells, 1984), thus higher pe values are likely to be underestimated. Furthermore, when the redox potential is measured in soil
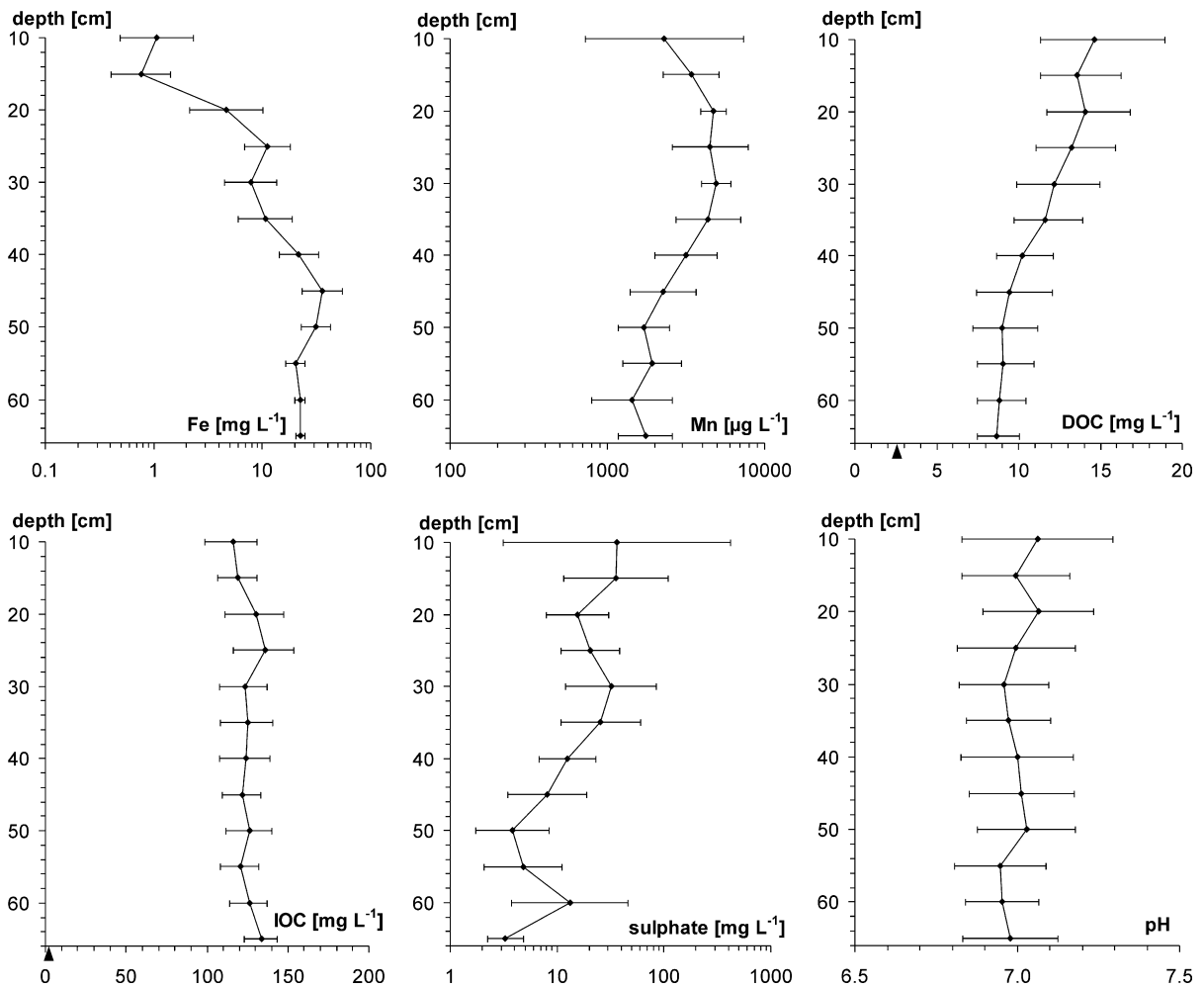
Fig. 4 (continued)

