Solid-solution partitioning of heavy metals in floodplain soils of the rivers Rhine and Meuse: Field sampling and geochemical modelling

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Abstract

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In the last century large amounts of heavy metals have accumulated in the embanked river floodplain areas of the Netherlands. Since the disposal of these contaminated sediments is costly, there is a need to understand more about the environmental risks that are linked to the presence of heavy metals in these soils.

In this study, the solid-solution partitioning of Cd, Cr, Cu, Ni, Pb, Zn and As in floodplain soils of the Dutch part of the rivers Rhine and Meuse is assessed by combining extensive field sampling with advanced geochemical modelling. The aim of this study was threefold: to develop tools to study the solid-solution partitioning of the heavy metals, to characterise the temporal and spatial variability of the partitioning including the effect of redox conditions, and to investigate the feasibility to predict the partitioning by geochemical modelling.

In a semi-field lysimeter containing a sandy soil with increasing Zn contents, pore water was collected *in situ* periodically during the growing season using Rhizons[®]. The pH and the Zn concentrations were affected by the precipitation pattern and the plant species growing on the plots. A geochemical model, fully parameterised by literature data, was able to predict the Zn concentrations within ±0.5 log-scale. The Zn^{2+} activity was mainly influenced by pH, whereas the total amount of Zn in soil had only a minor effect. For the modelling of Zn, generic average concentrations of dissolved organic carbon (DOC) and Ca in pore water were sufficient.

To characterise the concentrations of As, Cd, Cu, Ni, Pb, Zn, Mn, Fe, Ca, Cl and DOC in contaminated river floodplain soils, pore water was collected *in situ* three times during a year at 46 locations within the Dutch part of the Rhine and Meuse river systems. The concentrations of Cd, Cu, Ni and Zn in pore water varied by less than a half log-unit between the seasons. Metal concentrations extracted by 2.5 mM $CaCl_2$ showed a surprisingly good agreement with the pore water concentrations, and systematic differences between both methods can be explained by differences in pH and DOC concentrations. The extraction by $CaCl_2$ is a good measure to estimate the solid-solution partitioning of heavy metals in pore water, avoiding the problems of temporal variability.

To test the possibility to predict heavy metal partitioning by a geochemical model, 194 soil samples were collected at 133 floodplain sites. A strong correlation was found between the contamination by As, Cd, Cu, Cr, Ni, Pb and Zn and the organic matter content. Cu and Cd extractable by 2.5 mM $CaCl_2$ was predicted within one log-unit, whereas modelling of Zn and Pb needs adjustment of some model parameters. A statistical model, based on a small number of standard parameters, could describe the extractable metal concentrations within 0.32 log-units.

In a heavily contaminated river floodplain soil, pore water was collected 12 times *in situ* in a profile ranging from aerobic to sulphidic redox conditions. The concentrations of As, Cd, Cr, Cu, Pb, Zn, Mn, Fe, Ca, Cl, SO_4, DOC, IOC and the pH were measured. The variability of pH, IOC, DOC and Ca was found to be rather small during the year and within the profile. The temporal variability of the metal concentrations was small, too, whereas

changes with depth were distinct. The general patterns of Cd, Cu, Zn and As in the profile could be predicted well by mechanistic geochemical modelling. Metals strongly bound to organic matter were predicted better than metals mainly present as a mineral. The chemical behaviour of Pb is still not understood sufficiently.

To study the uptake of heavy metals, 119 plant samples from 28 different species were collected on 36 floodplains. The concentrations of Cd, Cu, Fe, Ni, Pb, Ti and Zn were measured. Differences in metal uptake were rather small between the plant samples, but significant seasonal differences in Cu uptake were found for several plants. For a number of plants, metal uptake was significantly correlated with the total amount or the metal fractions extractable 2.5 mM $CaCl_2$. Distinguishing four plant groups (monocotyls, leguminosae, willows and other dicotyls) resulted in a small enough intra-group variation to enable risk assessment of plant vegetation.

Geochemical modelling is found to be a useful tool for the investigation and understanding of metal availability in river floodplain soils. It is less precise than the applied statistical model but can be used for sensitivity analysis, to locate gaps in understanding, and to design further experimental studies or sampling campaigns.

Contents

Chapter 1

Introduction

1.1 The Rhine and Meuse river system

The Rhine and Meuse rivers are large European river systems covering several countries. Figure 1 shows the catchment area of the rivers Rhine and Meuse with a surface area of approximately 200,000 km^2. The river Rhine is 1320 km long and has its source in Switzerland. On its way to the North Sea, it passes through or along six European countries. Shortly after the Rhine enters the Netherlands, it splits up in three branches: the Waal, the IJssel and the Lower Rhine (Figure 2). The Waal is the major branch of the Rhine, transporting two-thirds of all water. The major outlet to the North Sea is the Nieuwe Merwede, a channel at the northern border of the Biesbosch area. The IJssel is the most northern branch that discharges in Lake IJssel. The Lower Rhine is the smallest branch, transporting only one-ninth of the Rhine water. Several locks regulate the water discharge and after it passes the Amsterdam-Rhine-channel, it is renamed into Lek. The river Meuse has a total length of 950 km and has its source in France. With a length of 300 km it is the longest river in the Netherlands, entering the country in the south and turns west close to Nijmegen, whereafter it is flows parallel to the Waal and Lower Rhine. Before it enters the North Sea, the Maas (now named Amer), joins with the Nieuwe Merwede.

FIGURE 1. Catchment area of Rhine and Meuse

The rivers Rhine and Meuse differ in several hydrological characteristics. The average water discharge of the Rhine is approximately ten times larger than the discharge of the Meuse (2200 m^3 s^{-1} and 230 m^3 s^{-1}, respectively). The water discharge of the river Rhine is the largest between January and April and the peak flow can be a factor of 10 larger than the average discharge. The discharge of the river Rhine is influenced by rainfall and snow melting in the Alps, whereas the river Meuse is an entirely rain-fed river.

FIGURE 2. Rhine and Meuse

Higher discharge results in an increase of the water level. Figure 3 shows the averaged and maximum water level of the Rhine and Meuse between 1990 and 2000, measured close to the Dutch border. In winter and spring season, the water level of the Rhine can rise by 5 m (Figure 3). The peaks in the Meuse river are smaller and usually have shorter intervals. Several locks in the Meuse keeps the water level constant in summer, whereas in the rivers Waal and IJssel locks are only present at the outlet to the North Sea.
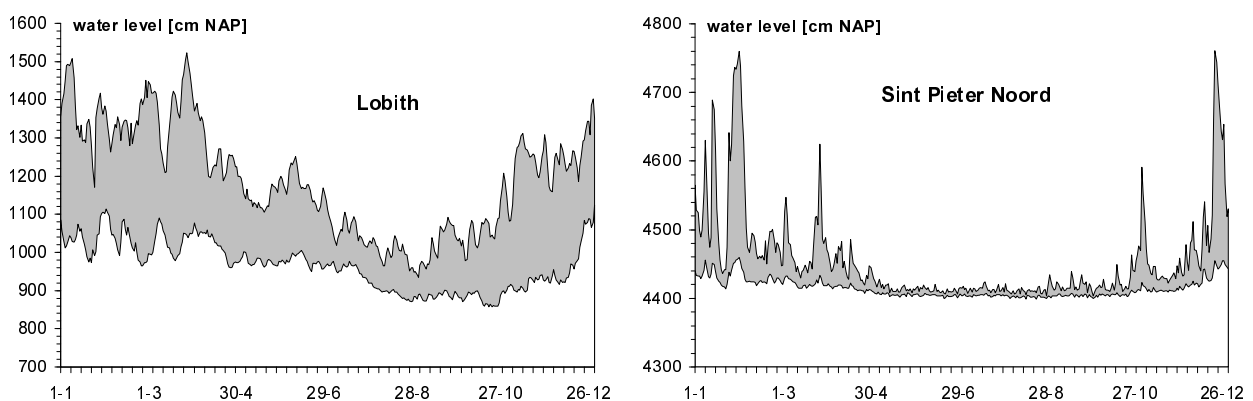
FIGURE 3. Ten-year average and maximum water level of the Rhine at Lobith and the Meuse at Maastricht. NAP is the Dutch reverence mean sea level (Source: Rijkswaterstaat)

Large parts of the Netherlands are situated below the mean sea level, and without protection by dikes more than 65% of the area would be flooded at high river water levels and high sea levels. Both rivers therefore constitute a severe threat of flooding. In the last nine centuries, tremendous efforts were done to protect the Netherlands against flooding. Except in the southern part of the Netherlands, the rivers are usually embanked by dikes. To be able to handle the large amount of water in the winter periods, the floodplain areas that surround the rivers are essential.
(Huisman et al., 1998; Middelkoop, 1997; Middelkoop, 1998, Van de Ven; 1996)

1.2 Floodplains

The floodplains cover an area of approximately 500 km^2 and are accessible during the larger part of the year, usually from April until December. Most floodplains are protected against smaller water peaks by a second, minor dike close to the river itself (Figure 4). The major part of the floodplain area is used for grazing cattle, but floodplains are also used for many other purposes (e.g. arable land, mining of clay and gravel, recreation, natural habitats).
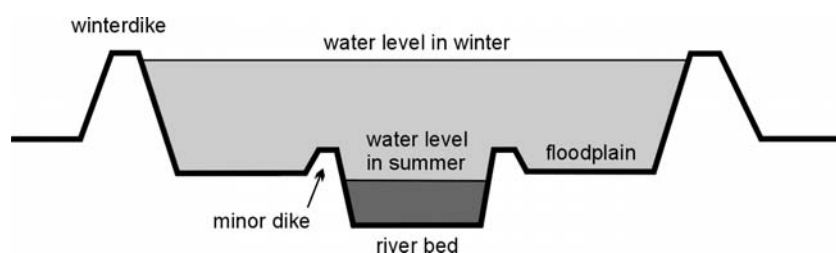
FIGURE 4. Typical shape of a floodplain. The minor dikes surround the rivers during the larger part of the year. At high water levels, the floodplains get flooded, which lead to an increased discharge area of the river

1.3 River contamination

Both Meuse and Rhine pass heavily industrialised countries with substantial industrial activities along the rivers, e.g. coal mining, steelworks and chemical industry. During the last century, enormous amounts of organic contaminants and heavy metals were emitted to the rivers. Förstner (1974) estimated, that in 1970 700 kg of Cd was emitted to the river Rhine, equivalent to 4% of the worlds total cadmium production. Also large amounts of other metals were drained off (Table 1). With the river water, approximately 3 million tons of sediments enters the Netherlands via the Rhine river every year, and about half of these sediments are deposited within the river system. Together with the sediments, large amounts of heavy metals were deposited in riverbeds, harbours, lakes and the delta areas of the Rhine and Meuse river systems. Parts of the contaminated sediments were deposited in the floodplain area. Middelkoop and Asselman (1998) estimated, that during the flooding

in 1993 7.7% of the annual sediment load was deposited in the floodplain area of the river Waal. However, sedimentation is a complex process, and the composition and amount of the deposited material can vary spatially and temporally (Asselman and Middelkoop, 1998).

TABLE 1. Estimated heavy metal emission to the river Rhine in 1970 (Förstner and Müller, 1974)

metal	amount emitted [t y^{-1}]	% of world production
Cd	15,000	4
Cr	1,700,000	0.2
Cu	6,400,000	0.1
Hg	10,000	1.2
Ni	500,000	0.4
Pb	3,500,000	0.1
Zn	4,600,000	1

In the sedimented layers of the floodplains, an increase of the concentrations of heavy metals since the beginning of the last century was measured. The highest concentrations of Cu, Zn and Pb were found to be deposited in the 1930s, and after a decrease during the Second World War a second peak is found in the 1960s (Middelkoop, 1997). In the last three decades, many effective measures were taken to reduce the emissions. Table 2 shows the annual metal load of the Rhine river between 1972 and 1993.

TABLE 2. Metal load of Rhine at the Dutch border (Huisman et al., 1998)

metal	1972	1985	1993
Cd [t y^{-1}]	167	9	2.8
Cr [t y^{-1}]	3,627	378	251
Cu [t y^{-1}]	2,018	473	314
Hg [t y^{-1}]	99	5	2.5
Ni [t y^{-1}]	*n.d.*	356	219
Pb [t y^{-1}]	2,000	441	346
Zn [t y^{-1}]	13,800	2,995	1,724

An important turning point in public awareness of the environmental problems connected to the river pollution was the Sandoz accident in Basel in 1986, where 30 tons of toxic waste, containing Hg and fungicides, entered the Rhine and killed approximately 500,000 fish. In 1950, the International Commission for the Protection of the Rhine (ICPR) was founded. Since environmental awareness growed only slowly, it took several decennia before effective measures where taken to control the emissions to the Rhine and Meuse

rivers. 1976, the first contract was signed by the littoral states of the river Rhine to reduce the emissions. Between 1972 and 1993, the amounts of heavy metals entering the Netherlands via the Rhine were reduced by more than 80% (Table 2).

However, pollution control is an important but not the only motive for international cooperation in the field of river management. The ICPR (2004) defines their targets as:

- Sustainable development of the entire Rhine ecosystem
- Guarantee the use of Rhine water for drinking water production
- Improvement of the sediment quality in order to enable the use or disposal of dredged material without causing environmental harm.
- Overall flood prevention and environmentally sound flood protection
- Improvement of the North Sea quality in accordance with other measures aimed at the protection of this marine area.

1.4 River protection and management

The rivers and the accompanying floodplains undergo continuous changes, not only due to natural sedimentation but also due to different demands and insights on the river management. Safety against flooding is clearly the most important aspect, but competing interests and the definition of new aims urge the need to reshape the river systems. The rivers are important waterways and 50% of all transboundary transport is carried out via these waterways. They also play an important role in the supply for drinking water, industrial and cooling water and in preventing the intrusion of brackish water from the North Sea. In addition, the role of the floodplain areas as a natural habitat plays a prominent role in the last decades.

The project "Maaswerken" aims to enlarge the discharge area of the river Meuse over a length of 170km to reduce flood risk, improve navigation, and develop natural areas (Hakstege et al., 1998; Provinvie Limburg, 1998). Several projects aspire to reinstall secondary channels and create different topologies of the water - soil interface (e.g. Posthoorn, 1998; Van der Perk, 1998). "Space for the rivers" ("Ruimte voor rivieren") is an ambitious project that strives to combine flood prevention with rehabilitation of old secondary channels of the Rhine branches (Silva et al., 2000). In 2001, the "Rhine 2020" act was signed, which aims to rehabilitate and protect the ecological functions of the river system, mainly by reactivation of the former network of habitats typical for the Rhine. The latest challenge in river management is to cope with the increasing sea level by the greenhouse effect: expert commissions expect a raise of sea level by 60 to 100 cm during the next century (Houghton et al., 2001).

For the management of the river systems it can be necessary to alter the river topology. A few examples of projects have been given in the previous section. In most cases, this results in moving or removing of sediment layers in the floodplains. Therefore the projects for river restoration and rehabilitation or flood protection have to consider the presence of contaminated sediments. The amounts of sediments that are affected are often large and can have a great impact on the costs of these projects: the cleaning of floodplain sediments

contaminated by heavy metals is not feasible at the moment and storing in landfill sites is costly.

The 4th *Nota waterhuishouding* (1998) therefore stimulates the reuse of slightly contaminated sediments within the river system, when this will not be harmful or hazardous. The question whether there is a potential or actual risk connected to contaminated floodplain sediments is a complex one. Therefore there is a urgent need to understand more about the environmental risks that are linked to the heavy metal contamination of floodplain soils.

1.5 Risk assessment of heavy metal contamination

1.5.1 Availability of metals

The simplest measure to judge a risk is the total amount of heavy metals present in soil. Environmental regulations of many countries are based on total amounts (Visser, 1993), but in risk assessment there is a general agreement that the "intensity" or "availability" of metals is more important than the total amount present in soils (Van Gestel, 1997; Gupta et al., 1996).

Many studies are done to quantify these "available" or "bioavailable" metal fractions, however, the "availability" of a metal in soil depends also on the plant or organism and is therefore not a unambiguous property of a soil. Therefore, several methods are used to quantify or link the available fractions of metals in soil with uptake in plants or organisms. A simple and successful tool to measure the "available" fraction of metals in soil is the use of "weak" extractants, e.g. 0.01 M $CaCl_2$, which was found to be strongly correlated with the uptake by plants (Sanders et al., 1987; Smilde et al., 1992; Van Erp et al., 1998).

The advantage of extractions is that they are easy to apply. But even if a strong correlation is present between extractable metals and uptake by plants, it can often not be related explicitly to the chemical composition and speciation of the soil or soil pore water itself. Therefore the suitability to extrapolate these results to other soil systems or other plants species or organisms is limited. Furthermore, by using soil extractions to assess the availability of metals, several features important for floodplain soils are lost. Extractions generally do not provide information about the temporal variability present under natural conditions. Due to the sample treatment, the redox condition of the soil samples can not be preserved.

Thus extractions may be well correlated with uptake, but the link with the solid phase and pore water chemistry is unclear.

1.5.2   Solid-solution partitioning

The solid-solution partitioning is a measure that links the amount in soil with the amount in solution by a partitioning coefficient

$$K_p \left[L \ kg^{-1} \right] = C_{soil} \Big/ C_{solution}$$ (Equation 1)

with C_{soil} the total concentration in soil and $C_{solution}$ the concentration in solution, ideally in pore water. This concept is successful applied in the risk assessment of organic contaminants, were the K_p value is a constant property of a compound. In contrast, for heavy metals the K_p value can vary to a large extent (Anderson and Christensen, 1988; Sauvé et al., 2003; Sauvé et al., 2000a). The reason is that, unlike for many organic contaminants, the amount of sorption sites that can bind cations or anions is limited and competition by other components is therefore essential. This also explains the strong pH dependency of the metal concentrations in solution. Moreover, heavy metals can form mineral phases. If a mineral is present in a system, it will tend to maintain a constant activity of the components. Thus, as long as a component *A* is constant, a mineral *AB* will keep the soluble concentration of a heavy metal *B* constant, too, independent from the total amount of the heavy metal *B* present in the system. Both, competition for sorption and mineral formation explains why the partitioning coefficient K_p will in most cases not be a constant (Sauvé et al., 2003).

Since the presence of sorption sites and the pH are usually the key factors for the metal behaviour in soil, often Freundlich- or Langmuir-type of functions are used to describe the partitioning of heavy metals (Lee et al., 1996; Oakley et al., 1981; Strawn and Sparks, 2000). Furthermore, to account for the sorption on more than one surface, these functions can be extended to multiple site functions (Anderson and Christensen, 1988; Degryse et al., 2003; Elzinga et al., 1999; Impellitteri et al., 2003; Janssen et al., 1997; Otte et al., 1999; Sauvé et al., 2000b).

These kind of functions are easy to fit and often describes a limited dataset well, but they are counterintuitive in a sense that the parameters that are fitted for a certain surface not necessarily give any information on the relevance of this surface on metal binding. Furthermore, the non-linearity introduced by the presence of sorption processes and mineral phases can also make it difficult to describe a dataset sufficiently by a linear combination of equations (Vulava et al., 2000).

More elaborated functions are presented in literature to enhance the applicability of this approach (Wang et al., 1997), however, the most convenient way to describe the complex interactions of sorption, speciation and mineral formation is by geochemical modelling.

1.5.3   Geochemical modelling in risk assessment

A major advantage of geochemical modelling is that it not only can be used to derive the solid-solution partitioning of heavy metals, but also can calculate the activity of an individual metal species. This can be useful when the uptake of a metal by a plant or an organism or toxic effects to theses should be studied in greater detail (Ge et al., 2002; Turner, 1995; Twiss et al., 2001; Vulkan et al., 2005).

The combination of metal speciation modelling 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 plants and organisms, can give useful insight in mechanisms and uptake behaviour in well-defined aquatic systems or nutrient solutions (Cambell, 1995; Di Toro et al., 2001; Janssen, et al., 2003; Paquin et al., 2002; Parker et al., 2001; Santore et al., 2001; Smiejan et al., 2003; Slaveykova and Wilkinson, 2002). Nevertheless, this approach is difficult to apply in soil systems. In the past, geochemical modelling of metals in soil systems led to unsatisfying results because of the lack of elaborate models that were able to describe adsorption processes to the soil matrix (Hesterberg et al., 1993; Mouvet and Bourgh, 1983). Several studies made use of Freundlich-type of sorption models, which were successful in fitting the experimental data (Römkens and Dolfing, 1998; Temminghoff et al., 1998; Tye et al., 2003). However, to be able to predict metal concentrations in pore water rather than matching measured data, we need sorption models in which all necessary parameters are known in advance. Recent improvements in sorption modelling makes it possible to study the complexation of metals by dissolved or soil organic matter (Kinniburgh et al., 1999; Milne et al., 2003; Tipping, 1993) or iron oxides (Hiemstra and Van Riemsdijk, 1996; Venema et al., 1996) in detail. These models describe metal sorption on molecular scale, taking into account the effects of pH, competition, ionic strength and background electrolyte on the metal binding. Several sorption models can be combined to describe the sorption in a complex soil system (Dijkstra et al., 2004; Lofts and Tipping, 1998). Weng et al. (2001) showed that integration of these sorption models to a multisurface model could successfully explain the speciation of a number of metals in soil.

However, a geochemical model that combines state-of-the-art sorption modelling, mineral formation and redoxchemistry to calculate the partitioning of several metals simultaneously under natural conditions, is to our knowledge never published before.

1.6 Aim and outline of this thesis

In this thesis we present the results of our study on the chemical behaviour of Cd, Cr, Cu, Ni, Pb, Zn and As in floodplain soils of the Dutch part of the river Meuse and the three branches of the river Rhine. We combined extensive field sampling with advanced geochemical modelling and assessed the usefulness of this tool to understand and predict metal behaviour in soil.

The aim of this study was threefold:
- to develop tools to study the solid-solution partitioning of heavy metals and As in river floodplain soils for the risk assessment
- to characterise the solid-solution partitioning of heavy metals and As in the floodplain soils of the river Meuse and the three branches of the river Rhine including the temporal and spatial variability and the effect of the redox condition on the partitioning
- to investigate the feasibility to analyse and predict the solid-solution partitioning of heavy metals and As by geochemical modelling

To do this, the following approach was followed during this study:
1. Acquisition of field data: the solid-solution partitioning of heavy metals in soil was quantified and the parameters influencing the partitioning were elaborated
2. Monitoring of temporal variability: the variability of the metal partitioning under natural conditions and the parameters influencing the metal partitioning were assessed
3. Developing of a geochemical model: the parameters and processes relevant for the modelling of the solid-solution partitioning of heavy metals were identified
4. Comparing modelling results and field data: the heavy metals that can be described by geochemical modelling were evaluated and the suitability of geochemical modelling as a tool to predict the partitioning was tested. Gaps in understanding or thermodynamic data were identified

Chapter 2 summarises a case study to test a method to sample pore water repeatedly *in situ* with minor disturbance to the soil system. The main focus of this case study was to find out if pore water is a good starting point for the risk assessment and if geochemical modelling is able to predict the pore water partitioning of heavy metals in a soil system under natural conditions. At the same time, data on the spatial and temporal variability of Zn and other parameters influencing the metal speciation were collected. The geochemical model that is presented was fully parameterised by literature data and included speciation, mineral formation and advanced sorption modelling. The modelling results were compared with the measured concentrations of Zn and the influence of several parameters on the modelling outcome was tested.

In Chapter 3, we compare two methods to assess the solid-solution partitioning in floodplain soils. A weak extraction by 2.5 mM $CaCl_2$ was used as an efficient method to approximate the pore water composition in floodplain soils. The method was compared with pore water sampled *in situ* at 46 location in the floodplains of the river Meuse and the three branches of the river Rhine. To estimate the seasonal variability of the pore water composition, pore water was sampled in spring, summer and autumn. The influence of Ca, Cl, DOC and the pH on the solid-solution partitioning of heavy metals was assessed. Both methods were compared and the use of both methods for risk assessment is discussed.

In Chapter 4, we summarise the outcome of a large sampling campaign comprising almost 200 samples from 133 sample points in floodplains covering the entire Dutch part of the river Meuse and the three branches of the river Rhine. The soluble fraction of metals and other parameters were measured by an extraction with 2.5 mM $CaCl_2$. Several characteristic properties of floodplain soils were elaborated from this dataset to derive a simplified input for the geochemical model calculations. The geochemical model of Chapter 2 was extended to predict the solid-solution partitioning of As, Cd, Cu, Pb and Zn in floodplain soils. The modelling results are compared with the metals extractable by 2.5 mM $CaCl_2$.

In Chapter 5, we focus on the influence of the redoxchemistry on heavy metal partitioning. Pore water was monitored for two years *in situ* in a redoxsequence from aerobic to sulphidic with a high spatial resolution. The geochemical model of the previous chapter is extended to cope with the redoxchemistry of metals. Again, we compared modelling results and measurements and discussed the applicability of the model.

In Chapter 6, we assess the uptake of heavy metals by a plant vegetations. The total amounts of Cd, Cu, Ni, Pb and Zn and the extractable fractions of these metals were

compared with the uptake by 28 different plant species. The temporal and spatial variability of the plant uptake was assessed and the differences in uptake between the plant species.

The results of the previous chapters are summarised and integrated in Chapter 7. A general overview of the metal contamination in the river floodplain soils is outlined and the methods to assess the solid-solution partitioning are discussed. The usefulness of these methods for risk assessment is discussed and consequences for the risk assessment were considered.

Chapter 2

In situ monitoring and modelling of the solid-solution partitioning of zinc in a lysimeter with different plant covers

2.1 Introduction

Relating metal speciation with uptake by plants and other organisms is one of the key problems in the risk evaluation of heavy metal contamination of the environment. Often denoted as *availability* or *bioavailability*, the link between metal contamination and uptake consists of a sequence of several processes (Peijnenburg et al., 1997; Pinheiro and van Leeuwen, 1999; Slaveykova and Wilkinson, 2002; Van Leeuwen, 1999). Depending on system properties, any of these processes can be limiting for the heavy metal uptake. The combination of metal speciation modelling 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 behaviour in well-defined aquatic systems or nutrient solutions (Di Toro et al., 2001; Parker et al., 2001; Santore et al., 2001; Smiejan et al., 2003; Slaveykova and Wilkinson, 2002), even if it fails to fully explain the uptake patterns (Hassler and Wilkinson, 2003; Hudson, 1998; Miramanoff and Wilkinson, 2000; Vink, 2002). However, the understanding of metal uptake in the complex system of soil rhizosphere still presents a major challenge in ecotoxicology.

An alternative to mechanistic modelling of metal speciation is the use of "weak" extractants, e.g. $CaCl_2$ (Sanders et al., 1987; Smilde et al., 1992; Van Erp et al., 1998) or metal ligands, e.g. DTPA (Singh and Narval, 1984), which supposedly mimics pore water composition or could represent the potential bioavailable fraction. These methods try to elucidate the available fraction in soil systems and are quite successful in describing metal uptake by organisms. But even if a strong correlation is present between extractable metals and uptake by organisms, it can often not be related explicitly to the chemical composition and speciation of pore water itself. Therefore the suitability to extrapolate these results to other soil systems or other organisms is limited. Furthermore, this method does not account for the temporal variability of pore water composition that occurs under field conditions (Del Castilho et al., 1993; Denaix et al., 2001; Farley and Fitter, 1999; Linehan et al., 1985; Linehan et al., 1989).

Even without understanding the precise mechanism of metal uptake by organisms, there is a general agreement that uptake behaviour is related to particular fractions of metals in pore water rather than the total concentration in soil (Campbell, 1995; Gerritse et al., 1983; Parker and Pedler, 1997; Sauvé et al., 1996; Shan et al., 2003). Therefore, the sampling of pore water can be a useful starting point to elucidate the link between metal content of soil and uptake in organisms. When pore water sampling is linked with geochemical modelling, two problems can be addressed simultaneously: pore water concentrations can be predicted from routinely measured soil properties and the distribution of metals in pore water over various species can be calculated and linked with the uptake in plants and organisms.