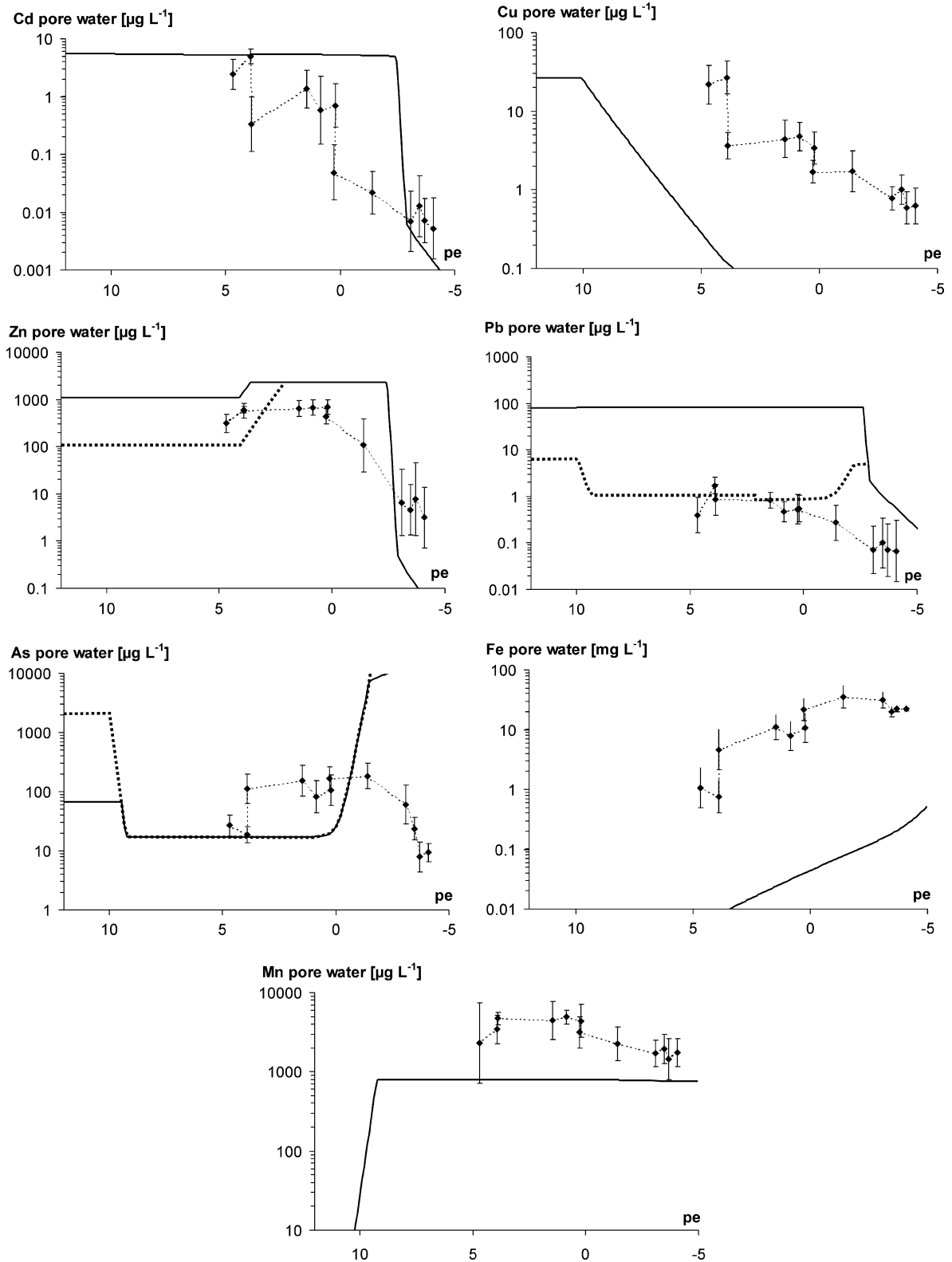**Table 4**
Values used for geochemical model calculations

SOC (%)	<2 μm (%)	Cd (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})	Pb (mg kg^{-1})	As (mg kg^{-1})	Mn (mg kg^{-1})	Fe (g kg^{-1})
11.1	32.2	15.4	288	2539	570	211	1007	41
P (mg kg^{-1})	S (mg kg^{-1})	Al (g kg^{-1})	pH [−]	DOC (mg L^{-1})	IOC (mg L^{-1})	Chloride (mg L^{-1})	Sulphate (mg L^{-1})	Ca (mg L^{-1})
2450	2100	25	7.00	11.4	126	78.6	27.3	159

aggregates, it may be lower than in the pore water itself.

Although Fe and Mn are not of foremost interest when focussing on the risk assessment of the contaminant metals, they still might have a significant effect on the partitioning of these metals. Iron and Mn form oxides that can sorb contaminant metals and high concentrations of both were measured in pore water (Fig. 3), so they might outcompete other sorbing phases. Fig. 5 shows that the soluble amounts of Mn and Fe are underestimated by the model by approximately one and more than two orders of magnitude, respectively. Assuming Fe to be in equilibrium with ferrihydrite or other Fe (hydr)oxides (Lindsay,

1979; Rickard and Morse, 2005) instead of goethite could not bridge this gap between predictions and measurements, since under equilibrium conditions soluble Fe^{3+} species can be neglected. Thus Fe and Mn appear to be oversaturated in relation to the soil system. The oxidation of Mn$^{(II)}$ and Fe$^{(II)}$ is well known to be kinetically limited (Stumm and Morgan, 1996). Another explanation for the high concentration may be the presence of Fe and Mn as soluble colloids (Stumm and Morgan, 1996). Wolthoorn et al. (2004) showed that the presence of Ca, DOC and other ions slows down the autocatalytic oxidation of Fe^{2+}. This can lead to large amounts of colloidal Fe particles that are small enough to pass through the membrane of the