In the past, geochemical modelling of metals in soil systems led to unsatisfying results because of the lack of elaborate models that were able to describe adsorption processes to the soil matrix (Hesterberg et al., 1993). Several studies made use of Freundlich-type of sorption models, which were successful in fitting the experimental data (Temminghoff et al., 1998; Römkens and Dolfing, 1998). However, to be able to predict metal concentrations in pore water rather than matching measured data, we need sorption models in which all necessary parameters are known in advance. Recent improvements in sorption

modelling makes it possible to study the complexation of metals by dissolved or soil organic matter (Tipping 1993, Kinniburgh et al., 1999; Milne et al., 2003) or iron oxides (Hiemstra and Van Riemsdijk, 1996; Venema et al., 1996) in detail. These models describe metal sorption on molecular scale, taking into account the effects of pH, competition, ionic strength and background electrolyte on the metal binding. Weng et al. (2001) showed that integration of these sorption models into a multisurface model could successfully explain the speciation of a number of metals in soil.

Besides metal sorption by the solid phase, in the last decades attention focussed on the importance of metal binding by dissolved particles (e.g. Reddy et al., 1995). Dissolved organic carbon (DOC) is a key factor to understand speciation and transport of a number of metals, e.g. Cu, Cd or Zn (Hesterberg et al., 1993; Weng et al., 2002a). One possible difficulty for the application of sorption models is the lack of simple methods to character-ise DOC in terms of particle size and concentration of binding sites: what usually is denoted as DOC, is in fact a poorly characterised heterogeneous mixture of organic compounds from different origins (Jones, 1998). In recent years, research has been conducted on size fractionation (Burba et al., 2001; Christl et al., 2001), coagulation behaviour (Weng et al., 2002b) and sorption behaviour (Filius et al., 2000; Tipping, 1981; Van de Weerd et al., 1999) of humic or fulvic acids in soil system. Nevertheless, a conclusive quantitative model description of DOC in terms of composition and soil-water partitioning is not available. To be able to calculate the solid-solution partitioning of metals in a soil system, measurement of DOC is therefore the best option, even when the fraction of fulvic and humic acids cannot be derived unambiguously.

In this paper, we combine pore water sampling with geochemical modelling to understand the factors influencing metal partitioning in natural soil systems. We tested if it is possible to predict the solid-solution partitioning of metal in the rhizosphere of a soil system by a geochemical model and assessed the variability of several key parameters under field conditions.
Pore water was collected *in situ* to monitor metal concentration and the variability of Ca, DOC and pH in time and depth. The metal we focus on is zinc, an essential nutrient but also a frequent environmental contaminant (Nriagru, 1980). We followed a comparable approach as Weng et al. (2001), which we extended by the presence of mineral phases but applied the model to pore water sampled under semi-field conditions. Unlike in other studies (e.g. Elzinga et al., 1999; Gustafsson et al., 2003; Römkens and Dolfing, 1998) our geochemical model involves no fitting but is fully parameterised by literature data to generate a purely predictive rather than fitting model. For a number of parameter where only ranges can be given, we tested the influence of these parameters on the model outcome.
The modelling outcomes were compared with the pore water measurements and we analysed the influence of the variability of Ca, DOC and pH one the model outcome. We discuss the relevant parameters needed to calculate Zn speciation in pore water and soil.

2.2 Materials and methods

2.2.1 Lysimeter set-up

The experiment was carried out at an outdoor lysimeter of the Vrije Universiteit of Amsterdam, The Netherlands. The lysimeters consist of six replicating plots, subdivided into 10 compartments of 1 m by 0.5 m. Each compartment was filled with 130 kg of a sandy soil (approx. 30 cm thickness), artificially contaminated by addition of up to 3200 mg kg^{-1} Zn as $ZnCl_2$. The addition of $ZnCl_2$ caused leaching of significant amounts of Zn through the profile during the first year. Further details and observations have been provided by Smit et al. (1997) and Van Beelen et al. (1996). Our experiment was performed five years after $ZnCl_2$ was added to the soil.

A drainage system kept the groundwater level in the lysimeters constant at 50 cm below the surface. Precipitation is interpolated by inverse distance method from meteorological stations at De Bilt, De Kooy and Vlissingen, The Netherlands (KNMI, 1999).

Experiments were done for two Zn concentrations: 1000 and 3200 mg kg^{-1} (nominal). Three model plants were planted out in randomly selected compartments three weeks before the sampling started: *Agrostis stolonifera* (creeping bentgrass) is a common grass species. *Trifolium repens* (white clover) is a dicotyl able to fix N_2 by the formation of Rhizobium nodules. *Brassica napus* (rapeseed) is chosen because the *Brassica* genus is known to be able to accumulate large amounts of heavy metals. We also monitored the pore water concentration in a single, not replicated plot covered by *Lolium perenne* (perennial ryegrass) at a nominal concentration of 1800 mg kg^{-1} Zn.

2.2.2 Pore water sampling

Rhizon soil moisture sampler (SMS MOM, Rhizosphere Research Products, Wageningen, The Netherlands) were placed in the root zone to sample pore water repeatedly with minimum interference to plant growth or the soil system. Unlike the extraction of pore water by centrifugation of soil samples, this non-destructive method minimises the problem of spatial heterogeneity in case of repeated sampling in time. 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 hours 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 $Ca(NO_3)_2$.

Prior to planting, the Rhizon samplers were inserted in the lysimeter horizontally at 10, 15, 20 and 25 cm depth in the rooting zone. The Rhizons were applied at three plant treatments and two Zn concentrations (1000 and 3200 mg kg^{-1}), resulting in 24 sampling points. Another set of 4 Rhizons was inserted at the plot with 1800 mg kg^{-1} Zn at 10, 15, 20 and 25 cm depth.

To extract pore water, a vacuum was build up inside the Rhizon sampler by a 10 mL syringe (300912, Becton Dickinson, EDC, Temse, Belgium). The vacuum was maintained overnight (16 - 18 h) and resulted in up to 9 mL of pore water, depending on moisture conditions. Desiccation can lead to reduced amounts of pore water samples, since natural

precipitation was the only source of water. Samples with less than 2 mL were rejected. Prior to sampling, the Rhizon samplers including the connecting tube systems were rinsed with 1 mL of sample solution (i.e., exceeding 3 * dead volumes). Pore water was sampled seven times during the growing season.

The pH was measured directly in the pore water samples. DOC was determined on a TOC analyser (SK12, Skalar, Breda, The Netherlands). Metal content of pore water was measured by ICP-AES (Spectroflame Modula, Spectro, Kleve, Germany).
The total amount of Zn, Ca, P and Fe in soil is determined by *aqua regia* destruction (NEN 6465, 1992) and measured on ICP-AES. The organic carbon content of the soils was analysed by wet oxidation with $K_2Cr_2O_7$ (Walinga et al., 1992). The pH-$CaCl_2$ was measured in a suspension of 0.5 mM $CaCl_2$ (1 : 10 v/v) after 2 h of shaking.

2.2.3 Geochemical modelling

Speciation calculations were done with the object-oriented modelling framework ORCHESTRA, which gives the user the possibility to extend the chemical model definitions by defining new objects (Meeussen, 2003). Equilibrium constants for soluble species and mineral phases (Table 1) were taken from Lindsay (1979). To calculate Zn adsorption to organic matter, we used the consistent *NonIdeal Competitive Adsorption* model (NICA), which was combined with a Donnan approach to describe the electrostatic interactions (Kinniburgh et al., 1999). The model accounts for the competition of metal sorption by Ca, the major background cation. Parameters were used from the generic NICA parameter set (Milne et al., 2003). The metal binding behaviour of humic and fulvic acid is found to be comparable (Christl et al., 2001), therefore we assumed for simplicity all reactive organic matter to be present as humic acid (HA).

TABLE 1. Mineral phases and *log* K values used for calculation (Lindsay, 1979)

mineral	*log* K
$ZnFe_2O_4 + 8H^+ = Zn^{2+} + 2Fe^{3+} + 4H_2O$	9.85
$Zn_3(PO_4)_2 \cdot 4H_2O + 4H^+ = 3Zn^{2+} + 2H_2PO_4^- + 4H_2O$	3.80
$ZnCO_3 + 2H^+ = Zn^{2+} + CO_2(g) + H_2O$	7.91
$ZnO + 2H^+ = Zn^{2+} + H_2O$	11.16
$\alpha\text{-FeOOH} + 3H^+ = Fe^{3+} + 2 H_2O$	-0.02
$Ca_5(PO_4)_3OH + 7H^+ = 5Ca^{2+} + 3H_2PO_4^- + H_2O$	14.46

All iron oxides were assumed to be present as goethite. The adsorption of Zn, Ca and PO_4^{3-} by goethite was calculated by the *Charge Distribution MUlti SIte Complexation* model (CD-MUSIC; Hiemstra et al., 1996). The amount of goethite calculated by the geochemical model was used directly for the sorption modelling. Clay adsorption of Ca and Zn is

described with a simple ion exchange model with a constant CEC (Appelo and Postma, 1994).

Relevant Zn mineral phases that were considered are $ZnFe_2O_4$ (franklinite), $Zn_3(PO_4)_2$ (hopeite), $ZnCO_3$ and ZnO (Table 1). The activity of Fe^{3+} was controlled by the presence of goethite, and the activity of PO_4^{3-} by hydroxyapatite. The total amounts of organic carbon, clay, Fe, P and Zn were used as input for the model. Calcite reaches equilibrium with soil solution only very slowly at neutral pH and was therefore not defined as mineral phase in the model (Appelo and Postma, 1994). The presence of calcite would lead to an overestimation of the Ca concentration in pore water; consequently we used the measured concentration of Ca in pore water as an input variable for the model.

A few assumptions had to be made for parameters that were not measured: Soil solution ratio is kept at 4 kg L^{-1}, equivalent with $\theta=0.4$ for the average bulk density of a sandy soil (1600 kg m^{-3}). To recalculate the measured carbon contents to organic matter content, we defined, for simplicity, a carbon content of organic matter of 50% (Schachtschabel et al., 1992). Since the fraction of humic substances in organic matter is variable, we tested values for the HA contents of organic matter, which ranged from 33 to 67%. We assumed clay to be present as illite with a CEC between 0.2 and 0.5 mol_c kg^{-1} (Schachtschabel et al., 1992) and we used an exchange coefficient $K_{Ca/Zn}$ of 1 (Bruggenwert and Kamphorst, 1982). For the specific surface area of goethite we used values ranging from 20 to 200 m^2 g^{-1} (Cornell and Schwertmann, 1996).

For the parameters, were a range of values can be assigned to, we tested the effect of the variability of these model parameters on the calculated Zn^{2+} activity by a Monte Carlo simulation.

2.3 Results

The soil properties are summarised in Table 2. The average organic carbon content is 9.2 mg kg^{-1} ($\pm$ 0.4 mg kg^{-1}). The total amounts of Zn measured were lower than the nominal values due to leaching. The values measured were approximately 25 to 30% lower than reported by Van Beelen et al. (1996) for February 1995. This difference can be explained by leaching: for an annual precipitation of 850 mm passing through the lysimeter soil, an average Zn concentration of 14 and 33 mg L^{-1} in pore water can be calculated (for 1000 and 3200 mg kg^{-1} Zn respectively), which is comparable to values reported by Van Beelen et al. in 0.01 M $CaCl_2$ extractions.

The $pH-CaCl_2$ decreases with increasing amounts of added Zn. The addition of $ZnCl_2$ during the set-up of the lysimeter leads to the exchange of protons, resulting in a concentration dependent pH. This characteristic side effect already reported by Van Beelen et al. (1996) was still prominently present in the system when our experiment was performed.

TABLE 2. Soil properties

Zn nominal [mg kg⁻¹]	pH-CaCl₂ [-]	Zn [mg kg⁻¹]	Ca [g kg⁻¹]	Fe [g kg⁻¹]	P [mg kg⁻¹]
1000	6.88	631	4.62	2.58	334
1800	6.72	959	*n.d.*	*n.d.*	*n.d.*
3200	6.52	1379	4.47	2.45	304

n.d. = not determined

The pore water samples extracted by the Rhizon results in a detailed picture of the dynamics of the DOC concentrations, the pH and the metal speciation in the rhizosphere. Two out of 28 Rhizon samplers could not be used due to technical failure. 12% of all samples contained less than 2 mL pore water and were therefore rejected. All other samples were used for analysis and model calculations. Figure 1 shows the interpolated precipitation during the experiment and the average amount of extracted pore water during the sampling. The quantity of extracted pore water is significantly correlated with the cumulative amount of precipitation during the three days prior to the sampling ($p < 0.02$).
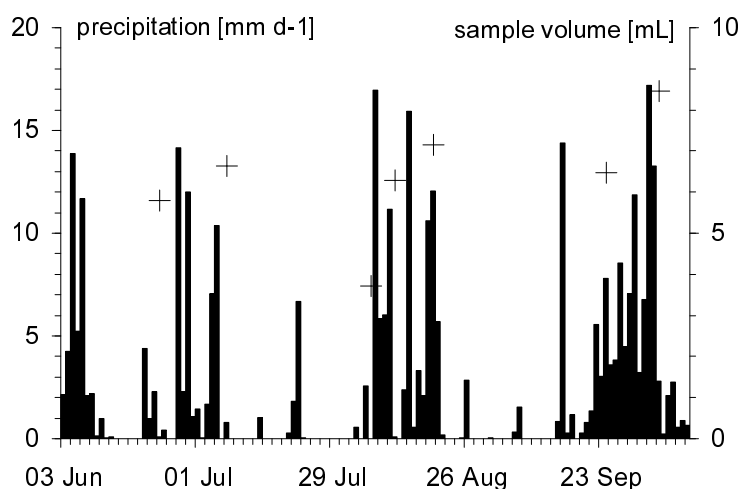
FIGURE 1. Daily precipitation during the experiment (KNMI, 1999). The plus (+) marker shows the average sample volumes (right vertical axis) at the indicated sampling dates (horizontal axis)

There was no significant trend of concentrations of Ca, Zn and DOC, or pH in pore water, either as a function of time or depth. Table 3 therefore presents the results of the pore water sampling as average values per treatment. Instead, we found a negative correlation between the precipitated amount three days prior to sampling dates and the average concentrations of *log*(Ca), *log*(Zn) and *log*(DOC) in all pore water samples taken at those dates (significant at $p=0.064$, 0.055 and 0.04, respectively). The pH was positively correlated with the precipitated amount ($p=0.04$).

TABLE 3. Average concentration and standard deviation of Zn, Ca, dissolved organic carbon (DOC) and pH in pore water. Values denoted with same character are not significantly different (p<0.05)

plant	Zn [mg kg^{-1}]	log Ca [mg L^{-1}]	log Zn [mg L^{-1}]	DOC [mg L^{-1}]	pH [-]
Agrostis stolonifera	1000	1.30 ±0.12^a	-0.08 ±0.17^a	25.0 ±12.4^a	7.39 ±0.17^a
Brassica napus	1000	1.35 ±0.16^a	-0.10 ±0.18^a	22.1 ±10.6^{ab}	7.58 ±0.18^b
Trifolium repens	1000	1.32 ±0.27^a	0.22 ±0.19^b	24.3 ±10.5^{ab}	7.31 ±0.17^{ac}
Lolium perenne	1800	1.05 ±0.16^b	0.30 ±0.11^b	21.3 ±9.7^{ab}	7.24 ±0.12^c
Agrostis stolonifera	3200	1.28 ±0.27^a	0.79 ±0.19^c	21.9 ±9.5^{ab}	7.03 ±0.23^d
Brassica napus	3200	1.29 ±0.26^a	0.98 ±0.19^d	18.5 ±5.8^b	6.93 ±0.16^{de}
Trifolium repens	3200	1.34 ±0.31^a	0.94 ±0.23^d	22.3 ±8.6^{ab}	6.88 ±0.18^e

For Ca, differences in concentrations between the treatments of 1000 and 3200 mg kg^{-1} Zn were small, but the variations as a function of time and within the root zone range up till a factor of two. Since calcite and hydroxyapatite are known to dissolve slowly at high pH (Appelo and Postma, 1994), we expect that the variability of Ca reflect the influence of dilution by precipitation. This is supported by the negative correlation between precipitation and the concentration of Ca and Zn in pore water. Ca is found to be significantly smaller in the plot covered by *L. perenne.*

The temporal and spatial variability of DOC in the different treatments was approximately ±50% of the average value. There is neither a significant difference between the treatments for each Zn level, nor is there a difference between different plant treatments.

The Zn concentrations at 3200 mg kg^{-1} are up to one order of magnitude larger than the concentrations measured at 1000 mg kg^{-1}. Zn concentrations in pore water differ significantly between plant species within the same treatment. The treatments with *T. repens*, which is known to reduce the soil pH due to the assimilation of N by Rhizobium (Marschner, 1993) showed a significantly increased Zn concentration in pore water compared with *A. stolonifera* and *B. napus* at 1000 mg kg^{-1}. At 3200 mg kg^{-1} the Zn concentration of the *B. napus* treatment was significantly higher, too. This is probably related to the observed toxic effects of Zn on *B. napus* and *T. repens* at this concentration (data not shown).

The pH of pore water in the plots with *T. repens* is the lowest of the three plant treatments for both Zn concentrations. However, this difference is only significant compared with *B. napus* at 1000 mg kg^{-1} and *A. stolonifera* at 3200 mg kg^{-1}.

The pH-dependent distribution of Zn in the water phase and the solid phase for the 1000 and the 3200 mg kg^{-1} treatment is summarised in Figure 2 and Figure 3, respectively. ZnO is not formed under the conditions prevailing in the lysimeter. ZnCO$_3$ was not relevant as a mineral phase below a pCO$_2$ of 0.01 atm. Hopeite is mainly formed at pH<7, whereas franklinite is the dominant mineral phase at pH>7.

Figure 2a shows that for pH<7, Zn binding to soil organic matter accounts for 50 to 65% of total Zn at 1000 mg kg⁻¹, whereas for higher pH-values, Zn is increasingly bound to franklinite. At 3200 mg kg⁻¹, organic matter binding is less important and accounts for approximately 30% of all Zn in soil for pH smaller than 7 (Figure 3a).

Hopeite accounts for up to 45 and 65% of all Zn present at a pH<7 in the 1000 mg kg⁻¹ and 3200 mg kg⁻¹ treatment, respectively. Binding to goethite and clay only plays a minor role (less than 8 and 5%, respectively) at both concentration levels.

FIGURE 2. Calculated distribution of Zn at 1000 mg kg⁻¹ as a function of the pH (a) in the solid phase and (b) in the water phase for average values of Table 4

At pH<7, Zn^{2+} accounts for over 70% of all Zn present in the water phase (Figure 2b). At pH>7, the fraction of Zn as $ZnCO_3$ increases with increasing pH, whereas $ZnOH^+$ increases from 2 to 20% in the entire plotted pH range. DOC-bound Zn accounts for 13 to 27% of all Zn present in pore water. The Zn distribution in pore water at 3200 mg kg⁻¹ is comparable to the 1000 mg kg⁻¹ treatment (Figure 3b).
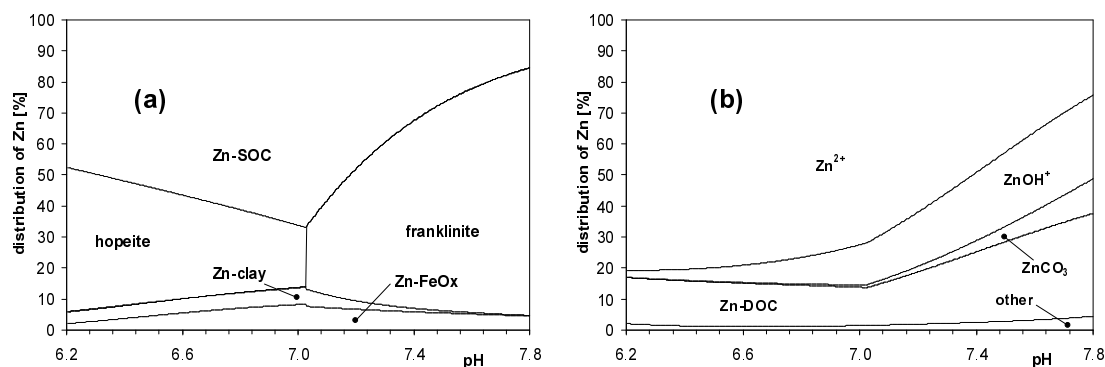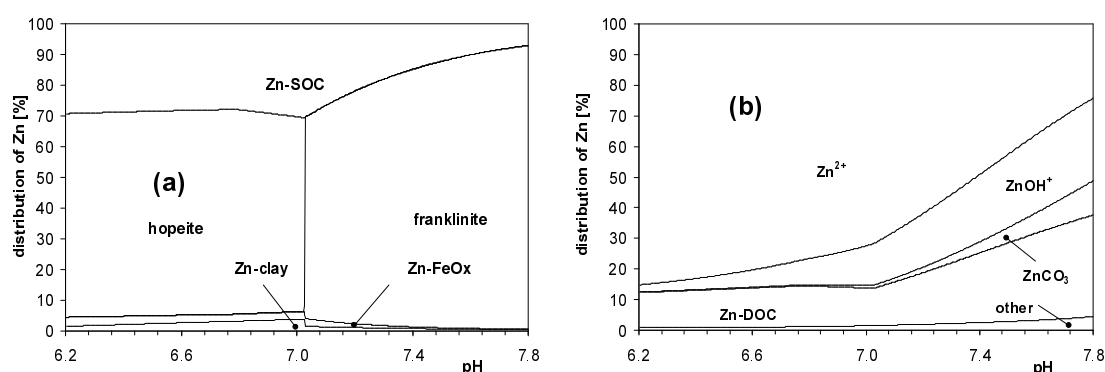

FIGURE 3. Calculated distribution of Zn at 3200 mg kg⁻¹ as a function of the pH (a) in the solid phase and (b) in the water phase for average values of Table 4

To evaluate the influence of the assumptions as described in the Material and Method section on the outcome of the model calculations, a Monte Carlo simulation was done.

Besides the range of possible values for model parameters discussed in the material and methods section, we tested the effect of the variability of the pH and the concentrations of Ca and DOC found in the pore water measurements (Table 3). Statistical analysis showed only weak relationships between pH, Ca and DOC when the individual data points were compared ($R^2 \leq 0.06$). The parameters and variables used for the Monte Carlo simulation are summarised in Table 4. We generated 10,000 random values for all parameter according to Table 4 and used this as input for the geochemical model. The calculations were performed for Zn concentrations of 1000 mg kg^{-1} and 3200 mg kg^{-1}.

TABLE 4. Parameter and variables varied in Monte Carlo simulation

parameter	average	range	distribution
log Ca pore water [mg L^{-1}]	1.27	1.04 .. 1.46	normal
SOC [mg kg^{-1}]	9.2	6.1 .. 12.3	uniform
DOC [mg L^{-1}]	25	7.8 .. 42	uniform
log pCO$_2$ [bar]	-2.9	-3.5 .. -2.5	uniform
goethite *log* surface area [m^2 g^{-1}]	1.9	1.3 .. 2.3	uniform
clay surface charge [mol$_c$ kg^{-1}]	0.25	0.2 .. 0.5	uniform
pH [-]	6.8	6.2 - 7.8	uniform

Figure 4 plots the results of the Monte Carlo simulations for the Zn^{2+} activity as a function of the pH. The grey marker represents the results of the simultaneous, independent variation of all seven parameters of Table 4 whereas the black markers show the same simulation with a constant concentration of Ca. For pH>7, the system behaviour is determined strongly by the presence of franklinite, leading to a decrease of the Zn^{2+} activity by two log-units per pH unit. For pH<7, hopeite competes for Zn binding with organic matter and therefore the Zn^{2+} activity is expected to be affected to a larger extent by the range of possible parameter values corresponding to the binding capacities of DOC, soil organic carbon (SOC), goethite and clay in Table 4. However, the main part of the variability of Zn^{2+} activity plotted in Figure 4a is due to the variation of Ca concentrations in pore water. Thus, when Ca is assumed to be constant, 95% of the calculated values can be found within a close range of ± 0.1 *log* (Zn^{2+}) which indicates that the other factors given in Table 4 affect the calculated Zn^{2+} activity only slightly.

Similar to the 1000 mg kg^{-1} treatment, at 3200 mg kg^{-1} and pH>7 the Zn speciation is determined by the presence of franklinite. Again, the activity of Zn^{2+} is mainly affected by the pH. Furthermore, comparison of the 1000 mg kg^{-1} and the 3200 mg kg^{-1} treatment showed no visible difference in the Zn^{2+} activity calculated for pH>7 (Figure 4a and 4b), which means that Zn^{2+} activity is independent of the total amount of Zn under these conditions.
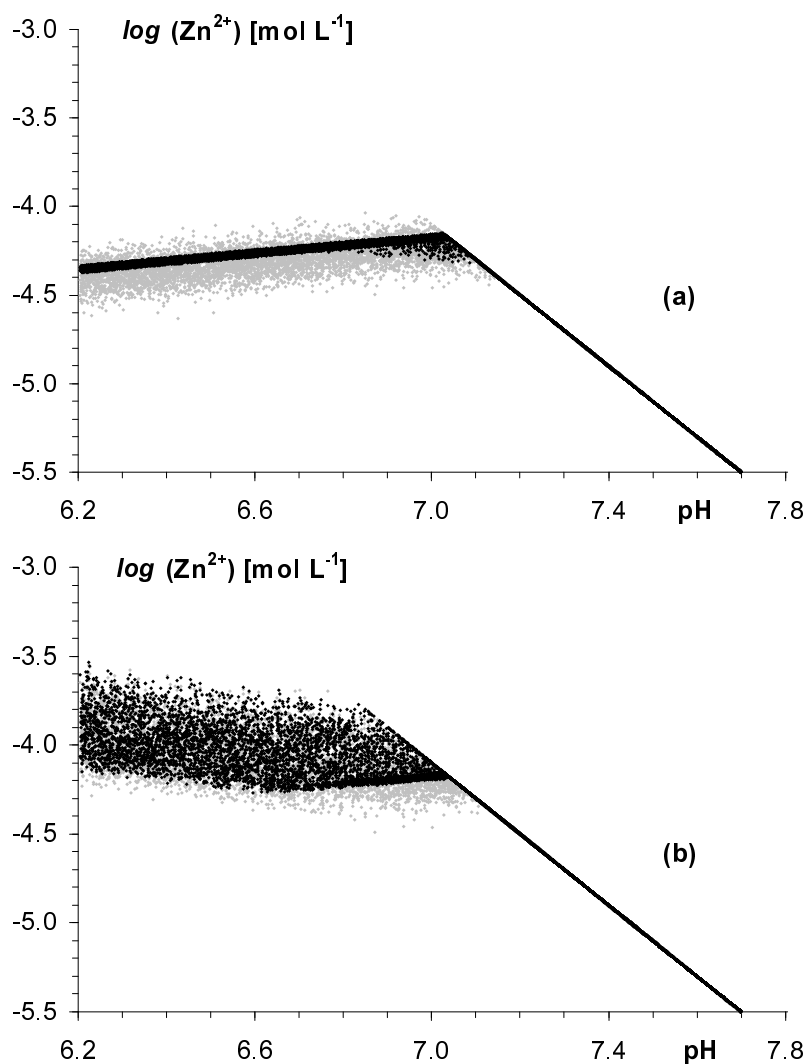
FIGURE 4. Monte Carlo simulation of Zn^{2+} activity (mol L^{-1}) as a function of the pore water pH. Parameters of Table 4 were varied simultaneously for (a) nominal concentration of Zn: 1000 mg kg^{-1} (b) nominal concentration of Zn: 3200 mg kg^{-1}. The grey marker represents a variable Ca concentration, black markers a constant Ca concentration

Below a pH of 7, the variability of Zn^{2+} activities in the 3200 mg kg^{-1} treatment were larger than for the 1000 mg kg^{-1} treatment; however, at 3200 mg kg^{-1} all pH values measured in pore water were above 7.