Fig. 5. Calculated and measured average concentrations of Cd, Cu, Zn, Pb, As, Fe and Mn in the soil profile at the Lage Hof site. Diamonds: measured geometric mean values of 12 sample dates and standard deviations as a function of the pe. Solid line: generic model. Dotted line: optimised model.
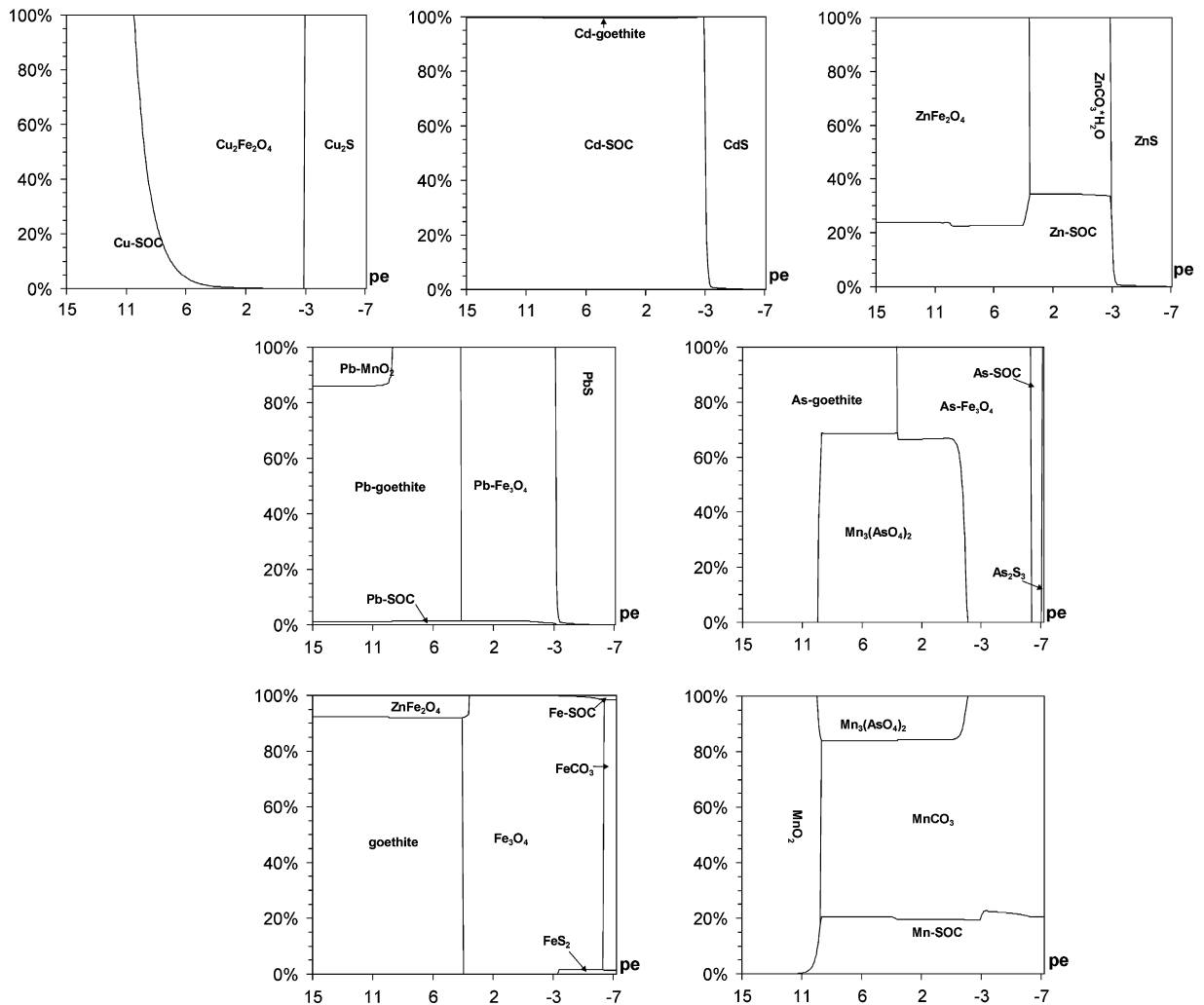
Fig. 6. Calculated distribution of Cd, Cu, Zn, Pb, As, Fe and Mn in the solid phase at the Lage Hof site.

Rhizon samplers (<0.2 μm). Which form Fe and Mn are present in pore water cannot be derived from the measurements in. But the measured concentrations in pore water can be used to calculate whether the presence as free cations or as colloids will influence the partitioning of the contaminant metals that are primarily being looking at. To test this, two additional calculations with opposing conjectures were conducted: in the first calculation, all Fe and Mn measured in pore water were assumed to be present as colloidal oxides with a specific surface area of 150 m^2 g^{-1}. In the second calculation, two extra species were defined with exactly the same sorption properties and soluble species as Fe^{2+} and Mn^{2+}. By defining no precipitation reactions for this species, the presence of large amounts of soluble Fe and Mn that are not in equilibrium with the mineral phase can be mimicked. Fig. 8 shows the results of the first calculation for Pb and As. The figures for Cd, Cu, and Zn are omitted since there was only a marginal difference with the generic model. For the second calculation, no relevant influence of soluble Fe and Mn on metal partitioning was found (data not shown).

The solid phase chemistry of Cd is clearly dominated by the adsorption to organic matter (Fig. 6). Under sulphidic conditions, Cd is immobilised by the formation of CdS and pore water concentrations decrease to concentrations close to the detection limit (6 ng L^{-1}). The model predicts an almost constant pore water concentration for pe-values larger than −3, whereas a slowly decreasing Cd concentration with increasing depth had been measured. The decrease of DOC in the profile by approximately 20% (Fig. 3), which was ignored in the calculations, can only partly explain the decrease of Cd. The contribution of Fe and Mn oxides to the binding of Cd according to the model is small (< 0.2%). Consequently, the two calculations using the measured values of Fe and Mn had barely any influence on the results (data not shown). But the surface complexation model of Tonkin et al. (2004) used in the model is known to strongly underestimate Cd binding to Mn oxides for a number of datasets. The coincidence of a second Cd peak in Fig. 3 in a soil layer where MnO$_2$ is being reduced (Fig. 6) suggests that the amount of Cd bound to MnO$_2$ was probably larger than calculated by the model.
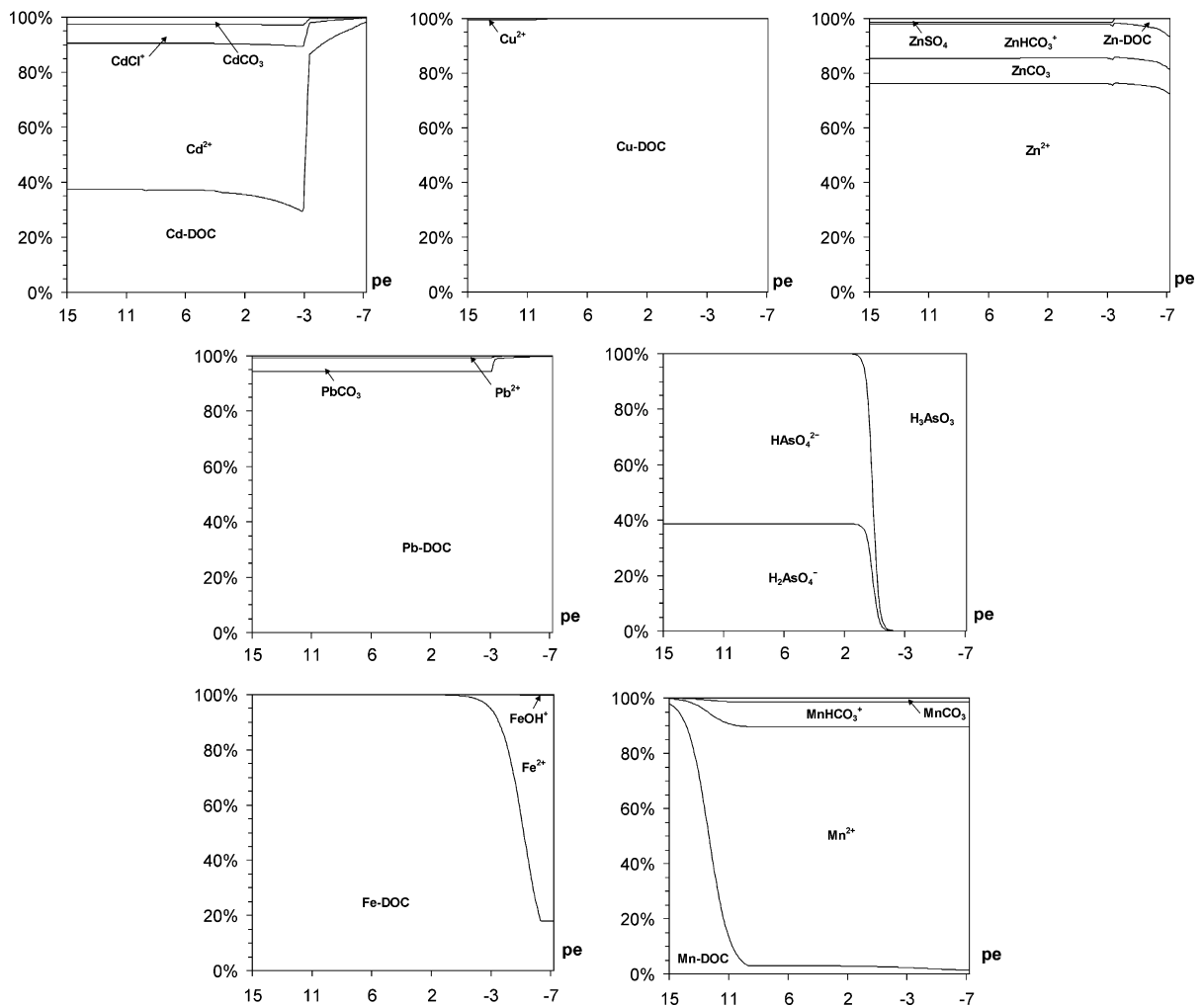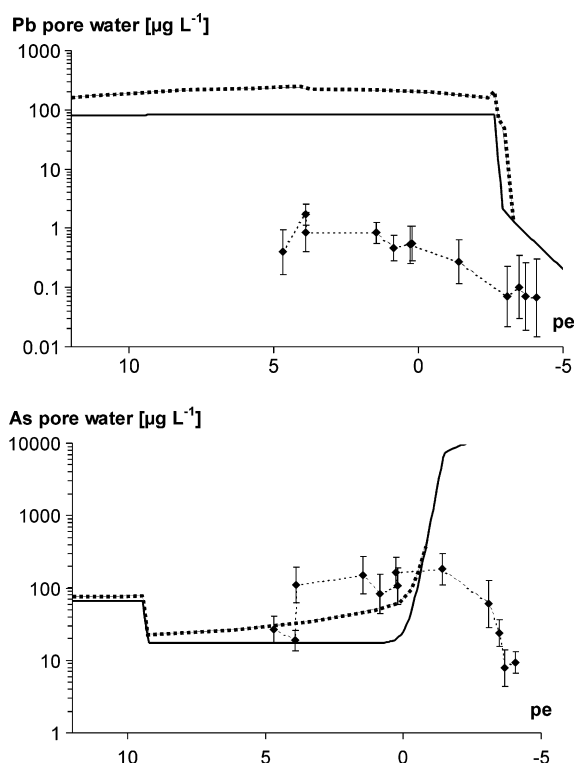
Fig. 7. Calculated distribution of Cd , Cu, Zn, Pb, As, Fe and Mn in the water phase at the Lage Hof site.