The concentration of Zn in pore water was stronger affected by the variations than the Zn^{2+} activity (Figure 5). This was mainly due to the binding of Zn to organic matter. However, the variability was limited to 0.3 log-units at 1000 mg kg^{-1} and to 0.2 log-units at the 3200 mg kg^{-1} treatment and pH values above 7.
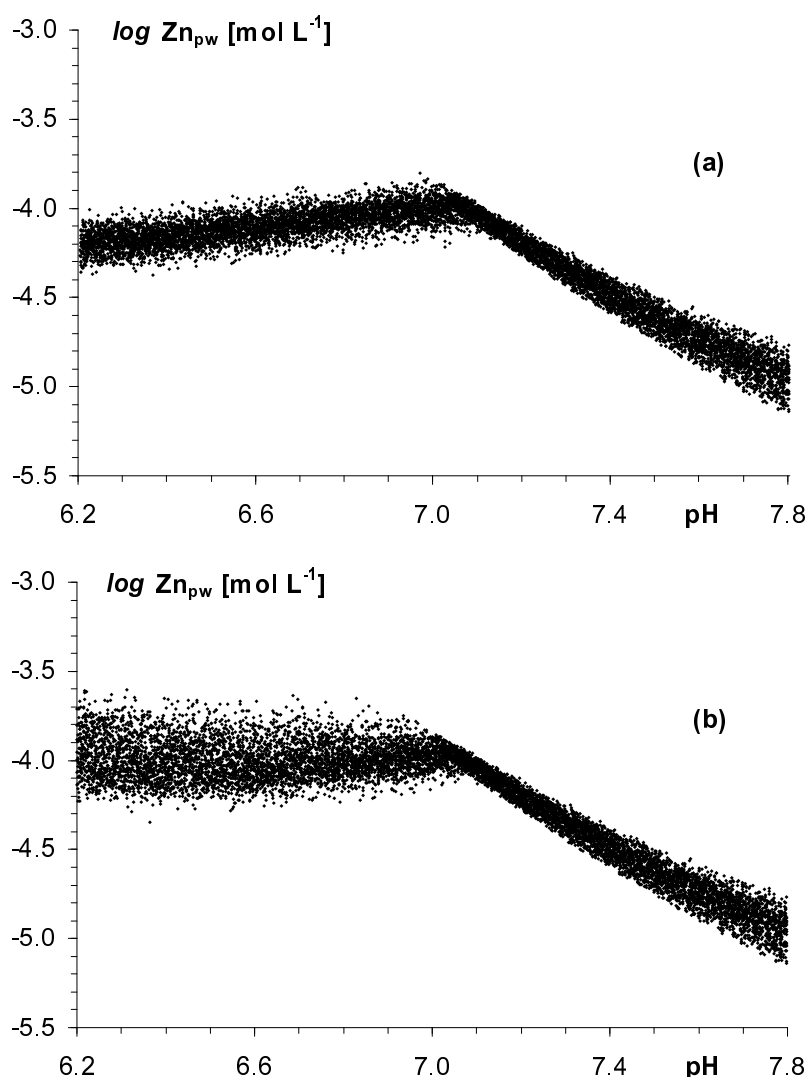
FIGURE 5. Monte Carlo simulation of the Zn concentration in pore water (mol L^{-1}) as a function of the pore water pH. Parameters of Table 4 were varied simultaneously for (a) nominal concentration of Zn: 1000 mg kg^{-1} (b) nominal concentration of Zn: 3200 mg kg^{-1}

Figure 6 shows the predicted and measured concentrations of Zn in pore water. It appears that 90% of the values fall in a band with a width of one log-unit. The fully parameterised generic model delivered a root mean square error (RMSE) of the *log*-transformed data of 0.284. The model overestimates the concentration of Zn in pore water at low concentrations; however, the Monte-Carlo simulation shows that the influence of the assumptions made on the results are rather small in the case of the 1000 mg kg^{-1} treatment (Figure 4a).
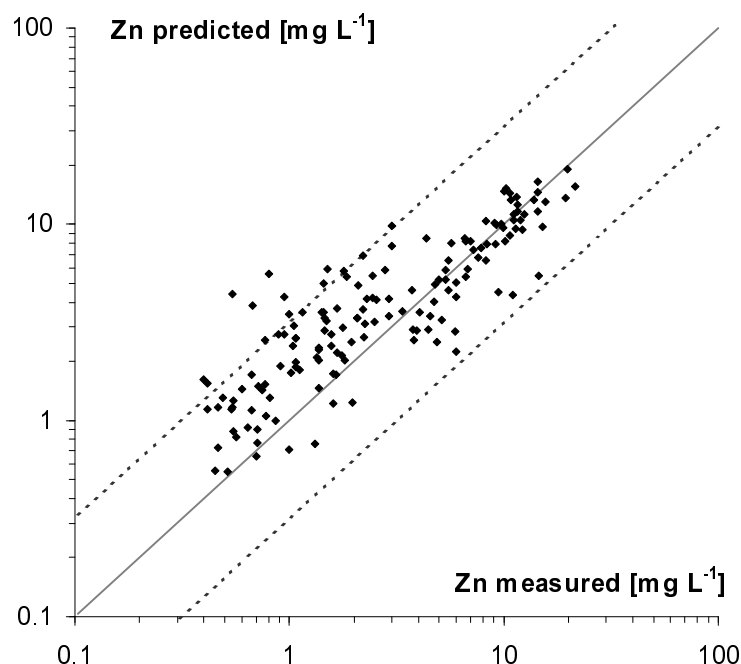
FIGURE 6. Predicted and measured Zn concentrations in pore water. The grey line and the dotted lines defines the 1:1 line and a range of ±0.5 log-unit, respectively

2.4 Discussion

The use of Rhizon samplers is an easy, fast and sensitive method to monitor pore water with minimum interference of the studied soil system. The influence of various plant species on pore water chemistry could be elucidated using this method. However, the lack of precipitation could be a major drawback for this method, because it can result in desiccation of soils with low water retention capacity, such as the sandy soil used in this experiment.

The variation of the pore water composition under natural conditions is found to depend on both biological processes and precipitation pattern. The amount of rainfall shortly before sampling correlates well with the concentrations of Ca, Zn, DOC and the pH. The relative contribution of this effect is pH = Ca > Zn > DOC (data not shown). The role of the non-equilibrium processes is therefore not negligible in a soil system studied on this scale, and the dilution of pore water by rainwater is not equilibrated fully within a day.

Unlike other studies, in which pore water composition was monitored under natural conditions (e.g. Linehan et al., 1985; Linehan et al., 1989), we could not find a significant trend of Ca, Zn, DOC, or pH as a function of time. One reason might be that the large short term variations due to the rainfall pattern overrule a possible trend.

Despite of these variations, the experimental set-up was sensitive enough to observe significant differences between different plant covers. As the analysis with the geochemical model showed, small changes in soil pH, which can be induced by plant root exudates, can affect the Zn^{2+} activity (Figure 4) and the measured Zn concentrations in pore water (Table 3). The measured differences of pH between the plant treatments were rather small,

but the Zn uptake of plants is known to be strongly dependent on the pH (Marschner, 1993).

System analysis showed that below a pH of 7, hopeite and organic matter compete as the major sink for Zn. We found from the Monte Carlo analysis that the distribution of Zn between these two phases is strongly dependent on the input values (data not shown). Therefore it will be difficult to quantify the exact contribution of these two phases to Zn binding by model calculations. However, as Figure 4 shows, this uncertainty has only minor impact on the calculated Zn^{2+} activity. Above pH 7, the pH has a strong influence on the Zn^{2+} activity. Accurate measurement of pH is therefore compulsory for a good prediction of the Zn^{2+} activity and Zn concentrations in pore water.

The total amount of Zn in soil is found to have only a small effect on the dissolved Zn^{2+} activity. Due to the partitioning of Zn between soil organic matter and dissolved organic matter, increasing total amounts of Zn in soil also increase the DOC bound fraction of Zn in pore water without necessarily shifting the Zn^{2+} activity in pore water to a large extent (Figure 5). Consequently, the assumptions made regarding the HA content of DOC and SOC have a larger impact on the total amount of Zn in pore water than on Zn^{2+} activity (Figure 4 and Figure 5). However, at the given pH range, DOC-bound Zn only accounts for approximately 13-26% of the total Zn present in pore water (Figure 2b and Figure 3b), therefore these assumptions have only a limited influence on the calculated pore water concentration.

With the fully parameterised model, we were able to predict the Zn concentration in pore water within ±0.5 log-unit for 90% of all samples. This is comparable with the results of Weng et al. (2001) at higher pH values. Besides processes that are kinetically limited, the modelling of metal adsorption to heterogeneous organic matter is a source of possible error. The generic NICA-parameters predict metal sorption generally within a factor of 3 (Milne et al., 2003). For the sorption parameter of Zn and Ca on humic acid Milne et al. reported a RMSE (of the *log*-transformed data) of 0.17 and 0.19, respectively. Evaluation of the modelling results shows, that all points that deviated more than half a log-unit are samples with low pH-values (pH<7) of the 1000 mg kg^{-1} treatment. It is unclear whether this is due to chemical alteration of the pH after sampling or some underestimation of pH-dependency by the model.

Whereas it is found to be essential that the pH is known for every sample, for DOC or Ca the mean concentrations can be used instead of individual measured values. When we used a constant average value for both DOC and Ca, the modelling error increased only slightly (RMSE=0.285 and 0.293, respectively). Since the modelling of calcite dissolution or DOC partitioning under natural conditions is beyond the reach of this work, a approximate knowledge of Ca and DOC concentration in pore water is therefore necessary to define the system. However, measuring Ca and DOC in individual samples will improve the accuracy of the prediction only slightly. This makes it also questionable whether an extension of the model, which accounts for the significant influence of the rainfall pattern we found on soil chemistry, will improve the model outcome substantially.

2.5 Conclusions

The sampling set-up introduced in this study showed the potential to monitor pore water *in situ*. The use of Rhizon sampler results in a detailed picture of the pore water chemistry in the root zone and avoids the problem of spatial heterogeneity of repeated sampling. This method also diminishes the influence on plant growth since no soil material is removed from the root zone. We were able to show significant effects of various plant species and the precipitation pattern on the speciation of Zn in pore water under semi-field conditions. However, we could not find a trend in time that affected the pore water chemistry. Instead, natural precipitation patterns can influence the equilibrium chemistry on short term by dilution.

Mechanistic modelling of soil chemical processes by the equilibrium approach with a fully parameterised model was successful in predicting pore water concentrations within a range of one log-unit without applying any further calibration, and we were able to demonstrate that the assumptions made for a number of parameter did not have a substantial impact on modelling results. Modelling also demonstrated the importance of the pH, and to a lesser extent of Ca and DOC, for the speciation of Zn in a soil system. Since DOC and Ca concentrations in pore water are difficult to model, they should be measured to enable the assessment of the availability and uptake of heavy metals accurately. However, the variability of DOC and Ca does not have a large influence on the model prediction. Average values of Ca and DOC were therefore sufficient to model the Zn behaviour, whereas the measurement of pore water pH is found to be essential.

Chapter 3

Risk assessment of heavy metals and As in floodplain soils: comparison of pore water sampling and a weak soil extraction

3.1 Introduction

In the last century, large quantities of heavy metals have accumulated in the embanked river floodplain areas of the Rhine and Meuse river system (Beurskens et al., 1993). To enable sustainable management of river floodplain areas, it is necessary to be able to predict adverse effects due to the heavy metal contamination of these floodplain soils. For the risk assessment of contaminated soils, understanding of the solid-solution partitioning and speciation of heavy metals is necessary as they affect both metal mobility and bioavailability.

In Chapter 4, we present a statistical and a geochemical model to predict the solid-solution partitioning of heavy metals in a large number of soil samples from river floodplains in the Netherlands. For the soluble fraction, we focused on the metals extractable by 2.5 mM $CaCl_2$. Extractions by $CaCl_2$ are known to be strongly correlated to plant uptake (Sanders et al., 1987, Smilde et al., 1992; Van Erp et al., 1998), which makes it a useful measure for the availability of heavy metals. To choose for an extraction of soil samples by $CaCl_2$ rather than the collection of pore water in the field was due to the large efforts necessary to collect pore water. Besides logistic and analytical aspects, a major drawback of the sampling of pore water is that the composition can vary in time (Farley and Fitter, 1999; Linehan et al., 1989). Therefore a single sample of pore water is most probably not a good estimator of the average composition of pore water on a location. In contrast, $CaCl_2$ extractions reflect rather time independent soil properties, and a single extraction is therefore sufficient to get a reproducible measure for metal availability in soil. In case a large number of samples have to be taken, e.g. to address the spatial heterogeneity of metal availability, the high cost efficiency of the $CaCl_2$ extraction is a clear advantage.

In spite of the advantages of $CaCl_2$ extractions, several relevant aspects for the risk assessment of heavy metals can only be determined by collecting pore water *in situ*. As indicated before, all information about the temporal variability of pore water under natural conditions is lost by extraction. Parameters that control metal partitioning, such as the pH or the concentration of dissolved organic carbons (DOC), are known to be influenced by seasonal variations and biotic processes (Dijkstra and Fitzhugh, 2003; Gupta and Rorison, 1974; Chapter 2). The importance of the temporal variability of these parameters for the metal partitioning may be limited for some situations (Chapter 2 and 5), but to be able to conclude this for a particular soil system, we must have sufficient data on the pore water composition under field conditions throughout the year.
Furthermore, an important feature of floodplains is the large fluctuation of the water level that affects the redox conditions in the soil profile. During continuous flooding, the lowered redox potential strongly affects the partitioning of heavy metals. The redox state of the soil is not preserved when samples are dried and therefore oxidised for the extraction by $CaCl_2$. However, the drying and remoistening of the soil samples for the extraction might lead to artefacts, too (Bartlett, 1981; Fierer and Schimmel, 2003).

Thus, compared with pore water, a weak extraction is a complex measure in a chemical sense and can not directly be related *a priori* to speciation and sorption processes as described by geochemical modelling. Since such models are increasingly being used to

screen bioavailability and leaching effects, the pore water composition is a more appropriate choice for the experimental variables with which modelling results has to be compared. Both methods have therefore their own advantages and obviously the choice which method to use is dictated by the specific question that has to be answered. If we would understand better how these two measures are related to each other, processes as bioavailability and leaching could be studied by the easily accessible $CaCl_2$ extraction.

In this paper, we compare two methods to assess the solid-solution partitioning of heavy metals and As in river floodplain soils of the Meuse and Rhine river system: *in situ* pore water extractions by Rhizons and soil extractions by 2.5 mM $CaCl_2$. There are two aims in this study: first, to quantify the temporal variability of As, Cd, Cu, Ni, Pb and Zn in pore water and the spatial as well as temporal variability of Ca, Cl, DOC and the pH. Second, to compare the pore water composition with soil extraction by 2.5 mM $CaCl_2$. We discuss the effect of Ca, Cl, DOC and the pH on the partitioning of heavy metals and assess how the results of both methods are related to each other.

3.2 Materials and methods

3.2.1 Field sampling

From 48 floodplains along the Dutch part of the river Meuse and the three major branches of the river Rhine presented in Chapter 4, we selected a subset of 24 locations for the extraction of pore water (Figure 1). Within every selected floodplain, we choose two sublocations to sample pore water *in situ*. At two smaller floodplains, we installed the Rhizons at one sublocation only, resulting in a total number of 46 sampling points. To collect pore water, we used Rhizon soil moisture samplers (SMS MOM, Rhizosphere Research Products, Wageningen, The Netherlands). 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 was 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 remain for 2 hours in 0.28 M HNO_3, before they were rinsed with 20 mL ultra pure water. Finally, they were rinsed with 30 mL 1 mM $Ca(NO_3)_2$ and stored overnight in 1 mM $Ca(NO_3)_2$.

The Rhizons were placed permanently in the floodplain sediments, which enabled us to sample pore water repeatedly with minimum interference of the soil system. At one sublocation in every floodplain, the Rhizons were inserted horizontally at 15 cm and 45 cm depth. At the other sublocations, they were installed at 15 cm depth only. All Rhizons were applied in duplicate in a rectangular angle with each other. The tubes and connectors were protected against grazing animals and farming machines by a 10 cm diameter PVC tube that was inserted in the soil vertically and closed up with a removable lid.

To extract pore water, a vacuum was build up inside the Rhizon sampler by a 10 mL syringe (Becton Dickinson, 10 mL LL). Depending on moisture conditions, up to 10 mL of pore water was sampled. Prior to sampling, the Rhizon samplers and the connecting tubes were rinsed with the first 2 mL of sample solution (i.e., exceeding 3 dead volumes). Pore water was sampled three times in 2002: in spring (2 May - 27 May), in summer (16 July -

5 August) and in autumn (21 October - 17 November). Samples with less than 3 mL volume where discarded.

Soils samples were collected by a gouche auger sampler (2.5 cm diameter) in 5 to 25 cm depth. The samples were dried at 40° C and sieved (<2 mm) before analysis.

FIGURE 1. Sampling locations in the Rhine-Meuse floodplain system

3.2.2 Chemical analysis

The pH of the pore water samples was measured immediately on the sampling location to prevent an alteration of the pH by oxidation. DOC was determined on a TOC analyser (Skalar SK12) after acidification to a pH of 3.0 to 3.5 by the addition of 0.28 M HNO_3. Concentrations of As, Cd, Cu, Ni, Pb, Zn, Mn, Fe, Ca and Cl were measured by ICP-MS (Perkin Elmer ELAN 6000) after 1:1 dilution with 0.28 M HNO_3 (Merck, suprapur).

$CaCl_2$ extractions were made according to a modified scheme of Houba et al. (1996). We used 2.5 mM of $CaCl_2$ rather than 0.01 M $CaCl_2$, because this composition is found to be in better agreement with the major ionic composition of pore water sampled in the floodplain soils. DOC was determined on a TOC analyser (Skalar SK12) at a pH of 3.0 to 3.5. Concentrations of As, Cd, Cu, Ni, Pb, Zn, Mn, Ca and Cl were measured by ICP-MS

(Perkin Elmer ELAN 6000) after 1:1 dilution with 0.28 M HNO_3 (Merck, suprapur). The pH was measured in the suspension of the 2.5 mM $CaCl_2$ extraction.

As, Cd, Cu, Ni, Pb, Zn, Mn, Fe, P and Al concentrations in *aqua regia* (NEN, 1992) were measured by ICP-AES (Spectros, Spectro Flame) and ICP-MS (Perkin Elmer, ELAN 6000). The content of soil organic carbon (SOC) was analysed by wet oxidation with $K_2Cr_2O_7$ (Wallinga et al., 1992). Clay content was measured by sedimentation according to Houba et al. (1997).

3.3 Results and discussion

During the three sampling campaigns in spring, summer and autumn, 64% of all locations were sampled successfully. In the other cases, pore water could not be collected due to natural conditions (flooding or desiccation) or technical problems. In total, 208 samples complied with the criteria of a sample volume larger than 3 mL and were used for analysis and calculation.

Table 1 shows the average concentration and standard deviation of Ca and Cl for the three sample campaigns. Whereas the average Ca concentrations did not differ much between the seasons, the average concentration of Cl increases significantly during the year. Figure 2 shows the Cl concentration of the pore water samples as a function of the Ca concentration for all seasons. The Cl concentrations in the pore water samples varied more than two orders of magnitude and the concentrations of Ca varies with more than one order of magnitude. For comparison, Figure 2 also shows the rather constant concentration of both elements measured in the $CaCl_2$ extractions. The ionic strength of 2.5 mM Ca, that was chosen for the extraction, agreed quite well with the measured average concentration of Ca (3.25 mM ±1.41) whereas the concentration of Cl in pore water was a factor of 4 lower than in the extraction (1.17 mM ±1.24).

TABLE 1. Average concentration and standard deviation of Ca, Cl, DOC and the pH of pore water samples collected in spring, summer and autumn. Standard deviations are given in parenthesis. Values denoted with the different characters are significantly different (p<0.05)

sampling campaign	Ca [mg L^{-1}]	Cl [mg L^{-1}]	DOC [mg L^{-1}]	pH [-]
spring	123.8 (51.5)[a]	16.1 (13.2)[a]	9.1 (4.8)[a]	7.01 (0.26)[ab]
summer	137.1 (59.7)[a]	44.6 (41.7)[b]	8.7 (4.3)[a]	7.03 (0.29)[a]
autumn	131.2 (58.4)[a]	63.7 (46.8)[c]	10.4 (6.1)[a]	6.92 (0.32)[b]

The concentrations of Cl and Ca in pore water can be influenced by the origin of the water: the pore water in flood plain soils originates either from river water or rain water, which have different compositions. The average concentration of Cl in rainwater is small (<5 mg L^{-1}) (Appelo and Postma, 1994) compared to the concentrations in river water

(approximately 70 mg L^{-1}). Ca concentrations in rain water are typically below 1 mg L^{-1} whereas the concentrations in river water are approximately 40 mg L^{-1} and 72 mg L^{-1} for the Meuse and Rhine river respectively. Samples with Cl concentrations below 70 mg L^{-1} and Ca concentrations below 72 mg L^{-1} (40 mg L^{-1} in case of the Meuse river) were therefore at least partially originating from rainwater. The variability of Ca and Cl were not of foremost interest for this study but might be helpful in interpreting the sampling results. Ca concentrations below 40 mg L^{-1} imply that the pore water is not equilibrated with the soil matrix. When the collected pore water was infiltrated into the soil only shortly before sampling, this might also affect the solid-solution partitioning of heavy metals. Furthermore, in dry periods evapotranspiration can increase the concentrations of ions in pore water leading to Ca concentration larger than 200 mg L^{-1}. This is consistent with the finding that pore water samples with large Ca concentrations needed longer to be extracted than other samples (data not shown). Evapo-transpiration will also lead to increased concentrations of Cl, explaining the significant correlation found between Ca and Cl for the samples in the upper right quadrant of Figure 2. How the variability of Ca and Cl affects the solid-solution partitioning of the heavy metals will be discussed later.
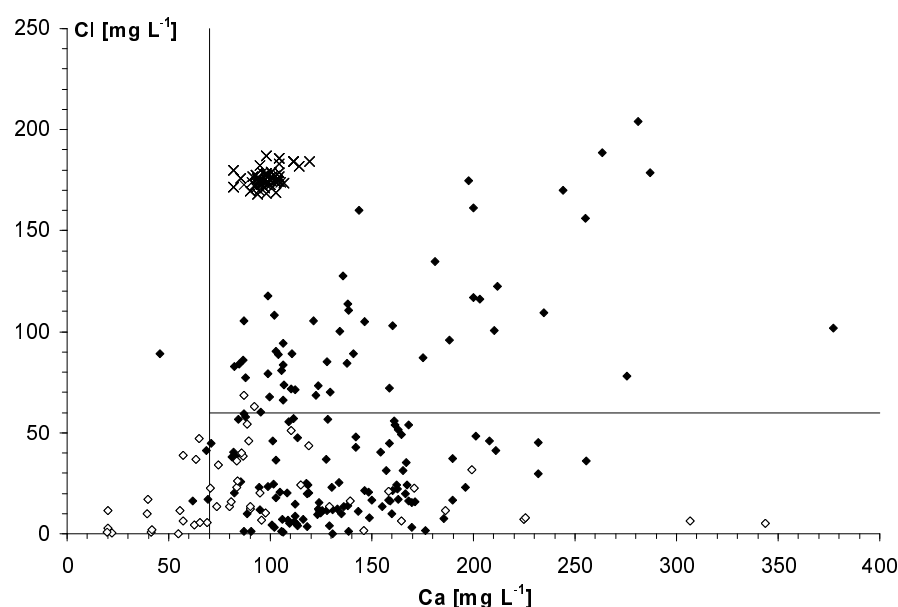
FIGURE 2. Concentrations of Cl in pore water as a function of the Ca concentrations. Closed diamonds: Rhine branches. Open diamonds: Meuse river. The horizontal and vertical lines represent average concentrations of Cl and Ca in river water. The (x) markers shows for comparison the concentrations measured in the samples extracted by 2.5 mM $CaCl_2$

Two important factors that control the solid-solution partitioning of heavy metals are the pH and the concentration of DOC (Sauvé et al., 2000b; Temminghoff et al., 1997). In Table 1, the average and standard deviation of the DOC concentration and the pH of the three sampling campaigns are summarised. The seasonal differences of the average pH and the average DOC concentrations are rather small, however, there was a small but significant difference of the average pH between the summer and autumn sampling. Figure 3 shows the time-averaged values of the pH and the DOC concentration for pore water

samples collected at one location as a function of the values in the extractions by 2.5 mM $CaCl_2$.
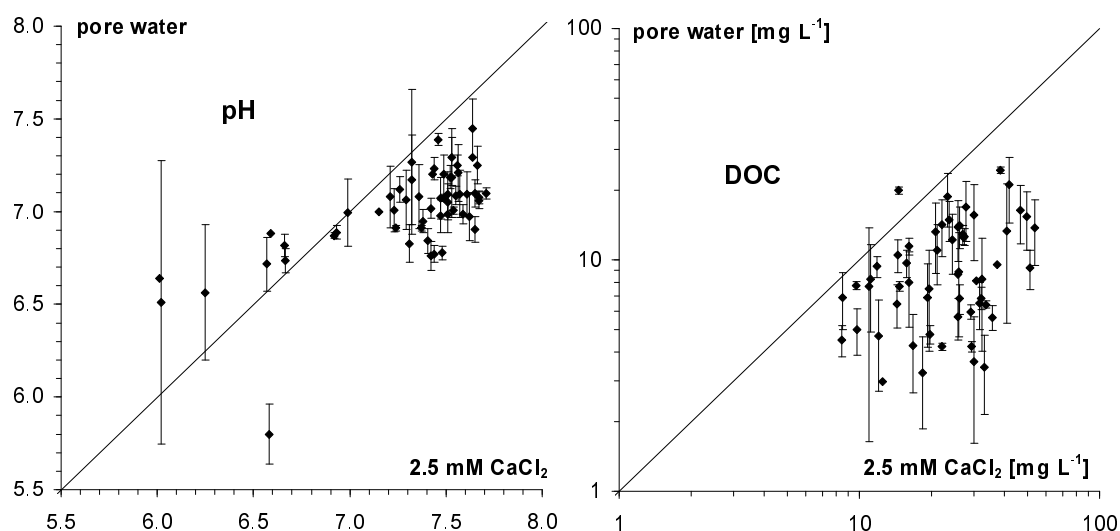
FIGURE 3. Average pH and DOC concentration and the standard deviations in pore water as a function of the 2.5 mM $CaCl_2$ extractable concentrations. The line represents the 1:1 line

On average, the pH in the 2.5 mM $CaCl_2$ extractions was approximately 0.3 units higher and the DOC concentration was approximately three times higher than in the pore water samples. Several factors might cause the differences in pH: the pH of the $CaCl_2$ extraction is measured in suspension, whereas the pore water pH is measured in solution. Under dry conditions, the collection of pore water required up to 16 h, and therefore oxidation may have altered the pH of the pore water samples. The pH in the $CaCl_2$ extract might also be affected by drying and rewetting of the soil samples. The differences in DOC concentrations can be attributed to the fact that the 2.5 mM $CaCl_2$ extractions were filtered by 0.45 μm, whereas the membrane of the Rhizons sampler had a pore diameter <0.2 μm.

Table 2 shows the average concentrations of heavy metals for all three sampling seasons. Except for Cd, the concentrations were the lowest in summer and the highest in spring. However, this effect was significant only for Pb.