In the soil solution, DOC complexation of Cd accounts for approximately 40% of all soluble Cd, the free cation Cd^{2+} accounts for another 50%, whereas $CdCl^+$, soluble $CdCO_3$ and all other species represented less than 10% of Cd in solution (Fig. 7). At low redox potentials the concentration of Cd^{2+} decreased due to the formation of CdS, increasing therefore the fraction bound to DOC.

The pore water concentration of Cu showed a decrease by an order of magnitude by 20 cm depth (Fig. 3), previous to the other metals and clearly above the sulphidic layer (pe values of +200 mV were measured). The model explains this decrease by the presence of α-$Cu_2Fe_2O_4$ (Fig. 6). The predicted trend and the measurements agree well, but the calculated decrease of Cu concentrations appears earlier in the profile than measured. Since the Pt-electrode is known to respond poorly to the O_2 redox couple to enable a quantitative analysis (Bohn, 1968; Lindberg and Runnells, 1984), this deviation can possibly be attributed to the measurement of the redox potential itself. In the upper layer, the measured redox potential was below +300 mV, while under aerobic conditions and in equilibrium with Mn oxide conditions the expected re-

dox potential should be around +800 mV (Bartlett and James, 1993; Lindsay, 1979). The presence of colloidal Fe or Mn does not influence the concentrations to a relevant extent (data not shown). Thus the equilibrium chemistry concept may overestimate the decrease of the Cu^{2+} activity by α-$Cu_2Fe_2O_4$, but it is likely that the redox potential measured was too low. In the sulphidic zone, Cu concentration decreases further to approx. $0.6\ \mu g\ L^{-1}$, which is still an order of magnitude above the detection limit. This shows that although Cu concentrations decreases by almost two orders of magnitude, Cu was not totally immobilised as Cu_2S as expected by the model calculations. The geochemical calculation with colloidal Fe or Mn could not explain this discrepancy, however, the presence of multinuclear clusters of Cu-sulphide may explain the measured value; concentrations of several μg of soluble Cu sulphides are reported in the literature (Rozan et al., 2000).

The speciation of Cu in the solution is dominated by the presence of DOC (Fig. 7). Only a minor part is present as Cu^{2+} (<0.34%), and this fraction decreases dramatically with the appearance of α-$Cu_2Fe_2O_4$.

Pb pore water [μg L⁻¹]
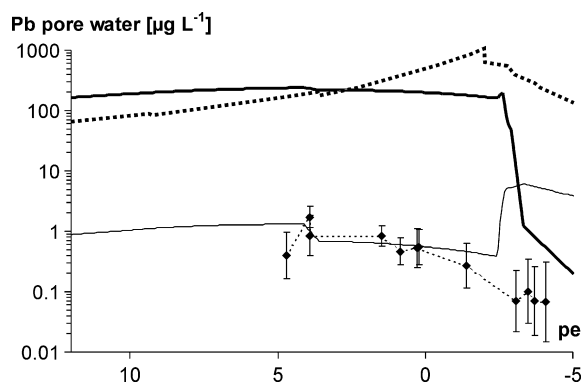

As pore water [μg L⁻¹]

Fig. 8. Calculated and measured time-averaged concentrations of Pb and As in the pore water profile at the Lage Hof site. Diamonds: measured average values and standard deviations as a function of the sample depth. Thick solid line: generic model. Dotted line: generic model, assuming all measured Fe and Mn present as colloidal oxides.

Copper is sensitive to a slight reduction of the redox potential, probably due to the formation of α-Cu$_2$Fe$_2$O$_4$. The Cu concentration may be already diminished before the peaks of Mn and Fe in pore water indicate the presence of reduced conditions. This behaviour could alter the availability of Cu even under conditions where the soil is not fully saturated, e.g. in the root zone.
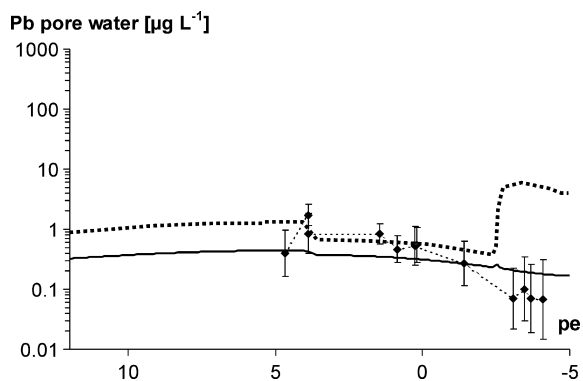
The distribution of Zn in the solid phase is dominated by minerals whereas binding to clay, Mn and Fe oxides is negligible. The two calculations based on the measured values of Fe and Mn in pore water therefore barely influence the outcome of the model (data not shown). When the modified log$K$ value for franklinite proposed in Schröder et al. (2005) was used, the Zn concentrations in the upper layers are underestimated by approximately a half order of magnitude (Fig. 5), however, the original log$K$ (Table 1) performed slightly better. At low pe, Zn is immobilised as ZnS and the soluble Zn concentrations decrease to values close to the detection limit. The distribution of Zn in the water phase is dominated by the soluble species Zn^{2+} > ZnHCO$_3^+$ > ZnCO$_3$ > ZnSO$_4$. Complexation of Zn by DOC played only a marginal role, increasing from 0.7% to 6.4% from oxic to sulphidic redox conditions.