TABLE 2. Average concentration and standard deviation of As, Cd, Cu, Ni, Pb and Zn of pore water samples collected in spring, summer and autumn. Standard deviations are given in parenthesis. Values denoted with the different characters are significantly different (p<0.05)

sampling campaign	As [μg L^{-1}]	Cd [μg L^{-1}]	Cu [μg L^{-1}]	Ni [μg L^{-1}]	Pb [μg L^{-1}]	Zn [μg L^{-1}]
spring	49.2 (243)[a]	0.93 (1.2)a	18.1 (17.2)[a]	6.5 (5.5)[a]	1.55 (3.3)[a]	76.3 (68.9)[a]
summer	10.5 (33)[a]	0.95 (1.5)a	12.9 (15.0)[a]	5.0 (3.2)[a]	0.24 (0.3)[b]	60.9 (87.2)[a]
autumn	41.8 (214)[a]	0.92 (1.5)a	14.1 (12.9)[a]	5.5 (4.9)[a]	0.43 (0.9)[c]	71.9 (95.6)[a]

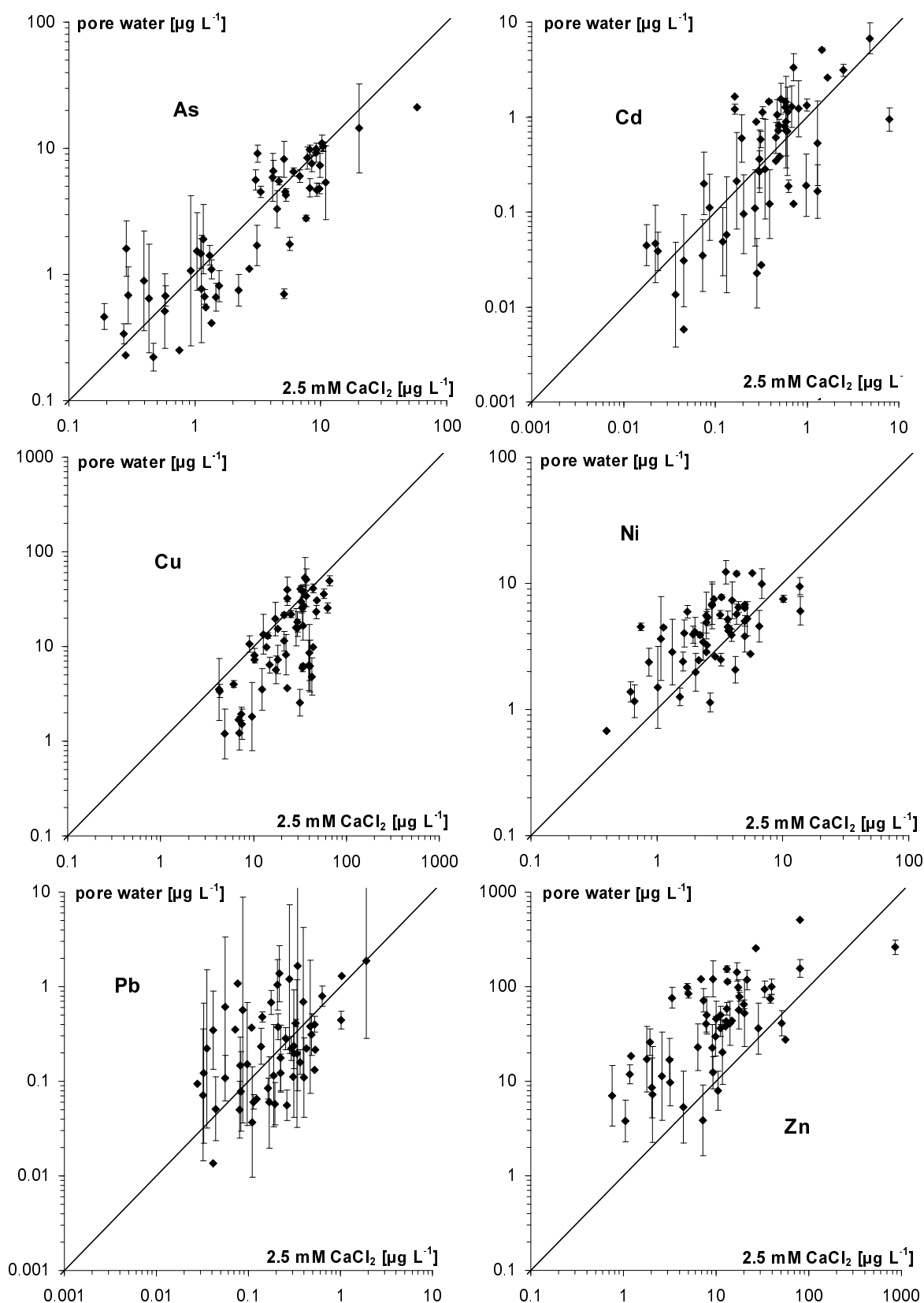**FIGURE 4.** Geometric mean and standard deviations of As, Cd, Cu, Ni, Pb and Zn in pore water samples collected on one location as a function of 2.5 mM $CaCl_2$ extractable concentrations. Samples with Fe>1 mg L^{-1} were not used for calculating the average. The line represents the 1:1 line

Reduced conditions can affect the partitioning of heavy metals in pore water (Chapter 5), but evidence of the reduced conditions is not preserved in the samples extracted by 2.5 mM $CaCl_2$. High concentrations of Fe in pore water samples commonly indicate the presence of reduced conditions in the soil layers that were sampled. Therefore, to be able to compare $CaCl_2$ extractions with pore water without a bias due to differences in redoxpotentials, we omitted all samples with Fe concentrations larger than 1 mg L^{-1} from the calculations in the next sections.

Figure 4 shows the pore water concentrations of As, Cd, Cu, Ni, Pb and Zn as a function of the concentrations measured in the 2.5 mM $CaCl_2$ extraction. The pore water concentrations of all sample points and depth are averaged over the three seasons. The extraction by $CaCl_2$ resembles the heavy metal concentrations measured in pore water well. Generally, the R^2 is high for all metals, but differences are apparent between the different elements.

Table 3 summarises the root mean square error (RMSE) of the *log*-transformed concentrations in pore water and 2.5 mM $CaCl_2$ extractions. The highest RMSE is found for Zn, mainly due to the systematic deviation from the 1:1 line. The large RMSE of Pb is due the large differences between the seasons. However, to separate deviations due to the scattering of data from systematic deviations, we defined transfer functions. To relate the concentrations measured in $CaCl_2$ to pore water concentrations, we used a simple regression function:

$$y = ax + b$$
(Equation 1)

The results are summarised in Table 4. The RMSE of the *log*-transformed data decreased by the application of this transfer function to values below 0.58 (Table 5). The largest benefit from this transfer functions obviously concerned the elements with the largest systematic deviations, Zn and Cu.

TABLE 3. Root mean square error (RMSE) of the *log*-transformed data of As, Cd, Cu, Ni, Pb and Zn in pore water and extractions by 2.5 mM $CaCl_2$

	As	Cd	Cu	Ni	Pb	Zn
log **RMSE**	0.34	0.53	0.50	0.30	0.63	0.71

Part of the differences between both methods can be explained by the difference in pH or DOC concentrations (Figure 3). Since virtually all Cu in solution is bound to DOC at the prevailing pH (Chapter 4 and 5), we can easily compare $CaCl_2$ extractable and pore water Cu concentrations by correcting the measured values for the different amounts of DOC in pore water and 2.5 mM $CaCl_2$ by:

$$\log Cu_{corrected} = \log Cu_{pore\ water} + \log \left[\frac{DOC_{CaCl_2}}{DOC_{pore\ water}} \right]$$
(Equation 2)

The corrected values lead to a better correlation between the Cu concentrations in pore water and the extraction (Figure 5), and result in a decrease of the RMSE of the *log*-transformed data from 0.50 to 0.29.

TABLE 4. Regression coefficients and R^2 of the transfer functions for As, Cd, Cu, Ni, Pb and Zn measured in 2.5 mM $CaCl_2$. All fits are highly significant ($p<0.001$). Standard error is given in parenthesis

pore water	a	b	R^2
log As [µg L^{-1}]	0.745 (0.04)	0.065 (0.03)	0.62
log Cd [µg L^{-1}]	0.942 (0.08)	-0.022 (0.05)	0.47
log Cu [µg L^{-1}]	1.041 (0.09)	-0.369 (0.12)	0.43
log Ni [µg L^{-1}]	0.510 (0.05)	0.391 (0.03)	0.34
log Pb [µg L^{-1}]	0.473 (0.12)	-0.306 (0.10)	0.09
log Zn [µg L^{-1}]	0.616 (0.06)	0.971 (0.06)	0.42

TABLE 5. Root mean square error (RMSE) of the *log*-transformed data of As, Cd, Cu, Ni, Pb and Zn in pore water and the concentrations in 2.5 mM $CaCl_2$ after correction by Equation 1

	As	Cd	Cu	Ni	Pb	Zn
log RMSE	0.31	0.52	0.36	0.23	0.58	0.38

For the other elements, a correction is more complex. Cd in pore water is only partially bound to DOC (Chapter 5) and the fraction bound to DOC varies with the pH (data not shown). Since the lower amount of DOC in pore water and the lower pH have an opposite effect on the Cd concentrations, the systematic deviation between both methods is small. In Chapter 2 and 5 we found a strong pH dependency of Zn due to the formation of a Zn-containing mineral. However, a correction for this pH-dependency is difficult, because it will only be valid as long as conditions are favourable for the formation of this mineral. Thus, the differences in pH can explain the higher Zn concentrations in pore water, but it is not possible to derive a simple correction as for Cu.

The differences in metal concentrations in pore water and in $CaCl_2$ were not significantly related to the concentrations of Ca or Cl in pore water. Samples with large differences between both methods could not be unequivocally linked to either high or low concentrations of Ca and Cl (data not shown). Thus, the influence of rainfall, flooding and evapotranspiration may be still recognisable in the concentration of Ca and Cl in a sample, but an influence on the metal partitioning could not be proven.
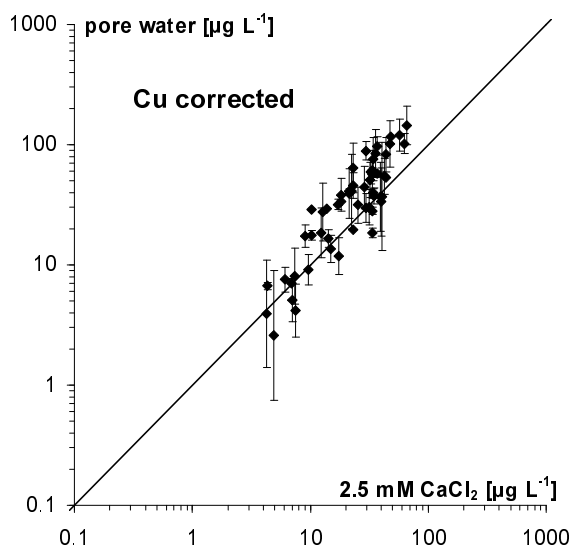
FIGURE 5. Geometric mean and standard deviations of Cu in pore water samples collected on one location as a function of concentrations extractable by 2.5 mM $CaCl_2$. The Concentration in $CaCl_2$ was corrected by Equation 2. Samples with Fe> 1mg L^{-1} were not used for calculation. The line represents the 1:1 ratio
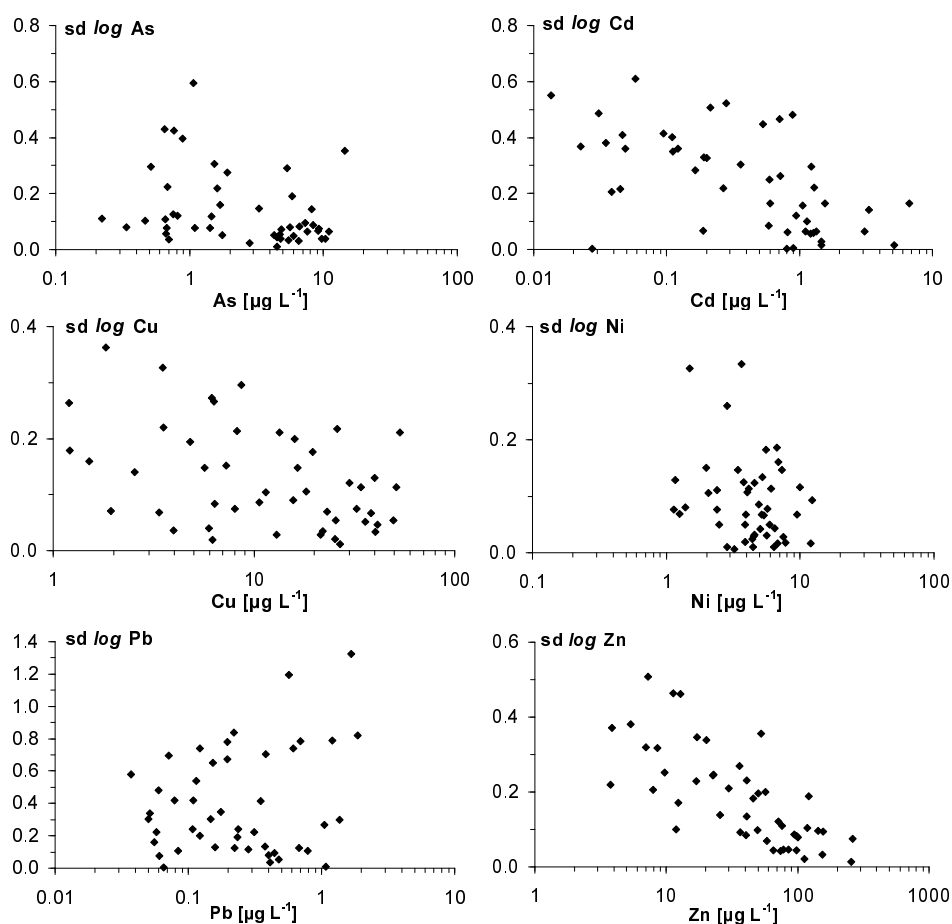
FIGURE 6. Standard deviations of Cd, Cu, Zn, Pb, Ni and As in pore water samples collected on one location in spring, summer and autumn. Samples with Fe>1 mg L^{-1} were not used for the calculations

3.3.1 CaCl₂ extractions compared with pore water

The concentrations of heavy metals in pore water and in the weak extractant were quite comparable. If the RMSE is compared with the standard deviations of the pore water samples collected in three different seasons (Figure 6), it is obvious that not in all cases the collection of a limited number of pore water samples will result in a better estimation of the average concentration than a $CaCl_2$ extraction corrected by Equation 1 or 2. The observed systematic differences could be partly explained by the differences in pH and DOC concentrations, but a suitable correction could only be derived for Cu. The different DOC concentrations were very likely due to the smaller pore diameter of the Rhizons, and a correction for DOC is consistent with the Cu concentrations in the two methods. The drying and rewetting of the soil samples does not lead to inexplicable artefacts, but the pH was significantly smaller in the extraction. Therefore we conclude that the extractions by 2.5 mM $CaCl_2$ were more than only a measure of bioavailability: they mimic to a good extent the composition of pore water for these river floodplain soils.

When the extractions can mimic pore water, geochemical modelling may deliver meaningful results for the solid-solution partitioning and can be used to compute detailed information about the speciation in the water phase, too. Both pore water sampling and $CaCl_2$ extractions are therefore useful tools to enable the modelling of uptake, toxicity and leaching of heavy metals in soils.

The monitoring of pore water gives an impression about the variability of the pore water composition present under natural conditions. The temporal variability of As, Cu, Ni and Zn is smaller than a half log-unit for almost all samples, which might be sufficiently small to use pore water extraction for risk assessment. However, for Pb the temporal variations can be larger than the differences we found between the least and most polluted sites. It is evident, that a single sample of pore water delivers a poor estimation of the mean Pb concentration in soil.

Pore water sampling is unavoidable when the temporal variability should be addressed. The use of Rhizon sampler *in situ* can overcome the problem of spatial heterogeneity since samples are taken at exactly the same location. Furthermore, only this method gives us any information about the influence of lowered redox conditions on metal partitioning. However, this method implies considerably more logistic efforts and the sampling of pore water can also be impeded by practical limitations: about one third of all samples could not be collected because of either desiccation or flooding of the location.

The pore water concentration collected at a particular time is the most direct measure of environmental effects, as it is the parameter that directly affects uptake and leaching at that moment. In view of the good agreement between pore water and extractable concentrations, extractions by 2.5 mM $CaCl_2$ appear to be a good measure for the concentration levels in the field. If this is the case, geochemical modelling can be used to derive the relationship between solid-solution partitioning and pore water concentrations and can therefore be used to predict changes in concentrations in scenario analyses.

Chapter 4

Modelling of the solid-solution partitioning of heavy metals and As in embanked floodplain soils of the rivers Rhine and Meuse

4.1 Introduction

In the last century large amounts of heavy metals have accumulated in the embanked river floodplain areas of the Dutch part of the Rhine and Meuse river systems. About 500 km^2 of floodplain soils are affected by the deposition of contaminated sediments. To enable decisionmaking with regard to river floodplain areas, it is necessary to be able to predict adverse effects due to the heavy metal pollution of these floodplain 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 (Pinheiro et al., 1999; Slavekoya and Wilkinson, 2002; Van Leeuwen, 1999). The combination of metal speciation modelling 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 behaviour in well-defined aquatic systems or nutrient solutions (Di Toro et al., 2001; Parker et al., 2001; Santore et al., 2001; Smiejan et al., 2003). However, modelling 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, geo-chemical speciation modelling of soil systems has not been satisfactory due to the complexity of sorption processes to the soil matrix (Hesterberg et al., 1993). To be able to use the many experimental data on metal sorption published in literature, understanding and accurate modelling 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 modelling make it possible to describe the complexation of metals by dissolved or soil organic matter (Kinniburgh et al., 1999; Milne et al., 2003; Tipping, 1993) or iron oxides (Hiemstra and Van Riemsdijk, 1996; Venema et al., 1996) 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 parameterised and therefore they can be applied directly to predict metal behaviour under a large range of conditions. Several studies combined a number of models to a "multisurface" approach (Cancés et al., 2003; Lofts and Tipping, 1998; Weng et al., 2001).

A more straightforward way to calculate solid-solution partitioning is the use of statistical regression formulas (Elzinga et al., 1999; Janssen et al., 1997; Sauvé et al., 2003). 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 modelling, 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 floodplain 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 parameterised by data available in literature, and a regression model based on the extensive dataset presented in this work.

To characterise the properties and heavy metal contamination patterns typical for river floodplain 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 a number of metals and nutrients (Sanders et al., 1987; Smilde et al., 1992; Van Erp et al., 1998).

For the geochemical model we used a multisurface approach similar to Weng et al. (2001) and Dijkstra et al. (2004) and extended it by also accounting for mineral phases. We parameterised the model by data given in literature, rather than fitting parameters to the dataset as done in other studies (Gustafsson et al., 2003; Lofts and Tipping, 1998; Hesterberg et al., 1993). 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.

4.2 Materials and methods

4.2.1 Field sampling

For field sampling, we selected 48 floodplains 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 fulfil two requirements, i.e., 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 landuse forms and ecosystem types. Within each selected floodplain system, we sampled two or three cores at different points, dependent on the size and heterogeneity of the floodplain. 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 5cm 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 5-35 cm and 57 samples from 35-60 cm) for analysis.
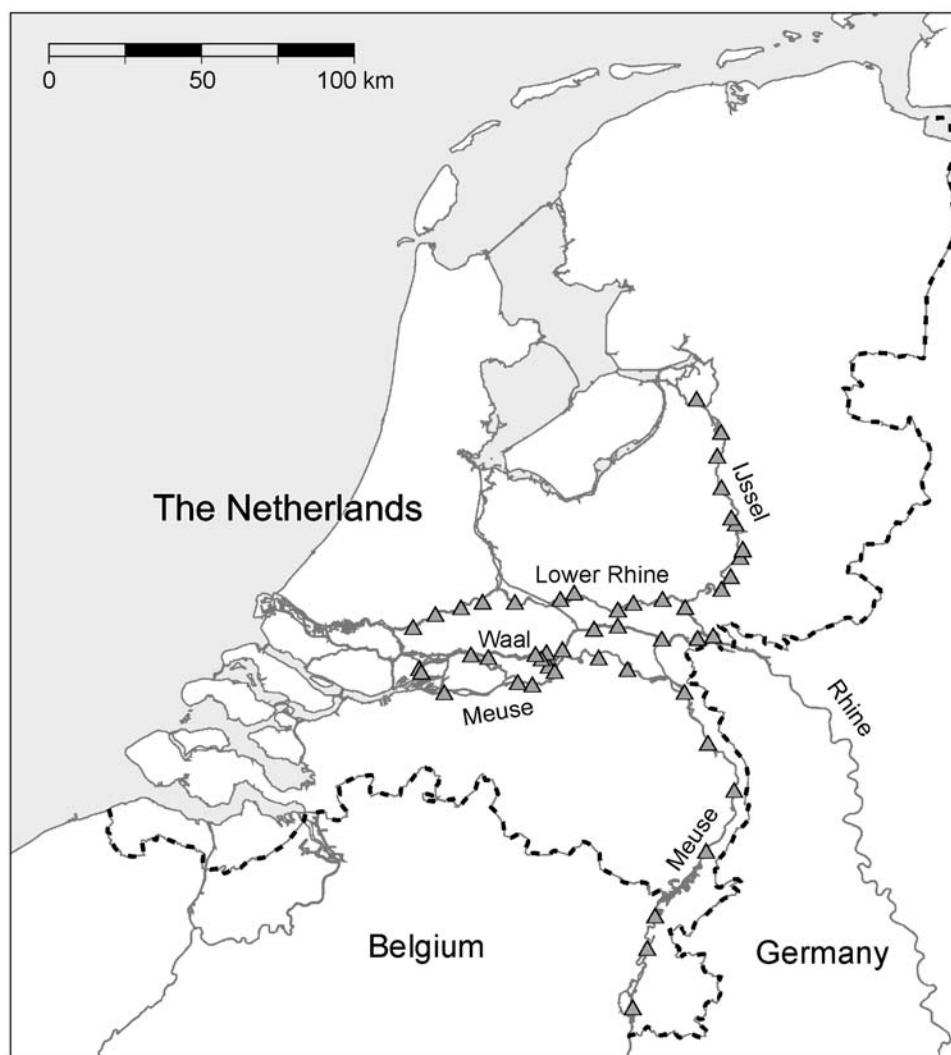
FIGURE 1. Sampling locations in the Rhine-Meuse floodplain system

4.2.2 Chemical analyses

Samples were dried at 40° C and sieved (<2 mm) before analysis. As, Cd, Cr, Cu, Ni, Pb, Zn, Mn, Fe, P and Al concentrations in *aqua regia* (NEN, 1992) were measured by ICP-AES (Spectros, Spectro Flame) and ICP-MS (Perkin Elmer, ELAN 6000). The content of soil organic carbon (SOC) was analysed by wet oxidation with $K_2Cr_2O_7$ (Wallinga et al., 1992). Clay content was measured by sedimentation according to Houba et al. (1997).

$CaCl_2$ extractions were made according to a modified scheme of Houba et al. (1996). 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 floodplains soils (data not shown).

The pH was measured in the suspension of the 2.5 mM $CaCl_2$ extraction (Houba et al., 1997). Dissolved organic carbon (DOC) concentration was measured in the extract by a TOC-analyser (Skalar, SK12) after the sample was diluted 5 times and acidified to a pH of

3.0 to 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).

4.2.3 Geochemical modelling

Speciation calculations were performed with the object-oriented modelling framework ORCHESTRA, a new geochemical program that gives the user the flexibility to extend the chemical model with appropriate sorption models (Meeussen, 2003).

Equilibrium constants for soluble species and mineral phases were used from the MINTEQA2 (Allison et al., 1991) recent database ver. 4.0. Equilibrium constants (K_{sp}) for mineral and soluble species from other sources are summarised in Table 1. Unlike in other studies (Weng et al., 2001; Dijkstra et al., 2004), we included in our model all minerals that are likely to occur under the prevailing conditions and allow them to coprecipitate with metals and to control the metal activity in solution. The activity correction was done with the Davis equation (Meeussen, 2003). 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 (Appelo and Postma, 1994). Instead, we defined a fixed background electrolyte of 2.5 mM $CaCl_2$ as input for the model calculations. The redoxpotential of the model system was defined by a constant $pO_2 = 0.20$ atm, assuming all samples to be in equilibrium with the atmosphere.

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

mineral	*log* K_{sp}	reference
$Ca^{2+} + Cl^- = CaCl^+$	-1.00	Lindsay, 1979
$Ca^{2+} + 2Cl^- = CaCl_{2(aq)}$	0.00	Lindsay, 1979
$Mn^{2+} + CO_3^{2-} = MnCO_{3(aq)}$	4.90	Stumm and Morgan, 1995
$Zn^{2+} + 2 CO_3^{2-} = Zn(CO_3)_2^{2-}$	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
$Zn_2Al(OH)_6Cl + 6H^+ = 2Zn^{2+} + Al^{3+} + Cl^- + 6H_2O$	23.50	Ford and Sparks, 2000
$Zn_2SiO_4 + 4H^+ = 2Zn^{2+} + H_4SiO_4$	15.33	Parkhurst and Appelo, 1999

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 (Kinniburgh et al., 1999). All model parameters necessary to describe adsorption on fulvic and humic acid were taken from the generic NICA parameter set (Milne et al., 2003). Organic matter consists of variable fractions of non-reactive matter, humic acid (HA) and fulvic acid (FA). Reliable data on the HA and FA fractions of organic matter are lacking in 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 non-reactive. To recalculate the measured carbon contents to organic matter content, we assume for simplicity a carbon content of organic matter of 50% (Schachtschabel et al., 1992).

Adsorption of metals and anions by iron oxide is calculated by the *Charge Distribution MUlti SIte Complexation* model (CD-MUSIC; Hiemstra and Van Riemsdijk, 1996). For the specific surface area of goethite, values are given from 20 to 200 m^2 g^{-1} (Cornell and Schwertmann, 1996). We assumed a specific surface area of 50 m^2 g^{-1} for iron oxide. The parameters used are given in the Appendix (Table 1 and 2). Sorption to manganese oxide is described by a surface complexation model of Tonkin et al. (2004). For the specific surface area of manganese oxide, a large range of values is given in literature (Tonkin et al., 2004). 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 modelling, 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 (Apello and Postma, 1994). 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} (Schachtschabel et al., 1992) and we used an exchange coefficient $K_{Zn/Ca}$ and $K_{Mn/Ca}$ of 1 (Bruggenwert and Kamphorst, 1982).

4.2.4 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 (Elzinga et al., 1999; Janssen et al., 1997):

$$\log Me_{CaCl_2} = \sum_i a_i \log X_i + const. \qquad \text{(Equation 1)}$$

where for the different i, X_i represent, 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.