As discussed previously in Schröder et al. (2005), the generic model can not predict the concentrations of Pb in pore water well. The decrease under sulphidic conditions is predicted well, but for a pe larger than −3 the model overpredicted the pore water concentrations by two orders of magnitude (Fig. 5). The speciation of Pb in both the solid and the solution phase is dominated by the binding to SOC and DOC (Figs. 6 and 7). In Schröder et al. (2005) a hypothetical PbPO$_4$ surface species on goethite was defined, which improved the model predictions. Fig. 5 shows that this hypothetical surface species gives good results for Pb for the entire redox range in the first instance. The distribution of Pb in the solid phase is now dominated by binding to goethite and magnetite, while the distribution in solution is comparable to Fig. 7 (data not shown). However, when the presence of colloidal Fe and Mn is taken into account, the hypothetical PbPO$_4$ species leads to Pb concentrations in pore water that were two orders of magnitude too high (Fig. 8) due to the binding of Pb to the colloidal Fe oxides. The solid–solution partitioning of organic C and Fe is comparable (Table 4 and Fig. 5), approximately 1000 L kg^{-1} and 1200–40,000 L kg^{-1} for organic C and Fe, respectively. Due to this partitioning, a shift from Pb bound to organic matter in the generic model to Pb bound to Fe oxides due to the definition of a PbPO$_4$ species can not explain the Pb concentrations found in pore water as long as significant amounts of the Fe measured in pore water are present as colloidal oxides. As discussed previously (Schröder et al., 2005), a Pb containing mineral that keeps the Pb^{2+} activity low enough to explain the results could not be found. Therefore the assumption was tested that Pb is present as a yet unknown form, labelled as PbX. A PbX mineral fixing the Pb^{2+} activity at ⩽10^{-13} M can explain the measured concentrations well also in the presence of colloidal Fe and Mn (Fig. 9). The peak of Pb concentrations at low pe was due to binding to colloidal Mn oxides. The model of Tonkin et al. (2004) did not define any complexation of Ca, Mg, or other major cations and anions for the YOH surface site, resulting in an almost complete saturation of the site by Pb. This is believed to be unrealistic given the presence of e.g. 2 mM of Ca^{2+} in solution. However, the definition of a YOCa$^+$ species with a low affinity (log$K$ = −3) is sufficient to explain the measured pore water profile within a half log scale unit (Fig. 10).

Pb pore water [μg L⁻¹]

Fig. 9. Calculated and measured time-averaged concentrations of in the pore water profile at the Lage Hof site. All model calculations assumed the presence of the measured concentration of Fe and Mn to be present as colloids. Diamonds: measured average value times and standard deviations as a function of the sample depth. Thick solid line: generic model. Thin solid line: generic model with PbX mineral phase. Dotted line: generic model with hypothetical PbPO$_4$ species on goethite.

Pb pore water [μg L⁻¹]

Fig. 10. Calculated and measured time-averaged concentrations of Pb in the pore water profile at the Lage Hof site. All model calculations assumed the presence of a PbX mineral phase and the measured concentration of Fe and Mn to be present as colloids. Diamonds: measured average times and standard deviations as a function of the sample depth. Solid line: optimised model with YOH – Ca species. Dotted line: generic model with PbX mineral phase.

The pattern of As in pore water shows an increase at a pe of 5 that was not predicted by the geochemical model (Fig. 5). However, the model predicted the As concentrations within one order of magnitude. The model used identical sorption properties for goethite and Fe_3O_4. The data of Dixit and Hering (2003) support this assumption in essence for As, however, currently a consistent dataset is lacking that comprises all relevant species to model the sorption behaviour of magnetite. The modelling of the presence of colloidal Fe in solution improved the predictions slightly above a pe of 0 (Fig. 8). The dissolution of Fe_3O_4 leads to a sharp increase of As in pore water. Since goethite and Fe_3O_4 were the only sorption sites for As defined in the model, virtually all As was soluble in the lower profile. Only a minor fraction of As was immobilised as As_2S_3 or, as uncharged H_3AsO_3 species, bound to the Donnan layer of SOC. The speciation of As at low redox potentials is still an unresolved problem. One possible sink might be the sorption of As to the edges of clay particles. Smedley and Kinniburgh (2002) proposed that Al oxides might be an important sink for As; Kinniburgh and Cooper (2004) suggest a simple model description for As sorption on $Al(OH)_3$, however a sorption model based on measured data is missing.