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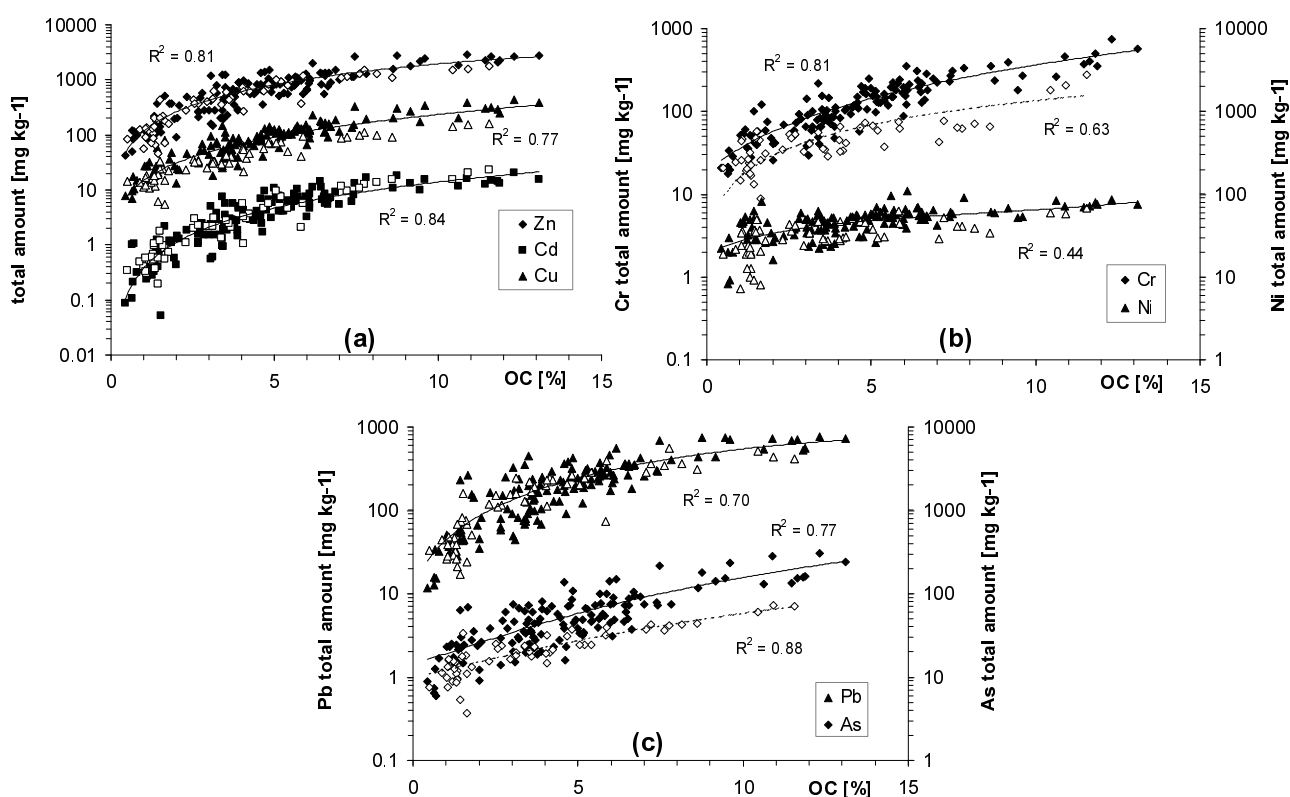
FIGURE 2. Heavy metal content of top soil layers (5-60 cm) as a function of the organic carbon content. (a) Zn, Cd and Cu (b) Cr and Ni (c) Pb and As. Open symbols: Meuse river. Solid symbols: Rhine river system. Fitted trendline functions and R^2 values are shown for all samples from both rivers. In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

Whereas the contamination patterns were quite comparable for the two rivers, the floodplain 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 ($\pm$11.2 g kg^{-1}) was measured, whereas in the Meuse floodplain the Ca concentrations were significantly smaller and more variable (9.2 g kg^{-1} $\pm$8.8 g kg^{-1}). Although the Ca content is not expected to influence metal behaviour 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. Due to sufficient amounts of Ca in the Rhine sediments the pH is high (7.47 ±0.16). In comparison, the pH values of the Meuse floodplain 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, the extractable metal fractions in the Meuse samples will be higher.
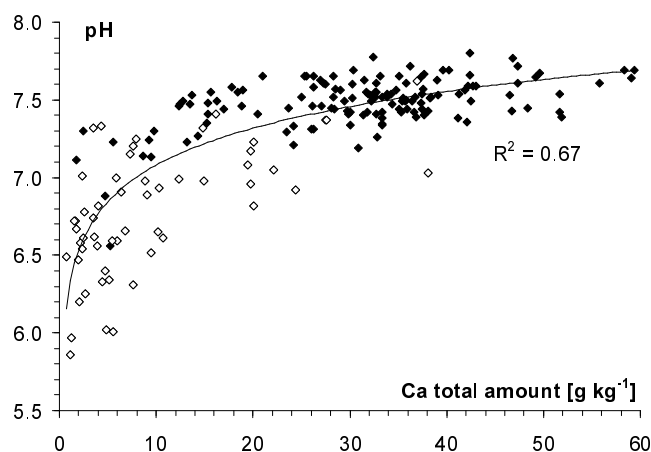
FIGURE 3. Soil pH as a function of Ca content of top soil layers (5-60 cm). Open squares: Meuse river, solid squares: Rhine river system

Figure 4 shows the measured concentrations in the 2.5 mM $CaCl_2$ extractions compared to the predictions of the fully parameterised geochemical model. We did not present geochemical calculations for Ni, because the thermodynamic data were of poor quality (Hummel and Curti, 2003), the data support for the NICA parameter was weak (Milne et al., 2003) 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 found to be 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 due to the low activity of Cd^{2+}, binding in diffuse double layers of organic matter, oxides and clay was negligible ($<1\%$). Manganese oxide can potentially bind large amounts of Cd (Zasoski and Burau, 1988). However, despite the use of four surface binding sites, the model of Tonkin et al. (2004)

fails to describe the available literature data on Cd binding to manganese oxides. The binding of Cd was largely underestimated in a number of 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 in order to improve our model.
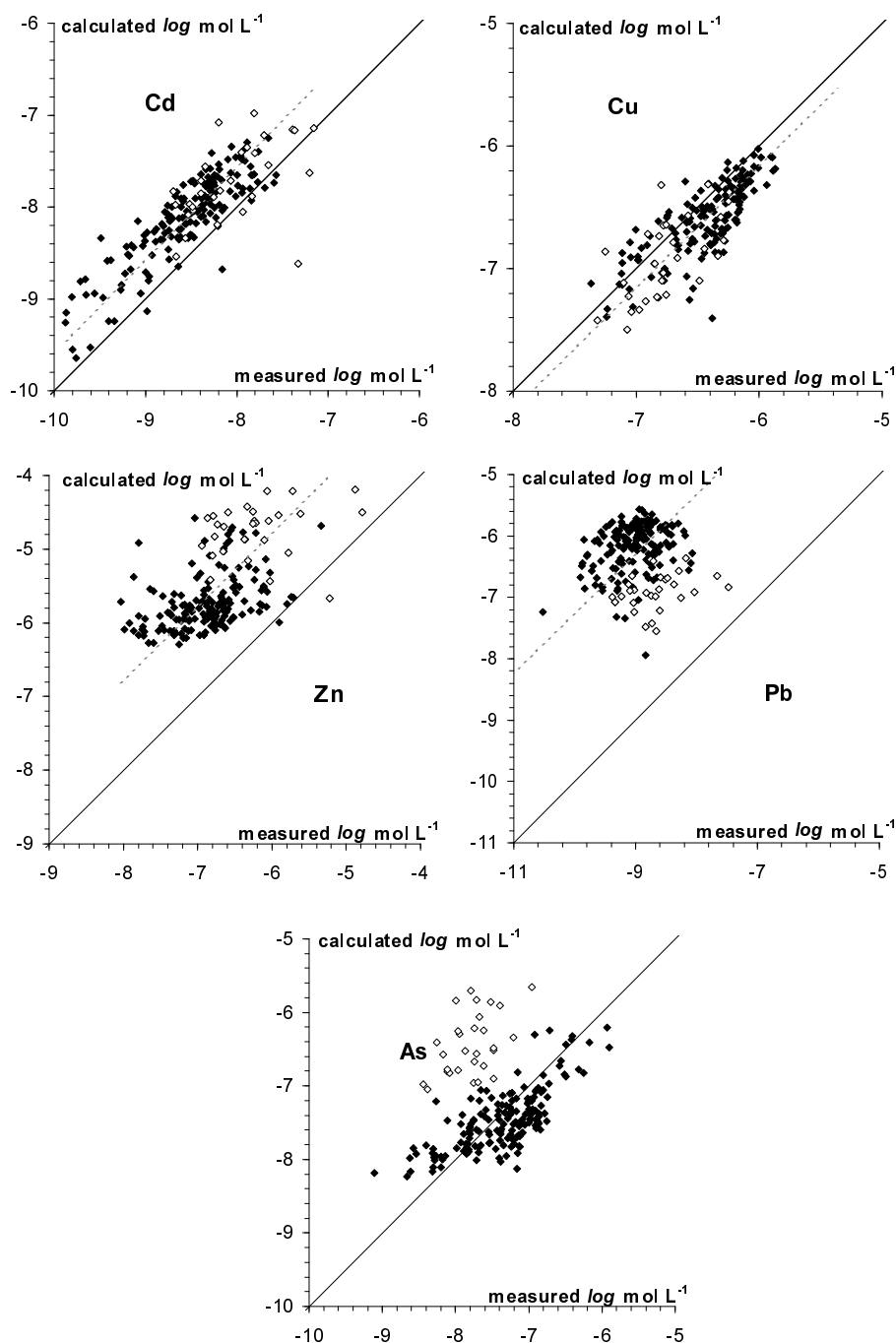
FIGURE 4. Concentrations of Cd, Cu, Zn, Pb and As extracted by 2.5 mM $CaCl_2$ and calculated by the geochemical model. Open symbols correspond to samples with a pH<6.8. The dashed line represents a trendline through the average values; the full line represents the 1:1 line

The extractable Zn concentrations were overestimated by more than one log-unit. For the speciation of Zn, organic matter binding is less important than in 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 (Scheinost et al., 2002; Manceau et al., 2000), 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 (1979) found that in soil the activity of Fe^{3+} can be larger than calculated in equilibrium with goethite. He recommends the use of an empirical "soil"-$Fe(OH)_3$ with a solubility between amorph iron oxide and goethite. In 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 can not prove which of the minerals is present in soil. However, since all of them have the same pH-dependency (log Zn^{2+} + 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.
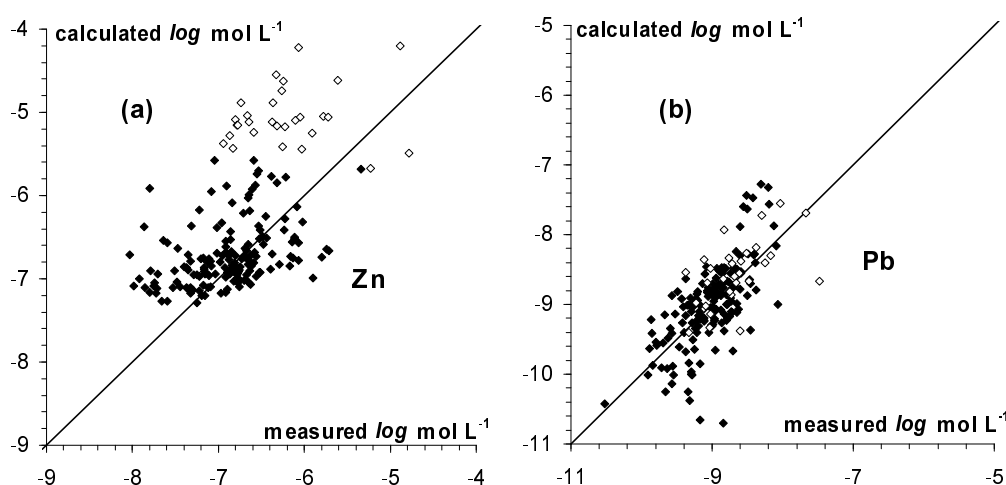
FIGURE 5. Concentrations of (a) Zn and (b) Pb extracted by 2.5 mM $CaCl_2$ and calculated by the modified model. Open symbols correspond to samples with a pH<6.8. The line represents the 1:1 line

Lead concentrations were profoundly overestimated too, a problem already discussed by Weng et al. (2001). In view of our model predictions for the extractable Pb fractions, which were more than two orders of magnitude too large, we estimated that only 1% of all Pb in soil can be bound to organic matter. Due to the high affinity of Pb to organic matter at high pH, the Pb^{2+} activity is too low to make it likely that mineral phases like chloropyromorphite or $PbHPO_4$ (Sauvé et al., 1998) can be formed under these conditions. Several studies imply that Pb can be sorbed to goethite not solely as a Pb^{2+} cation, but also as $PbCO_3$

(Villalobos et al., 2001; Ostergreen et al., 2000b), $PbSO_4$ (Ostergreen et al., 2000a), $PbCl^+$ (Barrow et al., 1981; Bargar et al., 1998) and $PbPO_4^-$ species (Ler and Stanforth, 2003; Weesner and Bleam, 1998). We used the data available in 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. (2003) but too small to describe the data of Weesner et al. (1998). However, in spite of the contradictory data, we hypothesise the formation of a $PbPO_4$ complex on goethite, recognising that we can not 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. (2002) suggest that at the given pH range, binding to Al hydroxides, which are present in floodplain soils at approximately 20 g kg^{-1} on average, might affect the solid-solution partitioning of As.

Table 2 and Figure 6 shows the results of the regression calculations of the statistical model. The statistical model shows better results than the fully parameterised 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 (Elzinga et al., 1999; Janssen et al. 1997). This can be attributed partly to the large size of the used dataset and partly to the limited and well defined area of this study, with soils of a comparable origin.

TABLE 2. Regression parameter for Cd, Cu, Zn, Pb, Ni and As extractable by 2.5 mM CaCl$_2$. *Me*$_{tot}$ is the total amount of the metal in question. *n.s.* = not significant

	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
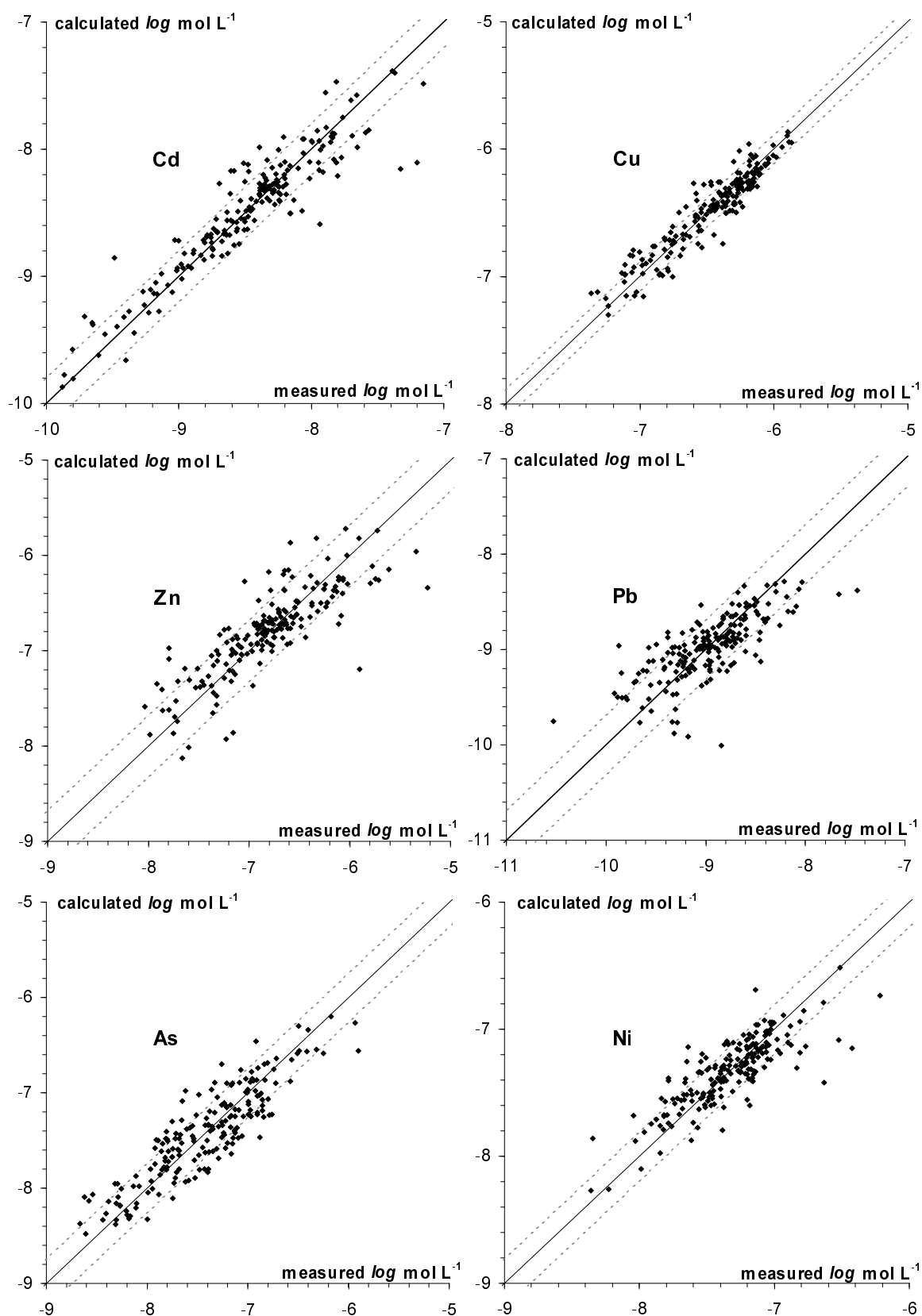
FIGURE 6. Concentrations of Cd, Cu, Zn, Pb, Ni and As extracted by 2.5 mM $CaCl_2$ as a function of the concentrations calculated by a regression model (Table 2). The full line represent the 1:1 line and the dashed lines the standard error of estimation

4.3.1 Reduction of input variables

Both statistical and geochemical model required an extensive input. Several options were explored to reduce the number of input parameters of the models. Table 3 summarises the effect of these simplifications on the RMSE of the statistical model. Table 4 summarises the regression parameters for the simplified models.

TABLE 3. Root mean square error (RMSE) of the statistical model for Cd, Cu, Zn, Pb, Ni and As in 2.5 mM CaCl$_2$. The RMSE is calculated from *log*-transformed concentrations. Me_{tot} is the total amount of the metal in question

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

TABLE 4. Simplified statistical model for Cd, Cu, Zn, Pb, Ni and As extractable by 2.5 mM CaCl$_2$. Me_{tot} is the total amount of the metal in question. *n.s.* = not significant

	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 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 al 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 to 0.13 log-units. Measuring of 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

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

The RMSE-values of the model that use equation (2) were comparable to the values of both the full model and the simplified model using the individual pH values, i.e., they vary less than ±0.03 log-units from both models.

In Table 5, we provide several generic input parameters based on 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 summarises the RMSE of the simplified geochemical models and the fully parameterised 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 5. Generalised input parameters for simplified speciation model. DOC values and pH are calculated according to equation 3 and 2, respectively

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}]
Equation 3	Equation 2	20,000	1000	900	30,000

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:

$$DOC = 1.0488 * 10^{-4} * SOC^{0.4545}$$

(Equation 3)
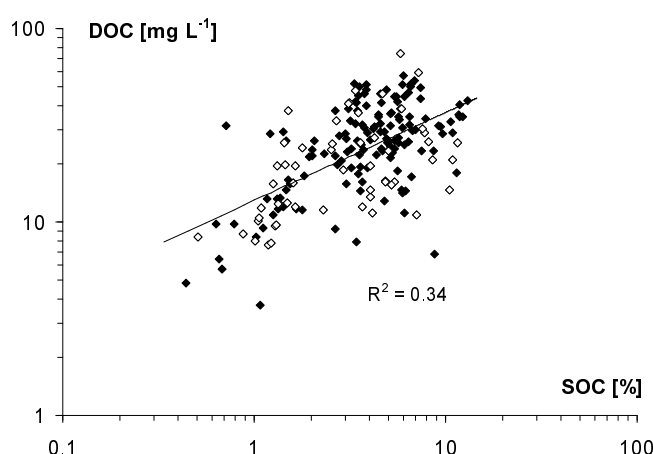
FIGURE 7. DOC concentration as a function of the organic carbon content. Open symbols: Meuse river. Solid symbols: Rhine river system

By calculating DOC concentrations with equation 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 Equation 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 literature (Tipping, 2002), and averaged DOC values are found to perform almost as well as individual measured samples for a single soil with different treatments (Chapter 2). DOC values calculated with equation 3 leads 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 (Equation 2), had a positive effect on the prediction of Pb and As (Figure 8) in the modified geochemical model. This substitution levelled 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.

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. The RMSE is calculated from the *log*-transformed concentrations. Me_{tot} is the total amount of the metal in question. Values in parenthesis are for samples with pH>6.8

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

After reduction of the numbers 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 floodplain soils to calculate the solid-solution partitioning with this simplified model.
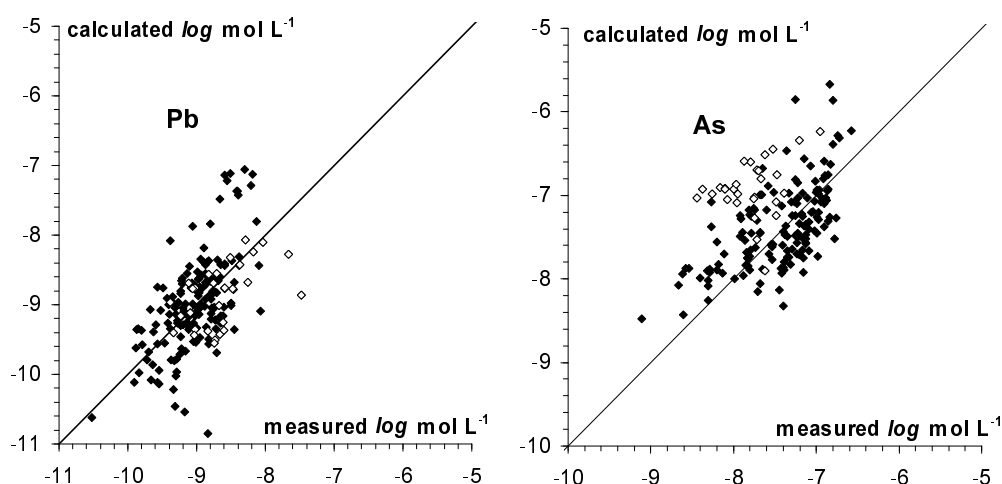
FIGURE 8. Concentrations of Pb and As extracted by 2.5 mM $CaCl_2$ and calculated by the simplified geochemical model with generic values for DOC, Al_{tot}, Mntot, Fe_{tot} and P_{tot}. The pH is calculated from Ca_{tot}. Open symbols correspond to samples with a pH<6.8

4.3.2 Geochemical modelling vs. statistical approach

We presented two models to predict solid-solution partitioning of heavy metals in oxic river floodplain 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 floodplain 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 a RMSE better than 0.74 log-unit. This is comparable to the results of other studies (Dijkstra et al., 2004; Weng et al., 2001).

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.

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 modelling of metal speciation in the soil solution is possible if metal complexation by DOC is taken into account (Sauvé et al., 2003; Weng et al., 2001). 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.

Chapter 5

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

(submitted)

5.1 Introduction

Large quantities of heavy metals have accumulated in the last century in the embanked river floodplain 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 heavy metal contamination of these floodplain soils. For the risk assessment of contaminated soils, information about the solid-solution partitioning and speciation of heavy metals is necessary as they affect both metal mobility and bioavailability. Geochemical speciation modelling is a potentially useful tool to quantify partitioning and speciation that can be integrated in a GIS environment to conduct scenario studies. Unlike in aquatic chemistry, the application of speciation modelling to soil systems faces extra 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 the dataset (Gustafsson et al., 2003; Römkens and Dolfing, 1998), but in this case the extrapolating capabilities to other soils and conditions, as might be important for scenario studies, become questionable. Recent advances of sorption modelling enables us to describe the complexation of metals by dissolved or soil organic matter (Kinniburgh et al., 1999; Milne et al., 2003; Tipping, 1993) or iron oxides (Hiemstra and Van Riemsdijk, 1996; Venema et al., 1996) in detail. These models can be combined to a "multisurface" approach (Dijkstra et al., 2004; Lofts and Tipping, 1998; Weng et al., 2001). The multisurface approach, combined with mineral precipitation reactions, may be well suited to improve geochemical modelling as underlying models are well parameterised (Chapter 4).

In a Chapter 4, we presented a geochemical model to predict the solid-solution partitioning of heavy metals in a large number of top soil samples from river floodplains in the Netherlands. For the soluble fraction, we focused on the metals extractable by 2.5 mM $CaCl_2$. Besides 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 redoxpotential in the profile under waterlogged conditions, therefore our approach can 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, we have to extend the geochemical model 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 equilibria and multisurface sorption under changing redox conditions is still relatively new. Redox processes influence the heavy metal speciation by precipitation and dissolution of metal containing minerals (Lindsay, 1979) or minerals that sorbs 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. The many chemical reactions that need to be accounted for in redox affected systems to our knowledge 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 can change during the year, a single sample of pore water gives only limited information about the availability of metals on a location. Parameters that strongly control the metal partitioning, such as the pH or the concentration of dissolved organic carbons (DOC), are known to be influenced by seasonal variations and biotic soil processes (Farley and Fitter, 1999; Linehan et al., 1989). 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 pore water is needed.

In this paper, we study the solid-solution partitioning of heavy metals in a soil profile of a floodplain situated along the Dutch Nieuwe Merwede river 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 heavy metals and As and other important variables in a soil profile ranging from oxic to sulphidic. For this, we monitored the pore water composition *in situ* over a period of two years. Second, we were interested to elucidate the processes influencing metal partitioning under different redox conditions. For this purpose, a multi-surface geochemical model is developed that predicts the solid-solution partitioning and computes the speciation of heavy metals in pore water and the solid phase. The model is fully parameterised by 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 geochemical model are presented.

5.2 Materials and methods

5.2.1 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 that connects the largest branch of the Dutch part of the Rhine, the river Waal, with the North Sea (Figure 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.

For pore water sampling, we used Rhizon soil moisture sampler (SMS MOM, Rhizosphere Research Products, Wageningen, The Netherlands). The Rhizon samplers were placed permanently in the floodplain sediment, which enabled us to repeatedly sample 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 hours 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 $Ca(NO_3)_2$.
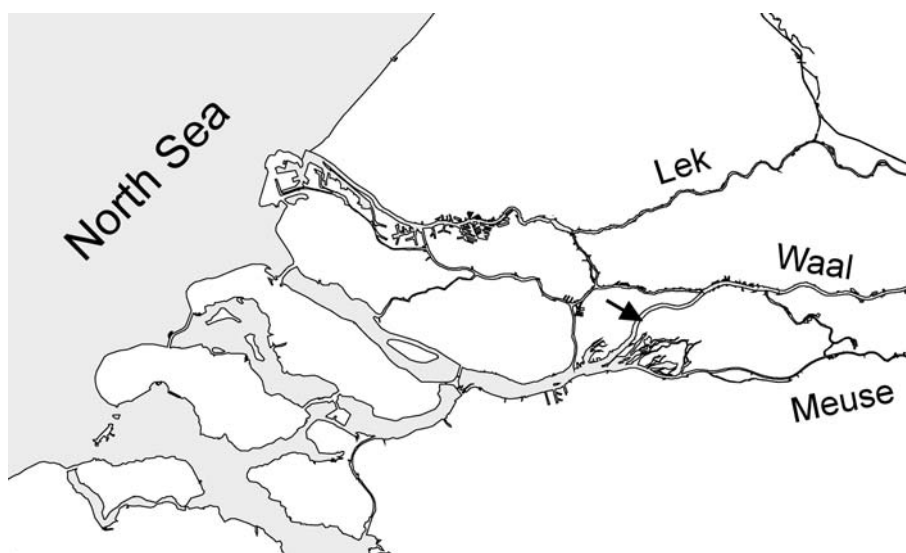
FIGURE 1. Monitoring location Lage Hof

The Rhizon samplers were inserted horizontally in the floodplain sediment from 10 to 65 cm depth with a 5 cm distance increment. From 45 to 65 cm depth, the Rhizons were applied in duplicate with a horizontal distance of 10 cm. To extract pore water, a vacuum was build up inside 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 takes 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 twelve times over a period of two years (Figure 2).

5.2.2 Chemical analysis

The pH of the pore water samples was measured immediately on location before oxidation affects the pH. Inorganic carbon (IOC) and DOC were measured on a TOC analyser (Skalar, SK12) within 24 h. For the analysis of DOC, samples were acidified to a pH of 3.0 to 3.5 by addition of 0.28 M HNO_3. As, Cd, Cu, Pb, Zn, Mn, Fe and Ca concentrations of pore water were measured by ICP-MS (Perkin Elmer, ELAN 6000). Sulphate and chloride 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 sulphur species in the pore water samples. Therefore we assume that the concentration of sulphate measured in the oxidised samples represents the total amount of S in pore water.

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

5.2.3 Geochemical modelling

Speciation calculations were done with the object-oriented modelling framework ORCHESTRA (Meeussen, 2003). The model set-up and parameterisation is based on Chapter 4. The previous model was already fully parameterised by literature data, but we had to extend the model definition by the species present at lower redox conditions. We included in our model all minerals that are likely to occur under the prevailing conditions and allowed them to coprecipitate with metals and to control the metal activity in solution. Equilibrium constants for minerals and soluble species from other sources than (Allison et al., 1991) are summarised in Table 1.

To calculate the adsorption of metals to solid phases and dissolved organic carbon, we used the consistent NICA model (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). We assumed 30% of soil organic carbon (SOC) to be present as HA and 50% of DOC to be present as FA. The remaining fractions of SOC and DOC were assumed to be non-reactive. To recalculate the measured carbon contents to organic matter content, we assumed for simplicity a carbon content of organic matter of 50% (Schachtschabel et al., 1992).

TABLE 1. Soluble and mineral species and *log* Ksp values used for calculation from other sources than (*22*)

species or mineral	*log* K_{sp}	reference
$Ca^{2+} + Cl^- = CaCl^+$	-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, 1995
$Fe^{3+} + H_2O + CO_3^{2-} = Fe(OH)CO_{3(aq)} + H^+$	-3.83	Bruno et al., 1992b
$Fe^{2+} + 2CO_3^{2-} = Fe^{(II)}(CO_3)_2^{2-}$	7.10	Bruno et al., 1992a
$Mn^{2+} + CO_3^{2-} = MnCO_{3(aq)}$	4.90	Stumm and Morgan, 1995
$Zn^{2+} + 2\,CO_3^{2-} = Zn(CO_3)_2^{2-}$	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

Adsorption of metals and anions by iron oxide is calculated by the CD-MUSIC model (Hiemstra and Van Riemsdijk, 1996). For the specific surface area of goethite, we assumed a specific surface area of 50 m^2 g^{-1} for iron oxide (Cornell and Schwertmann, 1996). The used sorption parameters are given in Chapter 4 and the Appendix (Table 1 and 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 manganese (hydr)oxides is described by the surface complexation model of Tonkin et al. (2004). For the model calculation we used a specific surface area of 50 m^2 g^{-1}. Clay adsorption of Ca, Zn and Mn is calculated by a simple ion exchange model with a constant CEC. We assumed all clay to be present as illite with a CEC of 0.35 mol$_c$ kg^{-1} (Schachtschabel et al., 1992) and we used an exchange coefficient $K_{Zn/Ca}$ and $K_{Mn/Ca}$ of 1 (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. SiO$_4^{4-}$ 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 in the model (Appelo and Postma, 1994). Instead, we used the total concentration of Ca measured in pore water as input parameter. The pCO$_2$ is calculated from the amount of IOC measured in pore water.

To address the complex chemistry of sulphur properly, we have chosen for a practical approach, which makes use of 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 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.

5.3 Results and discussion

Figure 2 on the next page 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 twelve times 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 for several weeks, only occur in the spring season.

Table 2 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 heavy metal contamination with increasing depth.

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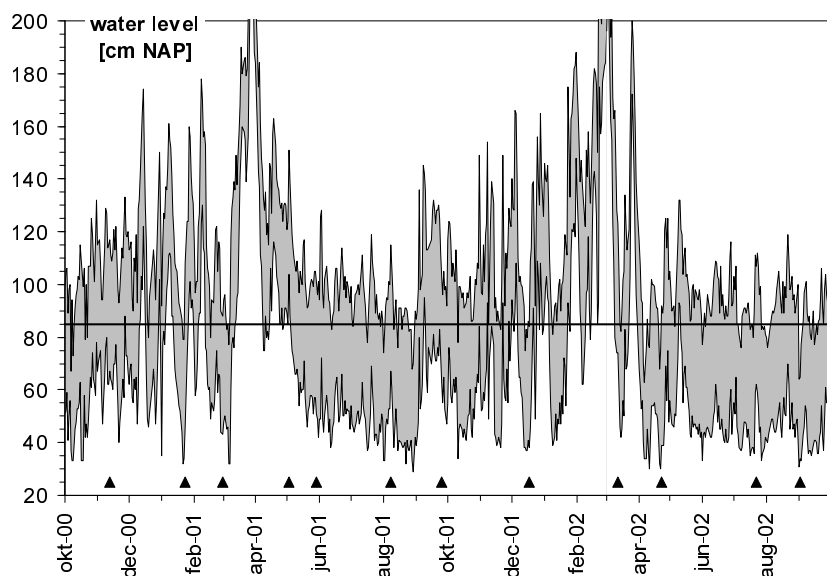
FIGURE 2. Daily minimum and maximum water level measured at Werkendam Buiten, The Netherlands. The water level is relative to the Dutch reference sea level (NAP). Triangles represent sampling dates, horizontal black line indicates the height of the sampling location. Source: Rijkswaterstaat, The Netherlands

Figure 3 presents the results of monitoring of the pore water composition (for SO_4 and Cl see Appendix, Figure 1). Whereas in the upper layers the concentrations of heavy metals and As are comparable to the extractable concentrations reported in Chapter 4, the heavy 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 iron peak.

The temporal variability of the 12 samples taken during the two years 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 (Figure 1 and 2, Appendix). 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). The small variability we 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 (Figure 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, we tested whether there is any correlation that links the variations of metal concentrations with the variations of these parameters. 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.
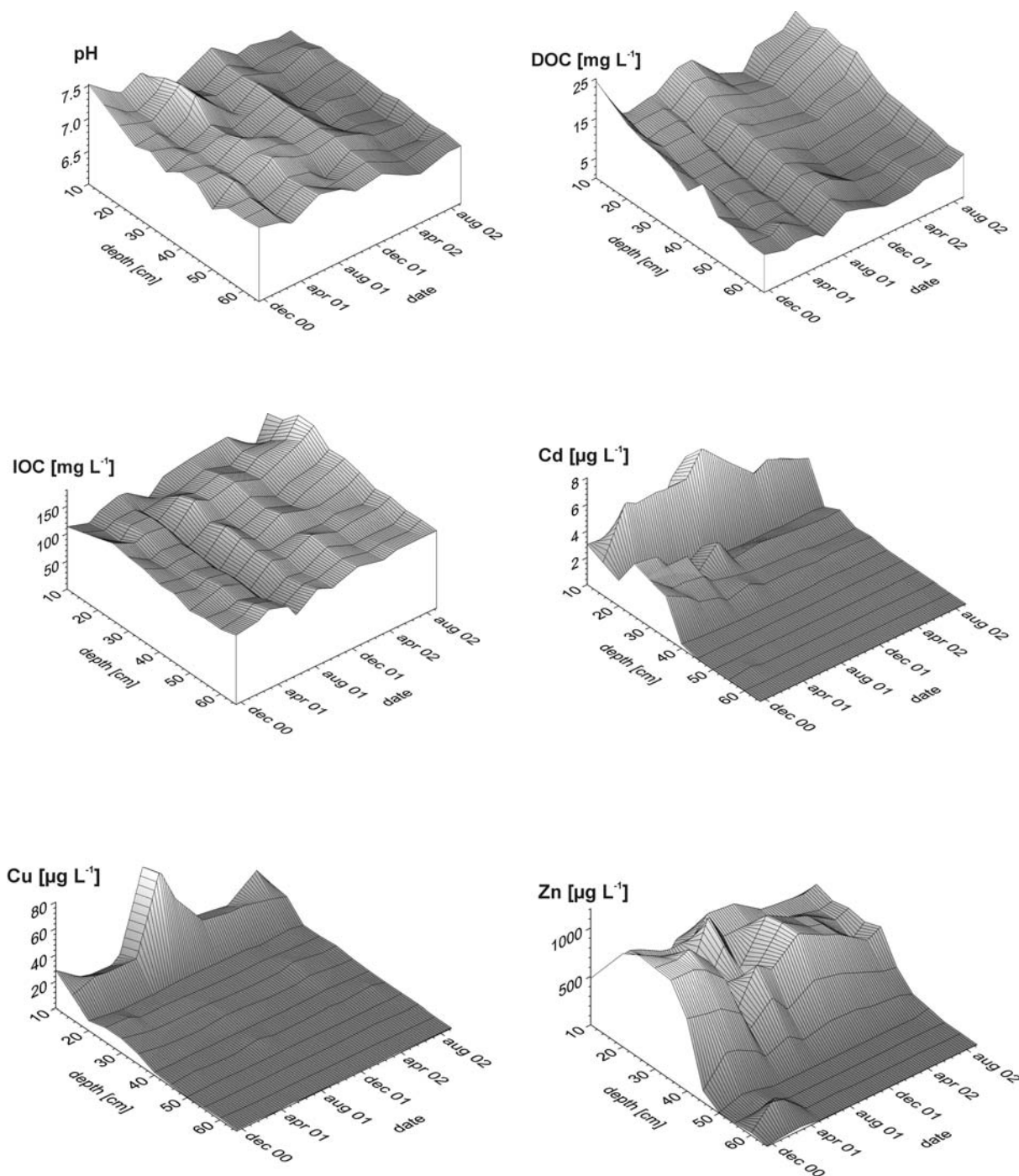
FIGURE 3. pH, DOC, IOC, Cd, Cu, Zn, Pb, As, Fe and Mn measured in pore water extracted at Lage Hof site as a function of sampling date and depth (continued next page)
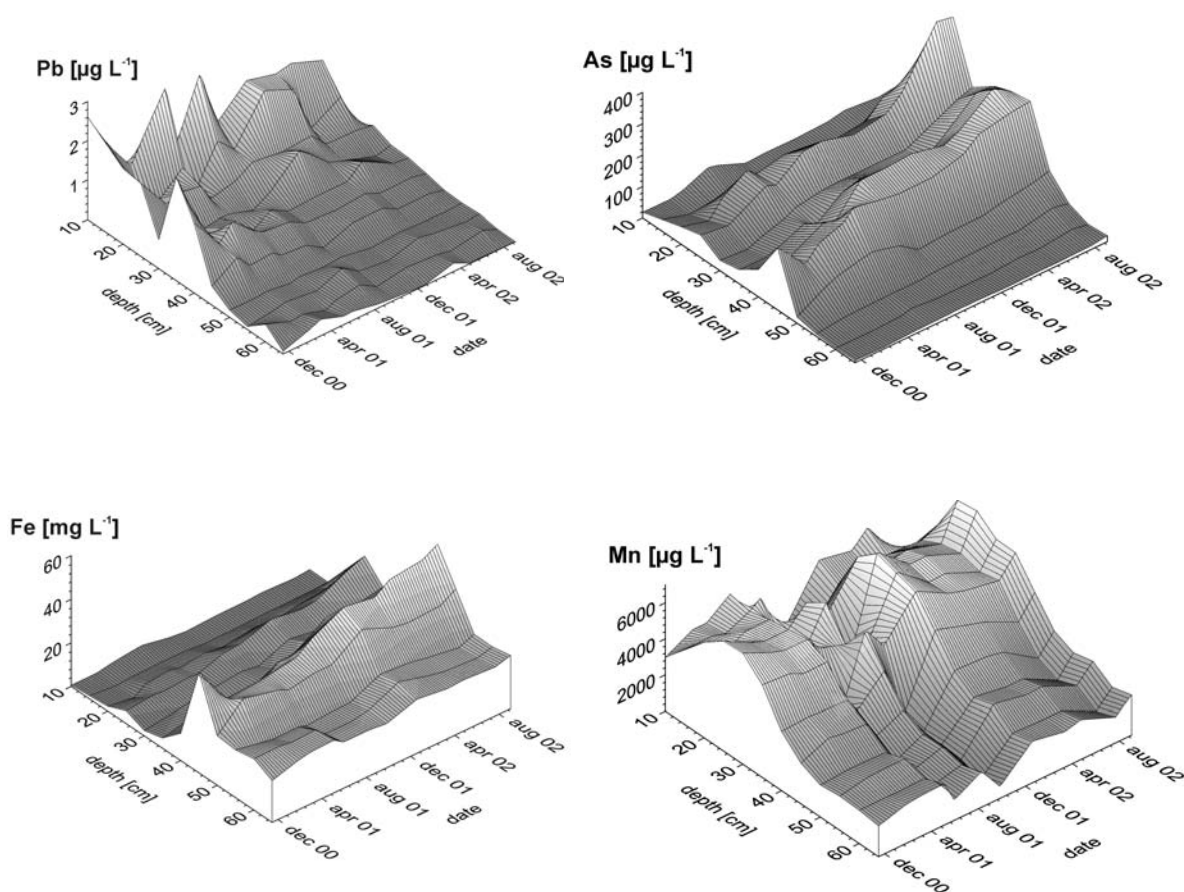
FIGURE 3 (continued from previous page). pH, DOC, IOC, Cd, Cu, Zn, Pb, As, Fe and Mn measured in pore water extracted at Lage Hof site as a function of sampling date and depth

Since the properties of the soil layers do not differ much (Table 2), we used the average value of all soil layers 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, too. Therefore we used their average concentrations of all samples in time and depth as a first estimate. By using the same input for all calculations, it is easier to present and discuss the results since the pe is the only variable left. In addition, it makes it superfluous to make any assumption about the redoxpotential present in a certain depth. Table 3 gives the values of the input parameters used for the geochemical speciation calculations.

TABLE 3. 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
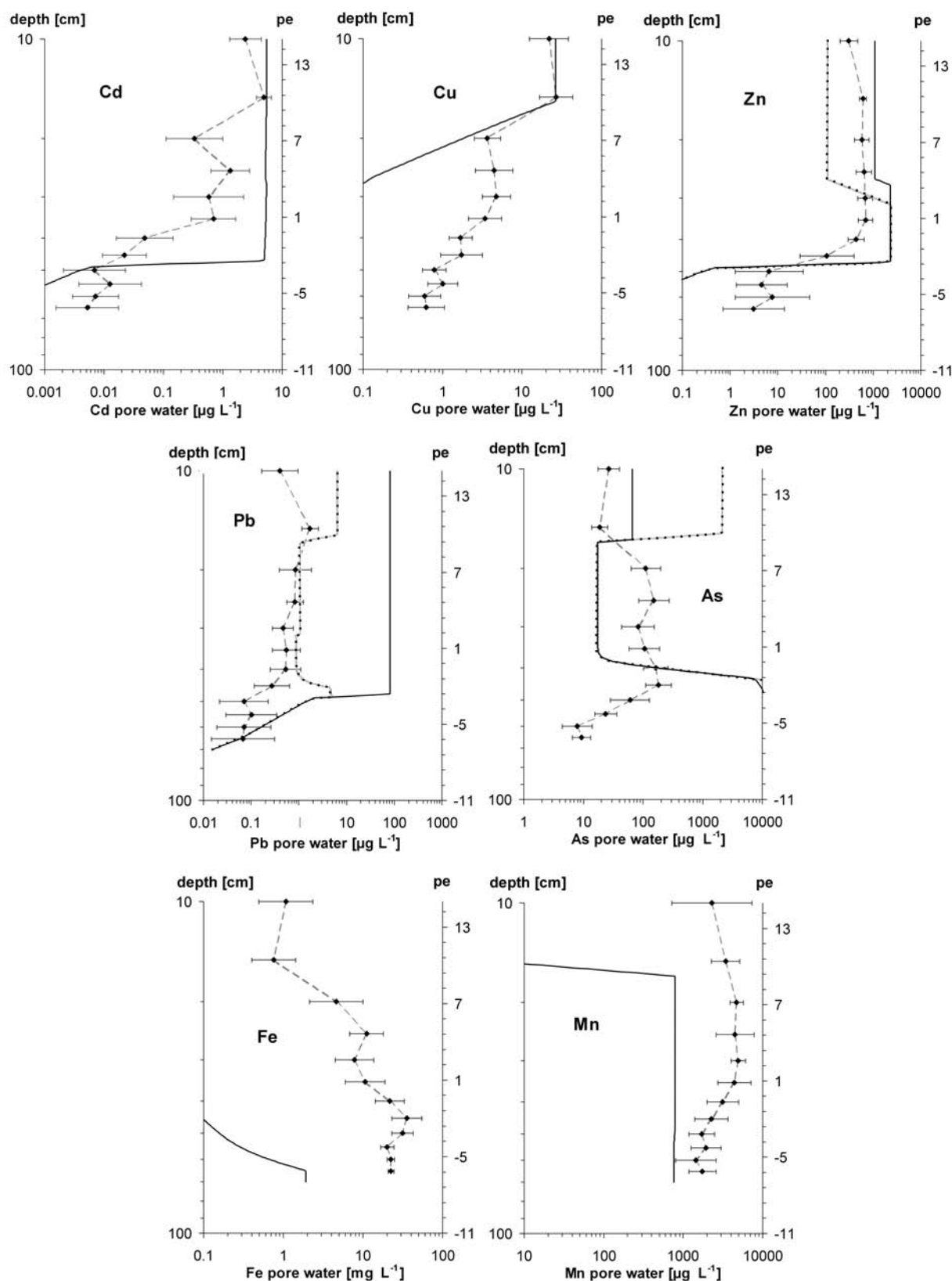
FIGURE 4. Calculated and measured average concentrations of Cd, Cu, Zn, Pb, As, Fe and Mn in the soil profile at the Lage Hof site. Diamonds: measured geometric mean values of 12 sample dates and standard deviations as a function of the sample depth. Solid line: generic model. Dotted line: optimised model. Note that the dotted lines are left out were not difference was visible

Figure 4 shows the calculated and measured concentrations of the heavy metals, As, Mn and Fe. The calculated values are expressed as a function of the pe and the measured values as a function of the depth in the profile. For the graphical presentation, we assumed the redoxpotential to decrease linearly with the logarithm of the depth with a pe of 15 at 10 cm and a pe of -7 at 70 cm depth.

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 calculated distributions of the metals over all relevant species in the solid and in the aqueous phase as shown in Figure 5 and 6 are useful to understand the speciation of the metals and indicates which species control the partitioning of these metals. But they can also be useful to elaborate the deviations found between the model predictions and measurements and to propose a way to improve the model as we will discuss in the next sections.
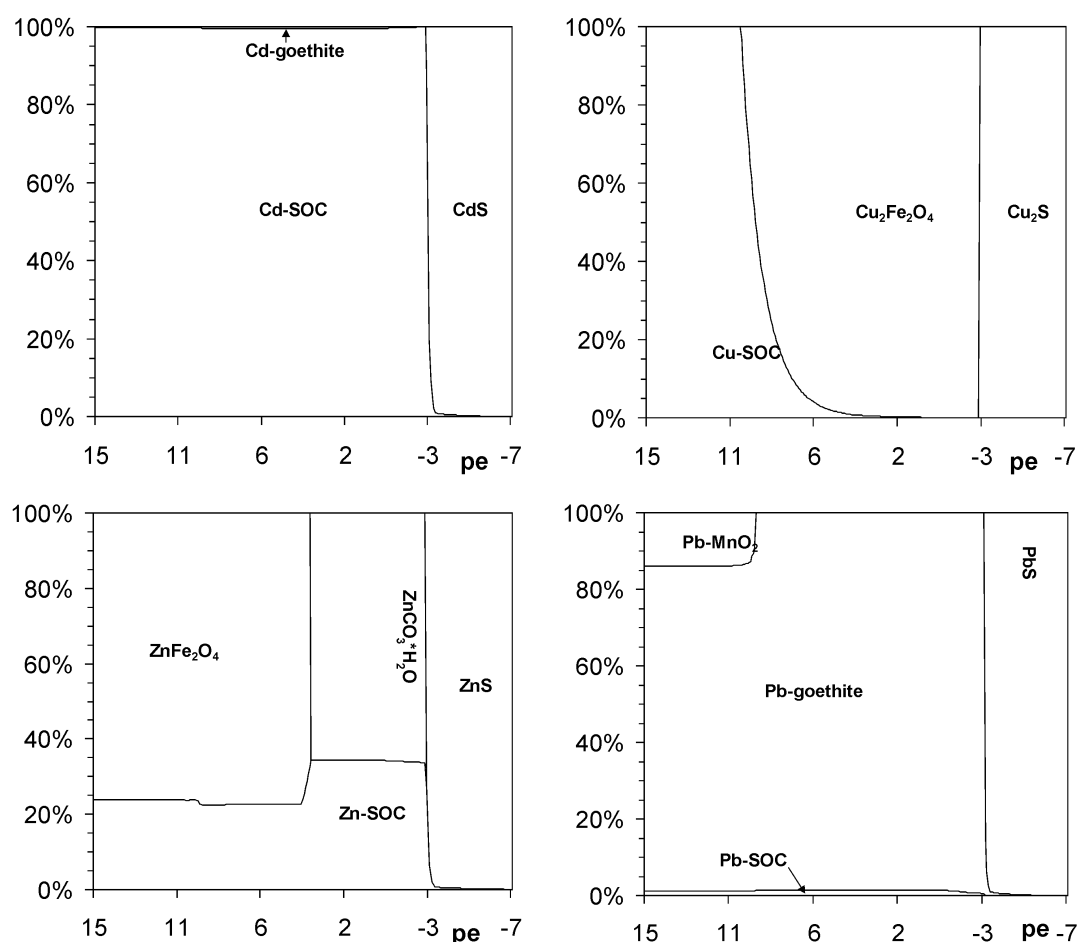
FIGURE 5. Calculated distribution of Cd, Cu, Zn, Pb, As, Fe and Mn in the solid phase at the Lage Hof site (continued next page)
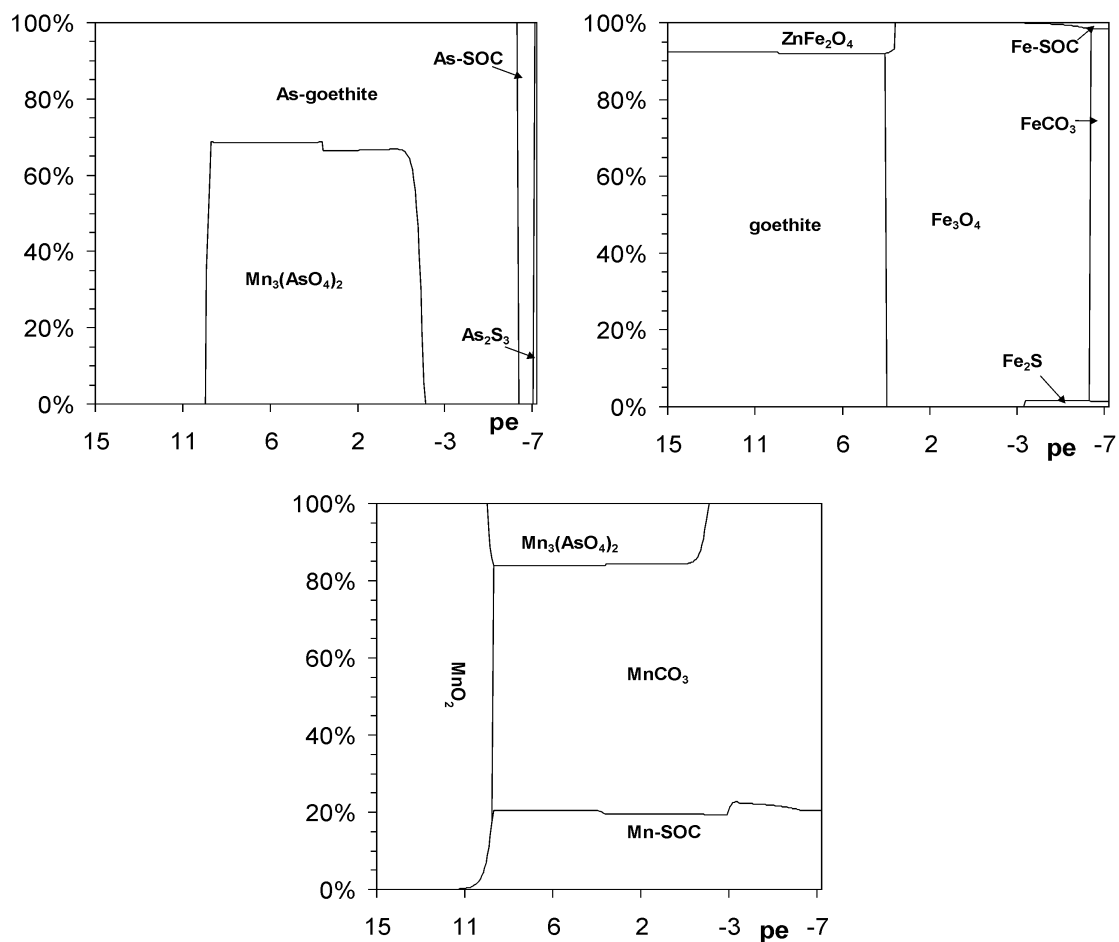
FIGURE 5 (continued from previous page). Calculated distribution of Cd, Cu, Zn, Pb, As, Fe and Mn in the solid phase at the Lage Hof site
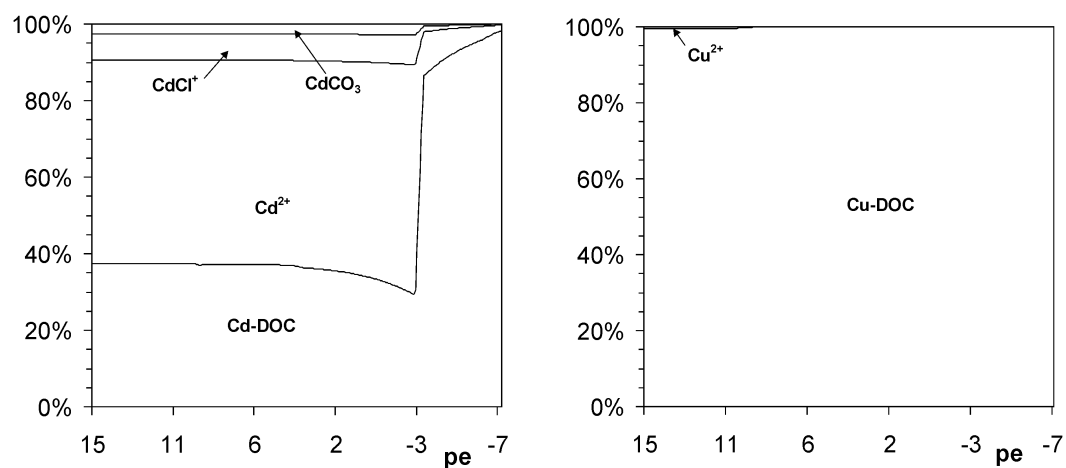
FIGURE 6. Calculated distribution of Cd , Cu, Zn, Pb, As, Fe and Mn in the water phase at the Lage Hof site (continued next page)
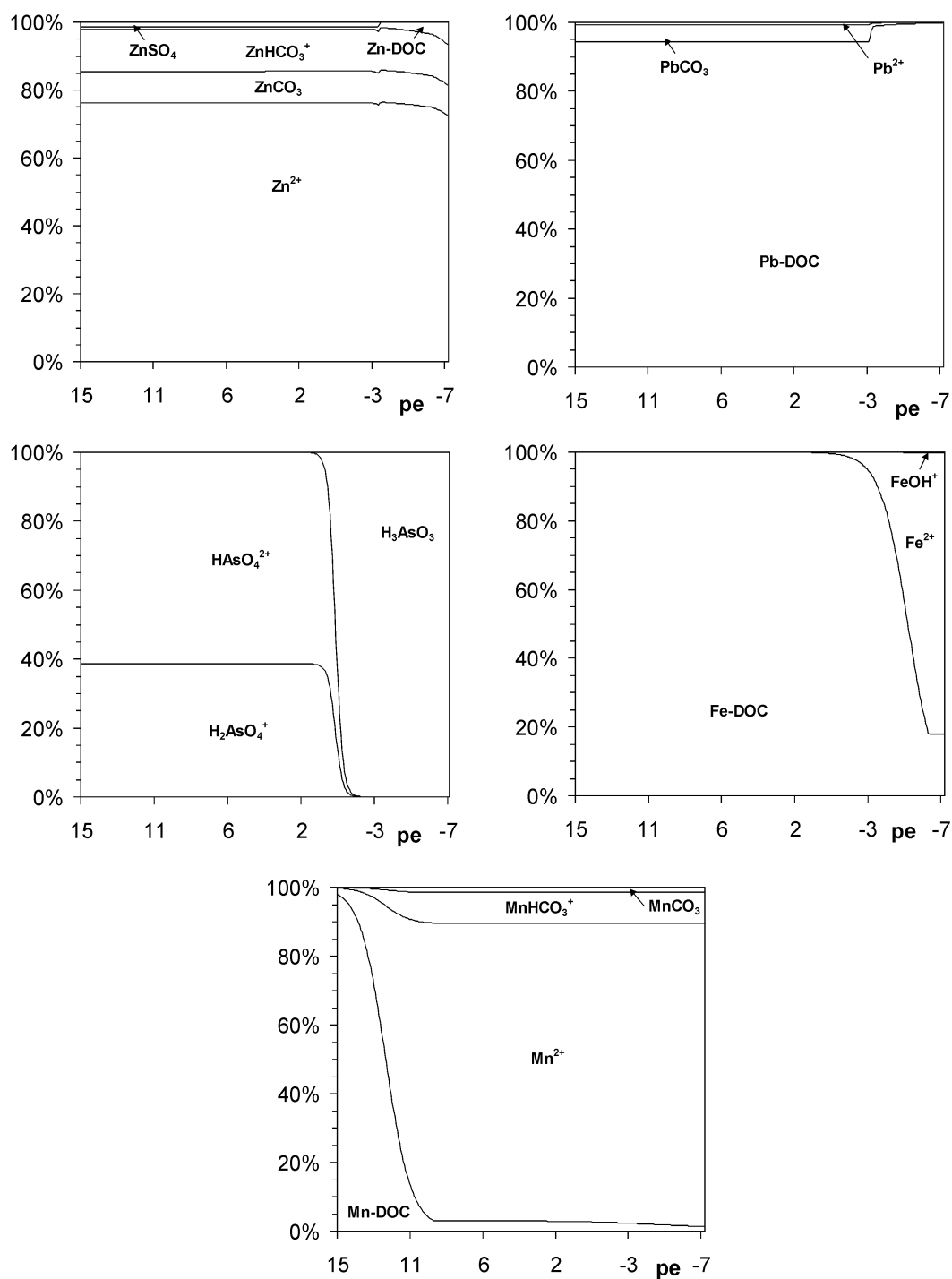
FIGURE 6 (continued from previous page). Calculated distribution of Cd , Cu, Zn, Pb, As, Fe and Mn in the water phase at the Lage Hof site

Although Fe and Mn are not of foremost interest when focussing on the risk assessment of the heavy metals, they still might have a significant effect on the partitioning of these heavy metals. Both metals form oxides that can adsorb heavy metals and for both metals we measured large concentrations in pore water (Figure 3), which might outcompete heavy metals on the other adsorbing phases. Figure 4 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. A possible interpretation for the underestimation by the model might be that Fe and Mn were not in equilibrium with the soil system. The oxidation of $Mn^{(II)}$ and $Fe^{(II)}$ is well known to be kinetically limited (Stumm and Morgan, 1995). However, another explanation could be that Fe and Mn were not present as soluble species but as colloids. 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 the membrane of the Rhizon samplers (<0.2 μm). We cannot decide from our measurements in which form Fe and Mn is present in pore water. But we can use the measured concentrations in pore water to calculate whether the presence as free cation or as colloid will influence the partitioning of the heavy metals that we are primarily looking at.