5. Conclusions

The 2-a monitoring of pore water profiles has resulted in a detailed picture of metal partitioning in a contaminated floodplain soil. Key parameters for the metal partitioning like the DOC concentrations or the pH showed a limited variability during the seasons. Consequently, the temporal variability of the concentrations of Cd, Cu, Zn, Pb and As is low, and the concentrations decrease in the sulphidic layer to values below the Dutch quality standards for shallow groundwater (Staatscourant, 2000). Considering the complexity of the problem, the rather simple reductionistic model predicts the solid–solution partitioning of Cd, Cu, Zn and As surprisingly well even under

changing redox conditions. Moreover, the calculations give a detailed picture of the metal(loid) speciation in soil. As a result of the large partitioning factors at the given pH, the free ion activities of most metals were too low to be measured in soil solution with the techniques available at present, but Weng et al. (2001) showed that with a comparable approach the speciation of contaminant metals in soil solution can in principle be calculated by geochemical modelling. The limitations of the equilibrium assumption are clearly visible in the case of Mn and Fe, which however did not influence the calculation results for the contaminant metals to a large extent. Metals mainly bound to organic matter were predicted better than metals predominantly present in a mineral phase. The model tends to underestimate solution concentrations in equilibrium with mineral phases in a number of cases (CdS, Cu_2S, α-$Cu_2Fe_2O_4$ and $ZnFe_2O_4$). Calibration of these $\log K$ values might be one option to improve the model, but by doing that the approach would loose its generality as a predictive tool. The integration of intermediate and more soluble Fe or sulphide phases into the model according to the Ostwald phase rule may be another option (Luther et al, 1996; Rickard and Morse, 2005; Rozan et al., 2000; Stumm and Morgan, 1996), but is beyond the scope of this study.

It is in principle possible to include in this approach the sorption of contaminant metal(loid)s to the colloidal fraction of oxides that are present in solution. This leads to a more detailed picture of the behaviour of Pb and As, but deriving surface areas of colloidal and soluble Mn and Fe by a standard procedure will be an analytical challenge. With the geochemical model, it was shown that the presence of colloids has a minor influence on the partitioning of Cd, Cu and Zn and that it improved the prediction of As. It also reveals that binding to organic matter and goethite both can not consistently explain the concentration profiles of Pb, which have been measured. In the case of the unknown sorbent for As under sulphidic conditions, it would be easy to construct a simple sorption equation that will result in a good fit of the data. However, since each mineral phase can act potentially as a sorption surface, every assumption not supported by the analytical data was omitted maintaining the concept of a fully parameterised model.

The results show that the mechanistic approach is principally useful to analyse and quantify metal partitioning in floodplain soils for risk assessment. The quality of the model results relies on the presence and quality of the thermodynamic data that is available in the literature, but integration of intermediate Fe or sulphide species may improve the model predictions. The results indicate what additional knowledge of soil chemical processes is necessary to understand the behaviour of contaminants like Pb in the environment. It enables performing of more specific experiments and judging the usefulness for further spectroscopic studies since it limits the number of potential elements and minerals of interest.

References

Allison, J.D., Brown, D.S., Novo-Gradac, K.J., 1991. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual. US EPA, Athens, Georgia.

Appelo, C.A.J., Postma, D., 1994. Geochemistry, Groundwater and Pollution. Balkema, Rotterdam, The Netherlands.

Bartlett, R.J., James, B.R., 1993. Redox chemistry of soils. Adv. Agron. 50, 151–208.

Bohn, H.L., 1968. Electromotive force of inert electrodes in soil suspensions. Soil Sci. Soc. Am. Proc. 32, 211–215.

Bruggenwert, M.G.M., Kamphorst, A., 1982. In: Bolt, G.H. (Ed.), Soil Chemistry B. Physico-chemical models. Elsevier, Amsterdam, The Netherlands, pp. 41–203.

Bruno, J., Stumm, W., Wersin, P., 1992b. On the influence of carbonate in mineral dissolution: II. The solubility of $FeCO_3$ (s) at 25 C and 1 atm total pressure. Geochim. Cosmochim. Acta 56, 1149–1155.

Bruno, J., Stumm, W., Wersin, P., Brandberg, F., 1992a. On the influence of carbonate in mineral dissolution: I. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at $T = 25\,°C$. Geochim. Cosmochim. Acta 56, 1139–1147.

Cornell, R.M., Schwertmann, U., 1996. The Iron Oxides. Structure, Properties, Reactions, Occurrence and Uses. VCH, Weinheim, Germany.

Dijkstra, J.J., Meeussen, J.C.L., Comans, R.N.J., 2004. Leaching of heavy metals from contaminated soils: an experimental and modelling study. Environ. Sci. Technol. 38, 4390–4395.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. Environ. Sci. Technol. 37, 4182–4189.

Farley, R.A., Fitter, A.H., 1999. Temporal and spatial variation in soil resources in a deciduous woodland. J. Ecol. 87, 688–696.

Ford, R.G., Sparks, D.L., 2000. The nature of Zn precipitates formed in the presence of pyrophyllite. Environ. Sci. Technol. 34, 2479–2483.

Gustafsson, J.P., Pechová, P., Berggren, D., 2003. Modelling metal binding to soils: the role of natural organic matter. Environ. Sci. Technol. 37, 2767–2774.

Hesterberg, D., Bril, J., Del Castilho, P., 1993. Thermodynamic modelling of zinc, cadmium, and copper solubilities. J. Environ. Qual. 22, 681–688.

Hiemstra, T., Van Riemsdijk, W.H., 1996. A surface structural approach to ion adsorption: the charge distribution (CD) model. J. Colloid Interface Sci. 179, 488–508.