To test this, we conducted two additional calculations with opposing conjectures: in the first calculation, we assume all Fe and Mn measured in pore water to be present as colloidal oxides with a specific surface area of 150 m^2 g^{-1}. In the second calculation, we defined two extra species with exactly the same sorption properties and soluble species as Fe^{2+} and Mn^{2+}. By defining no precipitation reactions for this species, we can mimic the presence of large amounts of soluble Fe and Mn that are not in equilibrium with the mineral phase.

The first calculation showed that competition by Mn or Fe did not influenced the metal partitioning to a relevant extent (Data not shown). Figure 7 shows the results of the second calculation for Pb and As. We omitted the figures for Cd, Cu and Zn since there was only a marginal difference with the generic model.

The solid phase chemistry of Cd is clearly dominated by the adsorption to organic matter (Figure 5). Under sulphidic conditions, Cd is immobilised by the formation of CdS and pore water concentrations decrease to close to the detection limit (6 ng L^{-1}). The model predicts an almost constant pore water concentration for values of the pe larger than 3, whereas we had measured a slowly decreasing Cd concentration with increasing depth. The decrease of DOC in the profile by approximately 20% (Figure 3), which was ignored in the calculations, can only partly explain the decrease of Cd. The contribution of iron oxide and manganese 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 our model is known to strongly underestimate Cd binding to manganese oxides for a number of datasets. The coincidence of a second Cd peak in Figure 3 in a soil layer where MnO_2 is getting reduced (Figure 5) suggests that probably the amount of Cd bound to MnO_2 was larger than calculated by the model.

In the soil solution, DOC complexation of Cd accounts for approximately 40% of all soluble Cd, the free cation of Cd^{2+} accounts for another 50%, whereas $CdCl^+$, soluble $CdCO_3$ and all other species represented less than 10% of Cd in solution (Figure 6). At low redox potentials the concentration of Cd^{2+} decreased due to the formation of CdS, increasing therefore the fraction bound to DOC.

FIGURE 7. Calculated and measured time-averaged concentrations of Pb and As in the pore water profile at the Lage Hof site. Diamonds: measured average values in time and standard deviations as a function of the sample depth. Thick solid line: generic model. Grey line: generic model, assuming all measured Fe and Mn present as colloidal oxides

Typically for the behaviour of Cu is a strong decrease of the pore water concentration already at 20 cm depth (Figure 3). The model explains this decrease well by the presence of α-$Cu_2Fe_2O_4$ (Figure 5). The predicted trend and the measurements agree well, but the calculated concentrations of Cu were smaller than measured. The presence of colloidal Fe or Mn does not influence the concentrations to a relevant extent (data not shown). The equilibrium chemistry concept probably overestimates the decrease of the Cu^{2+} activity by the formation of α-$Cu_2Fe_2O_4$. 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 decreases by almost two orders of magnitude, it was not totally immobilised as CuS as expected by the model calculations. Again, the presence of colloidal Fe or Mn could not explain this discrepancy.

The speciation of Cu in the solution is dominated by the presence of DOC (Figure 6). Only a minor part is present as Cu^{2+} (<0.34%), and this fraction decreases dramatically with the appearance of α-$Cu_2Fe_2O_4$.

Due to the formation of α-$Cu_2Fe_2O_4$, Cu is sensitive to changes of the redoxpotential. 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, manganese oxides and iron 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 we use the modified *log* K for franklinite as proposed in Chapter 4, the Zn concentrations in the upper layers are underestimated by approximately a half order of magnitude (Figure 4), 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 already in Chapter 4, the generic model can not predict the concentrations of Pb in pore water well. The decrease at low redox potentials is predicted well, but for pe larger than 3 the model overpredicted the pore water concentrations by two orders of magnitude (Figure 4). The speciation of Pb in both the solid and the solution phase is dominated by the binding to SOC and DOC (Figure 5 and Figure 6). In Chapter 4 we defined a hypothetical PbPO4 surface species on goethite, which improved our model predictions. Figure 4 shows that this hypothetical surface species gives good results for Pb for the entire redox range in first instance. The distribution of Pb in the solid phase is now dominated by the binding to goethite and magnetite, while the distribution in solution is comparable to Figure 6 (data not shown). However, the strong competition of this hypothetical PbPO4 species displaced As bound to goethite resulting in pore water concentrations of As that were two orders of magnitude too high (Figure 4).

Furthermore, when we take the presence of colloidal Fe and Mn into account, the hypothetical $PbPO_4$ species leads to Pb concentrations in pore water that were two orders of magnitude too high (Figure 8) due to the binding of Pb to the colloidal iron oxides. The solid-solution partitioning of organic carbon and Fe is comparable (Table 4 and Figure 4), approximately 1000 L kg^{-1} and 1200 to 40000 L kg^{-1} for organic carbon 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 solve the problem as long as significant amounts of the Fe we measured in pore water are present as colloidal oxides. As discussed in Chapter 4, we could not find a Pb containing mineral that keeps the Pb^{2+} activity low enough to explain our results. Therefore we suggest to assume that Pb is present as a yet unknown mineral, labelled as PbX. A PbX mineral fixing the Pb^{2+} activity at $\leq 10^{-13}$ M can explain the measured concentrations well also in the presence of colloidal Fe and Mn (Figure 8). The peak of Pb concentration at low pe was due to the 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. We believe this 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-unit (Figure 9).
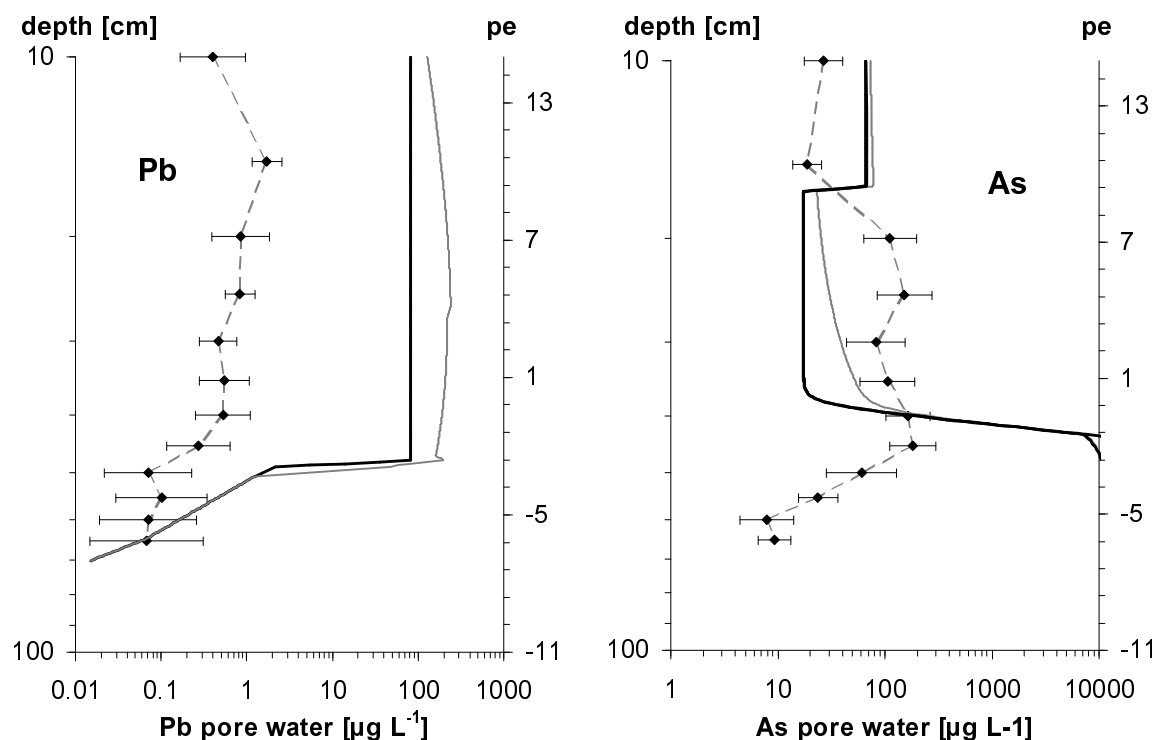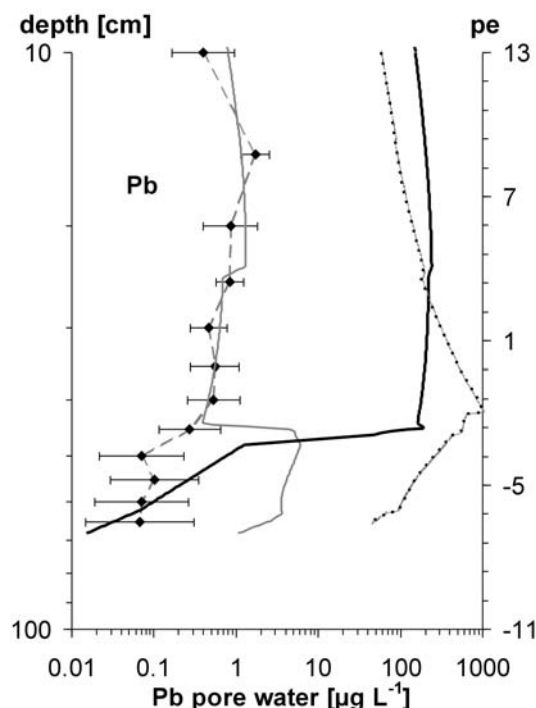
FIGURE 8. Calculated and measured time-averaged concentrations of in the pore water profile at the Lage Hof site. All model calculations assumed the presence of the measured concentration of Fe and Mn as colloids. Diamonds: measured average values in time and standard deviations as a function of the 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

At high pe values, the pattern of As in pore water predicted by the geochemical model disagreed with the measured concentrations (Figure 4). However, the model predicted the As concentrations within one order of magnitude. Our 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 (Figure 7) between 15 and 35 cm depth. 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 our 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 et al. (2002) proposed that aluminium oxides might be an important sink for As; Kinniburgh et al. (2004) suggest a simple model description for As sorption on $Al(OH)_3$, however a sorption model based on measured data is missing.
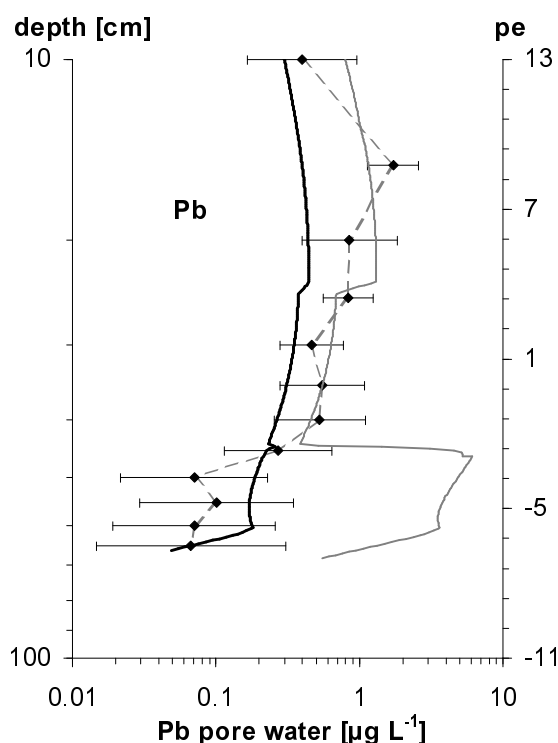
FIGURE 9. Calculated and measured time-averaged concentrations of in the pore water profile at the Lage Hof site. All model calculations assumed the presence of a PbX mineral phase and the measured concentration of Fe and Mn to be present as colloids. Diamonds: measured average times and standard deviations as a function of the sample depth. Thick solid line: optimised model with YOH - Ca species. Thin solid line: generic model with PbX mineral phase

Considering the complexity of the problem, our 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 speciation in soil. The free ion activities of most metals were too low to be measured in soil solution with the techniques available right now, but Weng et al. (2001) showed that with a comparable approach the speciation of heavy 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 heavy metals to a large extent. Metals mainly bound to organic matter were predicted better than metals predominantly present as a mineral phase. The model tends to underestimate solution concentrations in equilibrium with mineral phases in a number of cases (CdS, Cu_2S, α-$Cu_2Fe_2O_4$, $ZnFe_2O_4$). Calibration of these *log* K values might be an option to improve the model, but by doing that our approach would loose its generality as a predictive tool.

It is in principle possible to include in our approach the sorption of heavy metals 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 the fraction of colloidal and soluble Mn and Fe by a standard procedure will be an analytical challenge. With our geochemical model, we showed that the presence of colloids had 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 we have measured. In case of the unknown adsorbent for As under sulphidic conditions, it would be easy to construct a simple sorption equation that will result in a good fit of our data. However, since each mineral phase can act potentially as a sorption surface, we omitted every assumption to maintain the concept of a fully parameterised model.

The results show that our mechanistic approach is able to predict metal partitioning in floodplain soils. The quality of the model results relies on the presence and quality of the thermodynamic data that is available in literature. Our results points out which additional knowledge of soil chemical processes is necessary to understand heavy metal behaviour in contaminated soil systems.

Chapter 6

Uptake of Cd, Cu, Ni, Pb and Zn by a variety of plant species in embanked floodplains of the rivers Rhine and Meuse

6.1 Introduction

Large concentrations of heavy metals have accumulated in the last century in the embanked river floodplain area of the Rhine and Meuse river system (Beurskens et al., 1993; Middelkoop, 1997). To enable sustainable management of the river floodplains, there is a need to account for the effects of the contaminated sediments on the floodplain ecosystems. One possible route in which contaminated sediments can affect an ecosystem is via the uptake of heavy metals by plants. Besides toxic effects for the plants, the uptake of heavy metals represents a risk to herbivores and other organisms that accumulate heavy metals via the food-web (Van Straalen and Løkke, 1997). For ecological risk assessment, it is therefore necessary to understand the availability and uptake of metals by plants.

Whereas numerous papers consider the uptake of metals from potted soils or nutrient solutions, less work is done to elucidate the uptake by plants under field conditions. Only a limited amount of research is done on the uptake by economic less important plants in natural vegetation. Hence, a generalised approach that enables us to predict uptake by plants under field conditions on the basis of soil properties or extractable metal fractions is lacking.

Metal accumulation in plants can vary strongly between different plant species (Kayser et al., 2000; Qian, et al., 1999; Stoltz and Greger, 2002). However, data to give an *a priori* estimation of the variability in metal accumulation by different plant species are not available. Furthermore, the uptake can be limited by the chemical properties of the soil. In soils with a neutral pH, as present in floodplain soils, the metal uptake is reported to be limited even for hyperaccumulating plant species (Landberg and Greger, 1996; Kayser et al., 2000).

Several soil parameters such as the groundwater level, the pH and the concentrations of metals, anions and DOC vary during the year (Farley and Fitter, 1999; Linehan et al., 1989; Chapter 2 and 5) and such temporal variations may influence the metal uptake. This temporal variation is of particular interest for floodplain soils, which can get inundated every spring. However, it is not clear whether this variation significantly affects metal uptake under field conditions. Some evidence regarding seasonal variations of the heavy metal uptake by plant has been provided by Brekken and Steinnes (2004), who found lower plant uptake during the summer season. Metal uptake is proven to be affected by the temperature (Antoniadis and Alloway, 2001, Jastrow and Koeppe, 1980).

In this paper, we study the concentrations of Cd, Cu, Ni, Pb and Zn in the shoots of different plant species that are abundant in the floodplains of the Dutch part of the rivers Rhine and Meuse. Our aim was to elaborate an approach to estimate the heavy metal uptake of river floodplain vegetation consisting of a variety of plant species. For that we quantify the uptake by different plant species, its variability and seasonal changes under field conditions, and assess the relationships between uptake and different metal fractions in soil.

6.2 Materials and methods

6.2.1 Field sampling

This paper summarises the results from three field sampling campaigns. In November 1999 and June 2000, we collected plants from 4 different floodplains along the rivers Waal, Nieuwe Merwede and Meuse, all used for grazing cattle (Figure 1). At these locations, denoted by A, B, L and S, we collected seven plant species, i.e., perennial ryegrass (*Lolium perenne*), creeping bentgrass (*Agrostis stolonifera*), rough bluegrass (*Poa trivialis*), white clover (*Trifolium repens*), bitter dock (*Rumex obtusifolius*), creeping buttercup (*Ranunculus repens*) and white willow (*Salix alba*). These plants species were chosen because they were expected to be abundant in all 4 river floodplains, they are typical species for river floodplains, and because they belong to different plant families with a diverging physiology.

Additionally, in the second sampling campaign in June 2000 we collected a larger variety of plants species abundant on one or more locations (Table 4). In total, we collected 93 plant samples of 22 different species in the 1999 and 2000 sampling campaigns. To increase the geographical spreading and variation of soil properties, we collected in October 2001 another 26 plant samples (13 different species) from 26 floodplains along the Dutch part of the river Meuse and the three major branches of the river Rhine (Figure 1, Table 4).

The plant samples of 1999 and 2000 were collected randomly within plots of approximately 1500 to 2800 m^2. We collected four (in the smallest plot three) mixed soil samples to quantify the average metal concentrations and soil properties and to obtain a measure of the heterogeneity of the sampling area. In 2001, we sampled plants within a circular area of approximately 30 m^2 and collected a single soil sample in the centre of this area. All soil samples were collected from 5 to 25 cm depth with a gouche auger sampler (2.5 cm diameter).

From all plants, the above ground parts were collected, except for willows and elderberry, where we collected twigs and leaves only.

6.2.2 Chemical analysis

Plant samples were carefully rinsed with demineralised water and dried at 70° C. Plants samples collected in 2001 were rinsed with demineralised water, additionally soaked in 1 mM CaCl$_2$, and rinsed again with demineralised water afterwards. The samples were grounded and destructed by microwave digestion with HNO$_3$, H$_2$O$_2$ and HF (Temminghoff et al., 2000). Cd, Cu, Fe, Ni, Pb, Ti and Zn concentrations were measured by ICP-MS (Perkin Elmer, ELAN 6000) and ICP-AES (Spectros, Spectro Flame).

Soil samples were dried at 40° C and sieved (<2 mm) before analysis. Cd, Cu, Ni, Pb, Zn and Fe concentrations in *aqua regia* (NEN 6465) were measured by ICP-AES (Spectros, Spectro Flame) and ICP-MS (Perkin Elmer, ELAN 6000). Soil organic carbon content (SOC) was analysed by wet oxidation with K$_2$Cr$_2$O$_7$ (Wallinga et al., 1992). The clay content was measured by sedimentation according to Houba et al. (1997).

Soil extractions by CaCl$_2$ were made according to a modified scheme of Houba et al. (1996). 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 floodplains soils (Chapter 3).

The pH was measured in the suspension of the 2.5 mM $CaCl_2$ extraction (Houba et al., 1997). Dissolved organic carbon (DOC) concentrations of the $CaCl_2$ extract were measured by a TOC-analyser (Skalar, SK12) after 5 times dilution and acidification to a pH of 3.0 to 3.5 by the addition of 0.28 M HNO_3. Concentrations of Cd, 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).

Figure 1. Sampling locations in the Rhine-Meuse floodplain system

6.3 Results and discussion

Table 1 summarises the plant samples collected on 4 floodplain locations in 1999 and 2000. Not in all floodplains were the desired plant species abundant within the plots defined for sampling. In that case, we defined additional sublocations to collect them.

TABLE 1. Plant samples collected in October 1999 and June 2000 in four floodplains. Afferden-sche en Stiftse Waard (A), Beesel (B), Lage Hof (L) and Stiftse Waard (S). The numbers indicates different sublocations within a floodplain

plant species	location
Lolium perenne	A1, B1, L2, S1
Agrostis stolonifera	A1, B1, L1, S1
Ranunculus repens	A1, B1[+], L1, S1
Rumex obtusifolius	A1, B1, L1, S1
Poa trivialis	A1, B1, L1, S1
Salix alba	A3, B1, L1, S2
Trifolium repens	A2, L1, S1

[+] June 2001 only

The properties of the soil samples and extractions are given in Table 2 and 3 (1999 and 2000) and Table 3 and 4 of the Appendix (2001). The pH of the floodplain soils of the Rhine river system was high (7.6 ±0.2), whereas in the Meuse floodplain the average pH was lower (6.9 ±0.6). The heavy metal concentrations of the river floodplain soils follow a typical pattern with strong correlations between the organic matter content and the total amount of heavy metals (Chapter 4). The range between the lowest and highest concentration in soil was different for every heavy metal and varied between a factor of 5 and 59 for Ni and Cd, respectively (Table 2). The fractions of metals extractable by 2.5 mM $CaCl_2$ varied between a factor of 5 and 22 (Table 3).

TABLE 2. Soil organic carbon content (SOC), clay fraction (<2 μm) and total amount of heavy metals in soil. Afferdensche en Stiftse Waard (A), Beesel (B), Lage Hof (L) and Stiftse Waard (S). The numbers indicates different sublocations. Values in parenthesis are the standard deviations

location	SOC [%]	<2 μm [%]	Cd [mg kg^{-1}]	Cu [mg kg^{-1}]	Zn [mg kg^{-1}]	Pb [mg kg^{-1}]	Ni [mg kg^{-1}]	Fe [mg kg^{-1}]
A1	2.2 (0.03)	23.5 (6.1)	2.7 (0.5)	85.1 (20)	633 (191)	170 (39)	39.2 (10.3)	19185
A2	2.3	12.3	1.5	35.0	268	79	20.9	14064
A3	1.0	6.0	0.3	10.2	75	23	13.4	9028
B3	7.0 (0.34)	14.2 (1.9)	8.6 (1.1)	85.6 (6)	915 (118)	231 (43)	32.5 (1.9)	27670
L1	10.8 (0.65)	32.6 (1.4)	15.9 (2.5)	307 (37)	2442 (264)	709 (65)	68.8 (7.9)	41073
L2	2.5	26.4	2.5	49.5	489	131	40.0	24938
S1	2.2 (1.02)	18.5 (2.2)	1.8 (1.1)	43.9 (20)	354 (140)	116 (36)	30.8 (5.8)	20172
S2	5.9	24.5	5.9	114	795	222	51.4	30355

TABLE 3. Dissolved organic carbon (DOC), pH and concentrations of heavy metals extractable by 2.5 mM CaCl₂. Afferdensche en Stiftse Waard (A), Beesel (B), Lage Hof (L) and Stiftse Waard (S). The numbers indicate different sublocations

location	DOC [mg L^{-1}]	pH [-]	Cd [μg L^{-1}]	Cu [μg L^{-1}]	Zn [μg L^{-1}]	Pb [μg L^{-1}]	Ni [μg L^{-1}]
A1	14.2 (3.2)	7.86 (0.05)	0.30 (0.06)	27.7 (4.6)	7.53 (1.9)	0.10 (0.01)	1.40 (0.30)
A2	10.1	7.82	0.27	20.7	4.83	0.14	1.10
A3	3.7	8.05	0.07	6.01	2.33	0.06	0.73
B3	11.8 (1.3)	7.26 (0.11)	1.46 (0.10)	30.1 (1.6)	38.8 (7.2)	0.40 (0.11)	2.90 (0.61)
L1	22.5 (2.6)	7.58 (0.05)	1.59 (0.27)	55.3 (4.2)	56.0 (11.6)	0.43 (0.10)	5.42 (0.53)
L2	19.3	7.67	0.29	21.5	5.65	0.23	2.77
S1	9.6 (2.2)	7.98 (0.06)	0.17 (0.07)	16.8 (5.1)	4.94 (1.0)	0.06 (0.01)	1.05 (0.37)
S2	18.3	7.45	0.65	35.1	14.1	0.28	3.42

6.3.1 Contamination by soil particles

In Chapter 4, we have shown that the concentrations of metals extractable by 2.5 mM are rather small in floodplain soils. The solid-solution partitioning factors for the studied metals were between 3,000 and 1,000,000 L kg^{-1}. When the metal availability for plants is low, contamination of the plant samples by adhering soil particles might be a factor of significance. Elements, such as Ti, which are hardly taken up by plants, are suitable markers for the contamination by soil particles. Figure 2 shows the Ti concentrations in all plant samples. The additional soaking of the plant samples collected in October 2001 by a solution of 1 mM CaCl₂ reduced the Ti concentration below 20 mg kg^{-1}. However, for two metals this did not solve the problem fully as we discuss later.

Though in principle it is possible to correct for the contamination of the plant samples by soil particles, in the present case this is not well possible. In case of the floodplain soils in this study, it is very likely that the upper layer consists of recently sedimented material that is less contaminated than the layer of 5 to 25 cm, which we sampled for soil analysis (Middelkoop, 1997, Middelkoop and Asselman, 1998). A correction as mentioned resulted in negative metal concentrations for a large number of samples (data not shown). However, we still can make an estimation of the traces of soil that are attached to the plant samples despite the thoroughly rinsing with demineralised water. For this estimation we used Fe rather than Ti, since the destruction by *aqua regia* did not dissolve Ti in soil fully. Iron is present at high concentrations in floodplain soils (30 g kg^{-1} ±9.2) and is not strongly accumulated by plants.