Houba, V.J.G., Van der Lee, J.J., Novozamsky, I., 1997. Soil and Plant Analysis. Part 5B; Sub-department of Soil Quality. Wageningen University, Wageningen, The Netherlands.

International Organization for Standardization (ISO), 1992. ISO 10304-1. Water Quality – Determination Of Dissolved Fluoride, Chloride, Nitrite, Orthophosphate, Bromide, Nitrate and Sulphate Ions, Using Liquid Chromatography of Ions. Part 1: Method for Water with Low Contamination. ISO, Geneva, Switzerland.

Kinniburgh, D.G., Cooper, D.M., 2004. Predominance and mineral stability diagrams revisited. Environ. Sci. Technol. 38, 3641–3648.

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

Kuipers, S.F., 1984. Bodemkunde, Educaboek, Culemborg, The Netherlands.

Lindberg, R.D., Runnells, D.D., 1984. Ground water redox reactions: an analysis of equilibrium state applied to Eh measurements and geochemical modeling. Science 225, 925–927.

Lindsay, W.L., 1979. Equilibria in Soils. John Wiley & Sons, New York.

Linehan, D.J., Sinclair, A.H., Mitchell, M.C., 1989. Seasonal changes in Cu, Mn, Zn, and Co concentrations in soil in the root-zone of barley (*Hordeum vulgare* L.). J. Soil Sci. 40, 103–115.

Lofts, S., Tipping, E., 1998. An assemblage model for cation binding by natural particulate matter. Geochim. Cosmochim. Acta 62, 2609–2625.

Luther III, G.W., Rickard, D.T., Theberge, S., Olroyd, A., 1996. Determination of metal (bi)sulfide stability constants of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} by voltametric methods. Environ. Sci. Technol. 30, 671–679.

Meeussen, J.C.L., 2003. ORCHESTRA: an object-oriented framework for implementing chemical equilibrium models. Environ. Sci. Technol. 37, 1175–1182.

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

Nederlands Normalisatie-instituut, 1992. NEN 6465. Monstervoorbehandling van slib, slibhoudend water, luchtstof en grond voor de bepaling ven elementen met atomaire-absorptiespectrometrie. Ontsluiting met salpeterzuur en zoutzuur, second ed. Nederlands Normalisatie-instituut, Delft, The Netherlands.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's Guide to PHREEQC (Version 2). US Geol. Surv. Water-Resour. Invest. Rep. 99-4259.

Preis, W., Gamsjäger, H., 2001. (Solid + solute) phase equilibria in aqueous solution. XIII. Thermodynamic properties of hydrozincite and predominance diagrams for ($Zn^{2+} + H_2O + CO_2$). J. Chem. Thermodyn. 33, 803–819.

Rickard, D., Morse, J.W., 2005. Acid volatile sulfide (AVS). Marine Chem. 97, 141–197.

Römkens, P.F.A.M., Dolfing, J., 1998. Effect of Ca on the solubility and molecular size distribution of DOC and copper-binding on soil solution samples. Environ. Sci. Technol. 32, 363–369.

Rozan, T.F., Lassmann, M.E., Ridge, D.P., Luther II, G.W., 2000. Evidence for iron, copper and zinc complexation as multinuclear sulphide clusters in oxic rivers. Nature 406, 879–882.

Schachtschabel, P., Blume, H.P., Brümmer, G., Hartge, K.H., Schwertmann, U., 1992. Lehrbuch der Bodenkunde, 13th ed. Enke, Stuttgart, Germany.

Schröder, T.J., Hiemstra, T., Vink, J.P.M., Van der Zee, S.E.A.T.M., 2005. Modelling of the solid–solution partitioning of heavy metals and arsenic in embanked floodplains of the rivers Rhine and Meuse. Environ. Sci. Technol. 39, 7176–7184.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568.

Staatscourant, 2000. Circulaire streefwaarden en interventiewaarden bodemsanering, nr. 39. The Hague: Stadblad van het Koningrijk der Nederlanden.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry, third ed. John Wiley & Sons, New York.

Tipping, E., 1993. Modelling ion binding by humic acids. Colloids Surf. A 73, 117–131.

Tipping, E., 2002. Cation Binding by Humic Substances. Cambridge University Press, Cambridge, UK.

Tonkin, J.W., Balistieri, L.S., Murray, J.W., 2004. Modelling sorption of divalent metal cations on hydrous manganese oxide using the diffuse double layer model. Appl. Geochem. 19, 29–53.

Venema, P., Hiemstra, T., Van Riemsdijk, W.H., 1996. Multisite adsorption of cadmium on goethite. J. Colloid Interface Sci. 183, 515–527.

Wallinga, I., Kithome, M., Novozamsky, I., Houba, V.J.G., Van der Lee, J.J., 1992. Spectrophotometric determination of organic carbon in soil. Commun. Soil Sci. Plant Anal. 23, 1935–1944.

Weng, L., Temminghoff, E.J.M., Van Riemsdijk, W.H., 2001. Contribution of individual sorbents to the control of heavy metal activity in sandy soil. Environ. Sci. Technol. 35, 4436–4443.

Wolthoorn, A., Temminghoff, E.J.M., Weng, L., Van Riemsdijk, W.H., 2004. Colloid formation in groundwater: effect of phosphate, manganese, silicate and dissolved organic matter on the dynamic heterogeneous oxidation of ferrous iron. Appl. Geochem. 19, 611–622.