The estimated contamination was calculated by Equation 1:

$$\text{estimated contamination } [g\ kg^{-1}] = 1000 \times \frac{Fe_{plant}\ [mg\ kg^{-1}]}{Fe_{soil}\ [mg\ kg^{-1}]} \qquad \text{(Equation 1)}$$
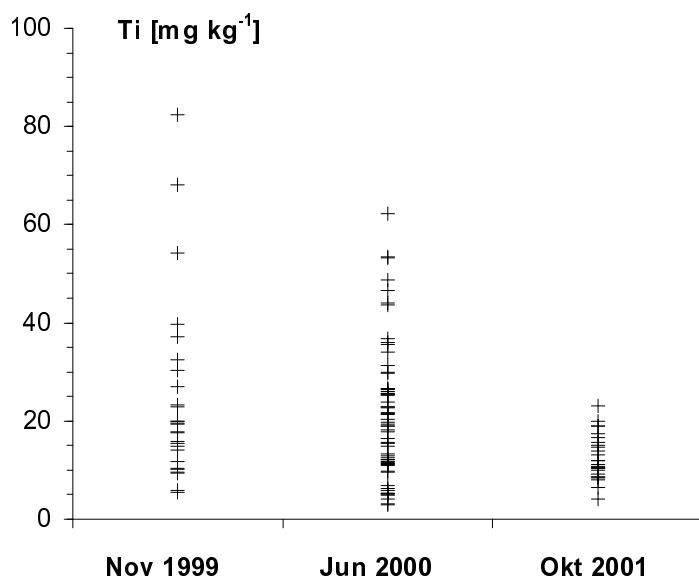
FIGURE 2. Ti concentrations in plant samples collected in 1999-2001

Figure 3 shows the distribution of the estimated contamination calculated by Equation 1. Of all samples, 76% was contaminated with less than 1% of soil particles, whereas only 8 samples were contaminated with more than 2%. It is obvious that this method leads to an overestimation, too, since this approximation assumes no uptake of Fe by plant. Therefore, to avoid interference due to contamination by adhering soil, we removed from further statistical analysis six samples with an estimated contamination exceeding 25 g kg^{-1} (>average + 2sd). The influence of the contamination on the metal concentration in plant will be discussed later.
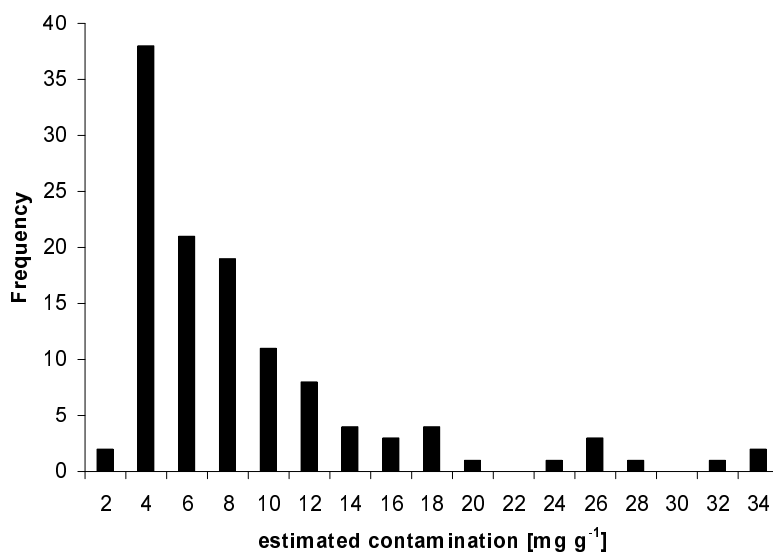
FIGURE 3. Frequency distribution of the estimated contamination of the plant samples by soil particles. The contamination is calculated by Equation 1

6.3.2 Seasonal differences

To assess seasonal influences on metal uptake by plants, we compared the metal content of the plants sampled in 1999 and 2000 (Table 1) by a T-test with paired samples. Figure 4 shows, that the samples collected in November 1999 had equal or significantly higher concentrations of Cd, Cu, Zn, Pb and Ni compared to the samples collected in June 2000, except for Zn in clover, which was higher in June (significant at p<0.1).
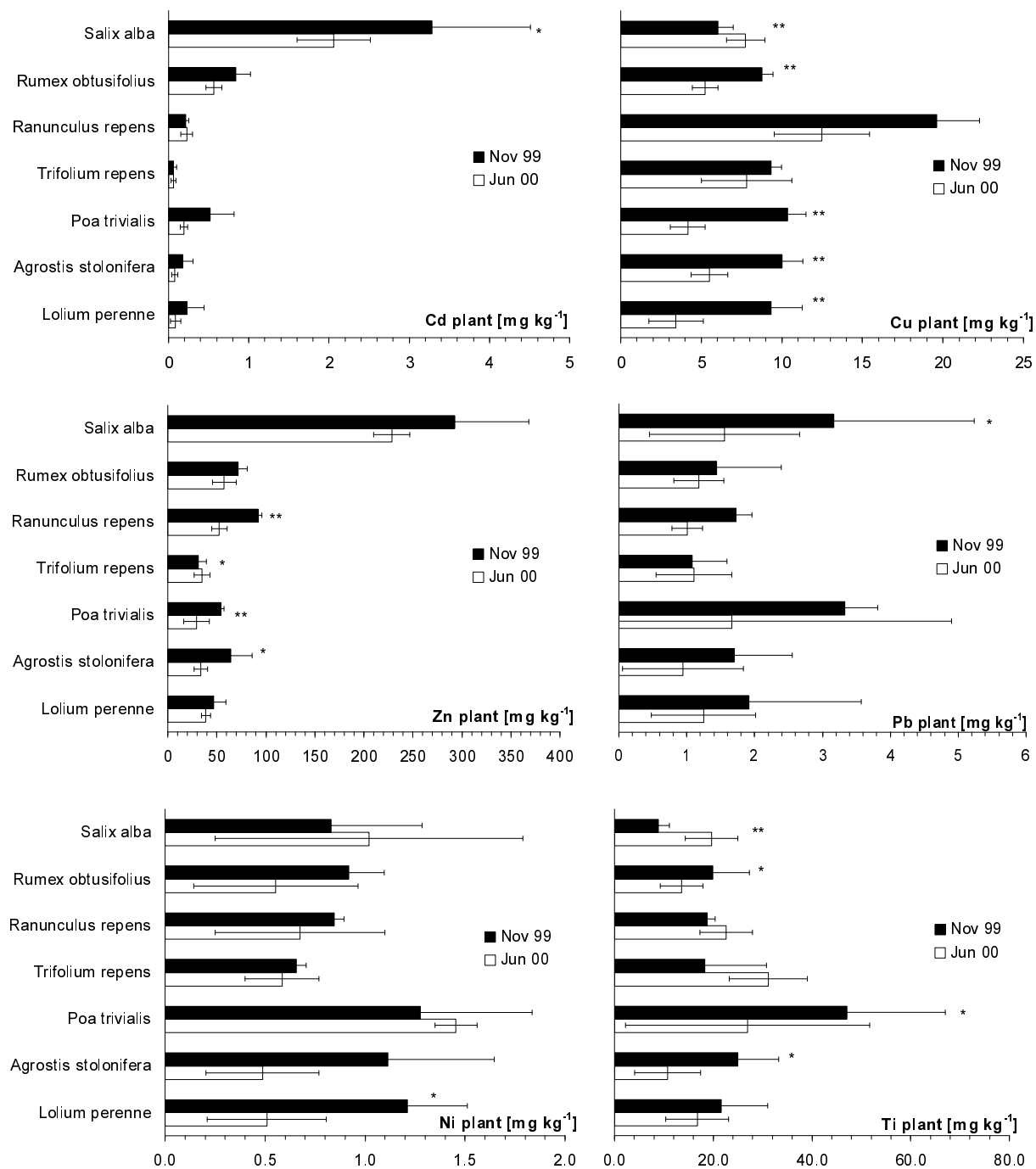
FIGURE 4. Average concentration and standard deviation of Cd, Cu, Zn, Pb, Ni and Ti in plant samples collected in November 1999 and June 2000. * significant different at p<0.1; ** significant different at p<0.05

The seasonal effect was best visible for Cu. Only part of this effect can be explained by the contamination of the plants by soil particles, as on average the Ti concentration was 32% higher in November whereas the heavy metal concentrations were 37% to 61% higher. For *T. repens*, *R. repens* and *S. alba* the concentrations of Ti were even lower in November (significant only for *S. alba*).

6.3.3 Species-specific uptake

Tables 4 shows the plants samples collected in June 2000 and October 2001 and Table 5 gives an overview of the average heavy metal concentration in plant species for all sampling campaigns. Generally, in dicotyls we observed higher metal concentrations than in monocotyls. The highest concentrations of Cd and Zn were found in *Salix alba* and *Salix viminalis* (white willow, basket willow) and the highest Cu concentrations were found in *Ranunculus repens* (creeping buttercup).

TABLE 4. Plant samples collected in June 2000 and October 2001

plant species	location
Agrostis stolonifera	IJ11A, R06A
Alopecurus geniculatus	A1, B1, L1, S1
Dactylis glomerata	B1, S1
Elymus repens	A1, B1, S1
Festuca arundinacea	L1
Lolium perenne	IJ01A, M24A, R03B, M11D, M11E
Phalaris arundinacea	W01A, W11B, W12C
Phragmites australis	W09C
Poa annua	B1
Phleum partense	B1
Cirsium arvense	A1, B1, L1, S1
Mentha aquatica	W01C
Plantago lanceolata	S1
Plantago major	A1, B1, L1, S1
Potentilla anserina	A1, L1, S1
Potentilla reptans	A1, B1, L1, S1
Ranunculus repens	IJ09A, M09A, M15A, R02A; R09B
Rorippa amphibia	L1
Rorippa sylvestris	A1
Rumex obtusifolius	W03B
Sambucus	M09B
Sinapis arvensis	B1
Trifolium pralense	S1, IJ05A, R08C
Trifolium repens	M17A, M24C
Vicia villosa	M11C
Salix alba	W02C, R13A, IJ05B
Salix viminalis	IJ04C

The observed concentrations of heavy metals were too small to expect toxic effects to the plants (MacNicol and Beckett, 1985). But since large parts of the floodplain areas are used as grassland, the uptake of heavy metals by grazing cattle or other herbivore is a point of concern.

TABLE 5. Average heavy metal content of plant samples collected in 1999 - 2001. n is the number of plant samples. Values in parenthesis shows the standard deviation

plant species	n	Cd [mg kg^{-1}]	Cu [mg kg^{-1}]	Zn [mg kg^{-1}]	Pb [mg kg^{-1}]	Ni [mg kg^{-1}]	Ti [mg kg^{-1}]
Agrostis stolonifera	12	0.14 (0.12)	8.55 (3.0)	50.1 (22)	1.19 (0.79)	0.74 (0.45)	16.6 (9.0)
Alopecurus geniculatus	3	0.25 (0.24)	5.73 (2.9)	68.5 (63)	0.97 (1.3)	0.47 (0.29)	12.0 (15)
Dactylis glomerata	2	0.15 (0.09)	2.93 (0.21)	24.2 (2.7)	0.54 (0.25)	0.57 (0.07)	8.99 (3.0)
Elymus repens	3	0.04 (0.02)	3.40 (0.44)	22.5 (2.9)	0.56 (0.46)	0.10 (0.08)	5.20 (1.1)
Festuca arundinacea	1	0.14	6.35	27.0	0.68	0.56	5.10
Lolium perenne	10	0.14 (0.13)	6.93 (3.4)	42.3 (12)	1.32 (1.1)	0.80 (0.37)	16.9 (6.6)
Phalaris arundinacea	3	0.10 (0.05)	7.5 (0.70)	140.5 (63)	1.09 (0.60)	0.77 (0.23)	12.5 (3.5)
Phragmites australis	1	0.15	3.73	28.2	0.47	0.18	4.18
Poa annua	1	1.08	7.42	76.1	2.10	0.89	21.6
Poa trivialis	6	0.35 (0.27)	7.63 (4.3)	43.4 (21)	3.03 (2.0)	1.43 (0.60)	381 (21)
Phleum pratense	1	0.08	3.18	35.0	0.56	0.44	5.38
Trifolium pralense	3	0.08 (0.05)	12.8 (5.9)	47.8 (27)	0.43 (0.23)	0.77 (0.60)	13.9 (6.5)
Trifolium repens	7	0.12 (0.11)	8.09 (1.6)	37.5 (9.8)	1.47 (1.1)	0.86 (0.53)	24.5 (14)
Vicia villosa	1	0.06	9.42	66.4	0.43	0.74	10.7
Cirsium arvense	4	1.74 (1.05)	13.2 (3.8)	82.2 (41)	1.00 (0.75)	0.51 (0.31)	31.8 (12)
Mentha aquatica	1	0.10	12.6	42.1	0.58	0.55	9.90
Plantago lanceolata	1	0.34	5.15	59.3	4.05	0.26	25.6
Plantago major	4	0.31 (0.18)	11.0 (2.6)	55.3 (8.9)	1.52 (1.1)	0.34 (0.08)	37.3 (14)
Potentilla anserina	3	0.92 (1.1)	5.69 (2.8)	88.6 (64)	1.69 (0.71)	1.34 (0.65)	25.9 (9.8)
Potentilla reptans	4	0.86 (0.09)	6.78 (1.5)	88.7 (16)	1.99 (1.7)	0.95 (0.37)	30.7 (11)
Ranunculus repens	11	0.54 (0.53)	20.4 (5.6)	77.6 (26)	1.59 (1.4)	1.07 (0.53)	26.2 (17)
Rorippa amphibia	1	0.47	4.72	70.8	0.35	0.16	15.5
Rorippa sylvestris	1	0.52	5.24	47.9	0.17	1.56	12.2
Rumex obtusifolius	10	0.63 (0.24)	7.20 (1.9)	61.1 (13)	1.25 (0.72)	0.71 (0.32)	17.6 (6.1)
Sambucus	1	0.08	6.70	61.2	1.14	1.24	8.46
Sinapis arvensis	2	0.55 (0.01)	3.08 (0.18)	47.8 (2.8)	0.37 (0.08)	0.18 (0.19)	16.8 (1.5)
Salix alba	15	3.45 (1.6)	7.73 (2.6)	247 (71)	1.91 (1.5)	0.77 (0.50)	12.5 (5.7)
Salix viminalis	1	3.09	9.61	551	0.74	0.44	7.97

To make a generic estimation of the heavy metal exposure of grazing cattle through plants, we group the plants species according to their physiology and metal uptake behaviour. First, we distinguished monocotyls and dicotyls. Since the concentrations of Cd and Zn in willows were 4 and 5 times higher than in the other dicotyls, we defined willows as a separate group. Leguminosae, that can form Rhizobium nodules (*Trifolium, Vicia villosa*)

were placed in a different group too, because the concentrations of Cd and Zn were more comparable to the monocotyls, whereas the concentrations of Cu were more comparable to dicotyls. This simple classification system is consistent with the grouping of Kuboi et al. (1986) on the basis of Cd accumulation pattern. Figure 5 summarises the average concentrations and standard deviations of the *log*-transformed concentrations for this four groups.
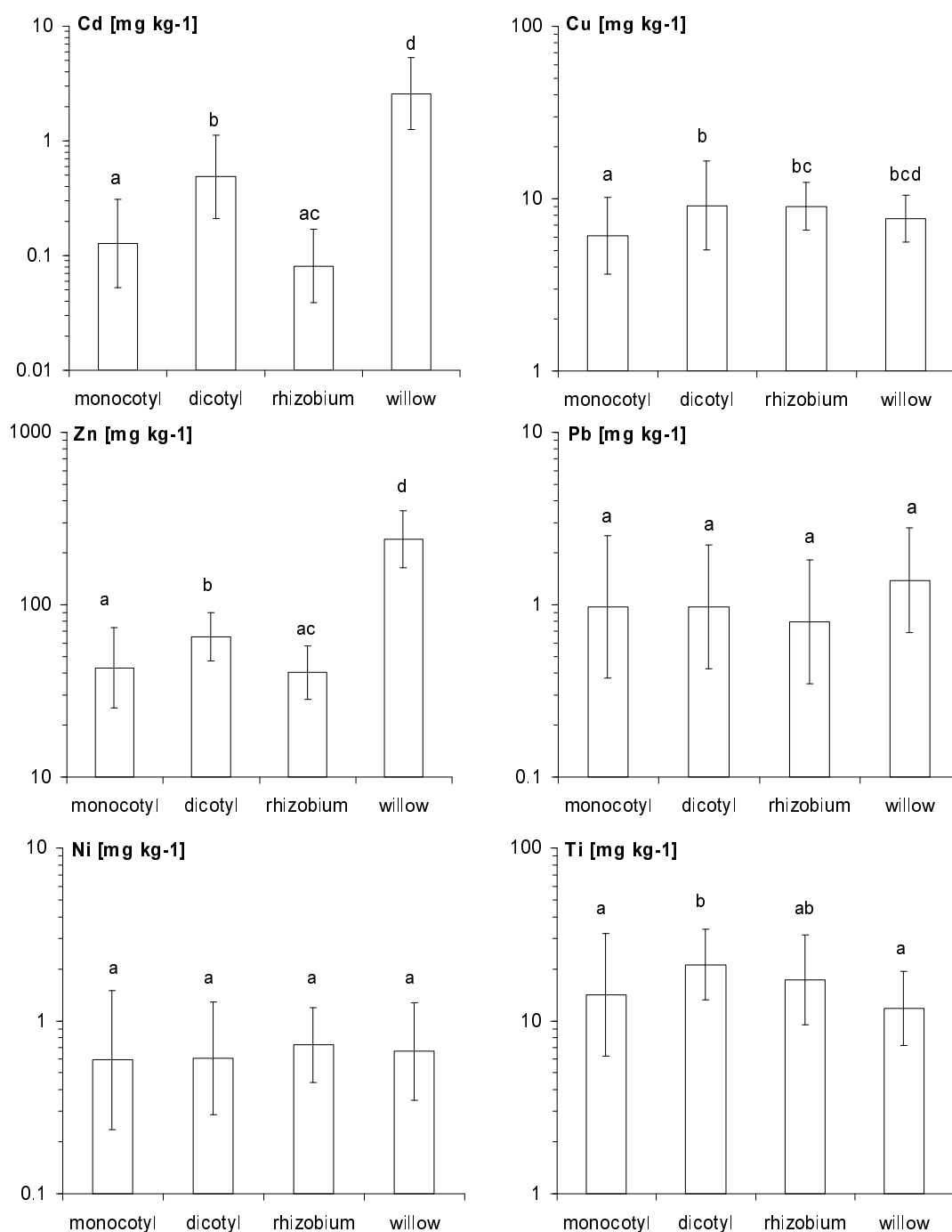
FIGURE 5. Geometric mean concentration and standard deviation of Cd, Cu, Zn, Pb, Ni and Ti in 4 different plant groups collected in November 1999, June 2000 and October 2001. Different letters indicates a significant difference at p<0.05

6.3.4 Plant-soil partitioning

Table 6 shows the average plant-soil partitioning factors of the heavy metals for all plant species (or bioaccumulation factors in case all metals is taken up by plant). Cu, Zn and Cd were the most strongly accumulated in the above ground parts of the plant, however, only *Salix alba* was able to accumulate Cd to higher concentrations than present in soil. On average, the concentrations of these metals in plant samples were 6 to 7 times smaller than in the soil samples. The plant-soil partitioning factors for Ni and Pb were even smaller: on average 0.02 and 0.007 g g^{-1} respectively. For these metals, attached soil particles can be a relevant part of the total metal concentration of the aboveground parts. We used Equation 1 together with Table 6 to estimate the fraction of metals in the plant samples that was probably not taken up, but was attached as soil particles. We did two calculations, one assuming that no Fe is taken up by plants and therefore clearly overestimating the contamination by soil particles, and the other assumed a shoot concentration of 100 mg kg^{-1} Fe (Ait Ali et al., 2002; Ait Ali et al., 2004; Schmidt and Steinbach, 2000). Both calculations assumed furthermore, that the metal concentrations in the upper layers were the same as in the sampled layers. Table 7 shows the ranges of contamination calculated by this method.

TABLE 6. Plant-soil partitioning of Cd, Cu, Zn, Pb and Ni for plant samples collected from 1999 to 2001. Values in parenthesis shows the standard deviation (continued next page)

plant species	Cd [g soil/g plant]	Cu [g soil/g plant]	Zn [g soil/g plant]	Pb [g soil/g plant]	Ni [g soil/g plant]
Agrostis stolonifera	0.029 (0.026)	0.111 (0.078)	0.075 (0.061)	0.0062 (0.006)	0.019 (0.013)
Alopecurus geniculatus	0.054 (0.007)	0.078 (0.022)	0.095 (0.051)	0.0046 (0.005)	0.014 (0.009)
Dactylis glomerata	0.037 (0.017)	0.051 (0.027)	0.049 (0.035)	0.0032 (0.0001)	0.018 (0.003)
Elymus repens	0.016 (0.015)	0.052 (0.019)	0.043 (0.026)	0.0039 (0.004)	0.0032 (0.003)
Festuca arundinacea	0.0087	0.021	0.011	0.00096	0.0082
Lolium perenne	0.068 (0.056)	0.192 (0.207)	0.129 (0.107)	0.0011 (0.008)	0.025 (0.012)
Phalaris arundinacea	0.029 (0.016)	0.109 (0.051)	0.252 (0.192)	0.0086 (0.008)	0.024 (0.017)
Phleum pratense	0.0088	0.037	0.038	0.0024	0.013
Phragmites australis	0.038	0.040	0.033	0.0022	0.0033
Poa annua	0.127	0.087	0.083	0.0091	0.027
Poa trivialis	0.049 (0.030)	0.068 (0.049)	0.044 (0.028)	0.0098 (0.006)	0.034 (0.015)
Trifolium pralense	0.050 (0.023)	0.315 (0.149)	0.143 (0.053)	0.0045 (0.002)	0.020 (0.017)
Trifolium repens	0.047 (0.043)	0.201 (0.130)	0.110 (0.084)	0.010 (0.006)	0.031 (0.025)
Vicia villosa	0.109	0.694	0.929	0.015	0.058
Cirsium arvense	0.357 (0.217)	0.143 (0.067)	0.102 (0.060)	0.0038 (0.003)	0.012 (0.004)
Mentha aquatica	0.015	0.107	0.047	0.0028	0.0080
Plantago lanceolata	0.192	0.118	0.167	0.035	0.0085
Plantago major	0.059 (0.035)	0.132 (0.072)	0.080 (0.051)	0.0055 (0.003)	0.0087 (0.004)
Potentilla anserina	0.129 (0.042)	0.059 (0.042)	0.097 (0.037)	0.0088 (0.006)	0.029 (0.001)
Potentilla reptans	0.251 (0.230)	0.086 (0.068)	0.129 (0.094)	0.0070 (0.004)	0.023 (0.007)
Ranunculus repens	0.131 (0.083)	0.371 (0.300)	0.142 (0.096)	0.0068 (0.004)	0.026 (0.011)
Rorippa amphibia	0.029	0.015	0.029	0.00049	0.0024

TABLE 6 (continued from previous page). Plant-soil partitioning of Cd, Cu, Zn, Pb and Ni for plant samples collected from 1999 to 2001. Values in parenthesis shows the standard deviation

plant species	Cd [g soil/g plant]	Cu [g soil/g plant]	Zn [g soil/g plant]	Pb [g soil/g plant]	Ni [g soil/g plant]
Rorippa sylvestris	0.191	0.062	0.076	0.0010	0.040
Rumex obtusifolius	0.159 (0.138)	0.085 (0.057)	0.087 (0.061)	0.0050 (0.003)	0.018 (0.012)
Sambucus	0.036	0.262	0.153	0.0074	0.052
Sinapis arvensis	0.065 (0.001)	0.036 (0.002)	0.052 (0.003)	0.0016 (0.0003)	0.0054 (0.006)
Salix alba	1.306 (1.851)	0.163 (0.256)	0.746 (1.394)	0.012 (0.018)	0.024 (0.038)
Salix viminalis	0.952	0.148	0.852	0.0043	0.010

TABLE 7. Estimated fraction of Cd, Cu, Zn, Pb and Ni in plant samples due to contamination of the plants by soil particles. The lower values assumes an uptake of 100 mg kg^{-1} Fe by plant, the upper value assumes no uptake of Fe

plant species	Cd [-]	Cu [-]	Zn [-]	Pb [-]	Ni [-]
Agrostis stolonifera	0.15 - 0.42	0.04 - 0.09	0.06 - 0.13	0.40 - 1.00	0.10 - 0.38
Alopecurus geniculatus	0.02 - 0.11	0.01 - 0.07	0.00 - 0.06	0.00 - 1.00	0.00 - 0.43
Dactylis glomerata	0.03 - 0.16	0.02 - 0.11	0.03 - 0.14	0.34 - 1.00	0.06 - 0.30
Elymus repens	0.00 - 0.43	0.00 - 0.07	0.00 - 0.10	0.00 - 1.00	0.00 - 1.00
Festuca arundinacea	0.01 - 0.27	0.00 - 0.11	0.00 - 0.21	0.00 - 1.00	0.00 - 0.29
Lolium perenne	0.05 - 0.17	0.03 - 0.09	0.04 - 0.09	0.22 - 1.00	0.13 - 0.42
Phalaris arundinacea	0.04 - 0.19	0.01 - 0.05	0.00 - 0.02	0.14 - 0.87	0.05 - 0.25
Phleum pratense	0.24 - 0.65	0.06 - 0.15	0.05 - 0.15	0.85 - 1.00	0.15 - 0.42
Phragmites australis	0.00 - 0.06	0.00 - 0.06	0.00 - 0.07	0.00 - 1.00	0.00 - 0.72
Poa annua	0.05 - 0.08	0.07 - 0.11	0.08 - 0.12	0.69 - 1.00	0.23 - 0.36
Poa trivialis	0.27 - 0.36	0.20 - 0.27	0.27 - 0.37	1.00	0.32 - 0.47
Trifolium pralense	0.08 - 0.19	0.01 - 0.02	0.03 - 0.06	0.58 - 1.00	0.11 - 0.40
Trifolium repens	0.24 - 0.40	0.07 - 0.11	0.12 - 0.19	0.75 - 1.00	0.34 - 0.54
Vicia villosa	0.00 - 0.05	0.00 - 0.01	0.00 - 0.01	0.00 - 0.37	0.00 - 0.09
Cirsium arvense	0.00 - 0.02	0.01 - 0.04	0.01 - 0.05	0.00 - 1.00	0.00 - 0.40
Mentha aquatica	0.01 - 0.16	0.00 - 0.02	0.00 - 0.05	0.04 - 0.86	0.01 - 0.30
Plantago lanceolata	0.01 - 0.03	0.01 - 0.06	0.01 - 0.04	0.04 - 0.19	0.18 - 0.76
Plantago major	0.04 - 0.12	0.03 - 0.07	0.05 - 0.11	0.19 - 1.00	0.22 - 0.70
Potentilla anserina	0.00 - 0.04	0.01 - 0.09	0.00 - 0.05	0.27 - 0.95	0.02 - 0.18
Potentilla reptans	0.05 - 0.08	0.11 - 0.17	0.07 - 0.11	0.79 - 1.00	0.23 - 0.42
Ranunculus repens	0.05 - 0.09	0.04 - 0.06	0.06 - 0.10	0.48 - 1.00	0.14 - 0.33
Rorippa amphibia	0.00 - 0.07	0.00 - 0.13	0.00 - 0.07	0.00 - 1.00	0.00 - 0.87
Rorippa sylvestris	0.00 - 0.01	0.00 - 0.04	0.00 - 0.04	0.00 - 1.00	0.06 - 0.07
Rumex obtusifolius	0.02 - 0.06	0.04 - 0.10	0.04 - 0.10	0.40 - 1.00	0.10 - 0.40
Sambucus	0.01 - 0.13	0.00 - 0.02	0.00 - 0.03	0.06 - 0.63	0.01 - 0.09
Sinapis arvensis	0.00 - 0.03	0.00 - 0.06	0.00 - 0.04	0.00 - 1.00	0.00 - 1.04
Salix alba	0.00 - 0.01	0.05 - 0.11	0.01 - 0.02	0.19 - 0.81	0.08 - 0.39
Salix viminalis	0.00	0.00 - 0.02	0.00	0.00 - 0.77	0.02 - 0.32

On average, less than 10% of Cu and Zn measured in plant samples were attributed to attached soil particles. The highest potential contamination was found in *Poa trivialis* (rough bluegrass), which hairy backside of the leaves might be responsible for the higher contamination. For Cd, contamination ranges between 4% and 16% on average, but might be more than 25% for *Poa trivialis*, *Phleum pratense* (timothy) and *Trifolium repens* (white clover). For Ni, contamination by soil particles accounts for approximately 50% of all measured metal. The accumulation of Pb is so small, that for almost all plant species the reported concentrations were likely to reflect mainly the contamination by soil.

6.3.5 Soil-plant relationships

To relate the concentrations of heavy metals in plants with the concentrations in soil, statistical regression calculations were done. We compared the concentrations in plants with the total amount in soil and the fraction extractable by $CaCl_2$, and made calculations for all plant species for which more than 4 samples were available. The regression parameters were calculated according to Equation 2 and 3:

$$log(Me_{plant}) \; [mg \; kg^{-1}] = a * log \, (Me_{total \; amount}) \; [mg \; kg^{-1}] + b \qquad \text{(Equation 2)}$$

$$log(Me_{plant}) \; [mg \; kg^{-1}] = a * log \, (Me_{CaCl2 \; extractable}) \; [\mu g \; L^{-1}] + b \qquad \text{(Equation 3)}$$

All results that are significant at $p<0.05$ and $p<0.1$ are given in Table 8. Cd is the metal with the largest range of 2.5 mM $CaCl_2$ extractable and total concentrations (Table 2 and 3, Appendix Table 3 and 4). We could find significant relations for the plant concentrations of Cd for all species except *R. obtusifolius*. In contrast, for Cu no significant regression parameters were found; the differences in plant concentrations between samples collected on different locations (Table 5 and Figure 4) were small with standard deviations between 0.14 and 0.26.

For Zn, two relations could be fitted significant at $p<0.1$. All significant regressions for Pb were related with the total amount in soil. This is not surprising, since our estimation of the contamination by soil particles (Table 7) shows that a major fraction of Pb in plant is probably due to adhering soil. For three plant species we could relate the Ni concentrations with the concentrations in $CaCl_2$.

In Table 9 we summarised the regression coefficients for the metal uptake in the four plant groups we defined before. In case of Cd and Pb, for all groups significant regressions could be fitted. For Cu and Zn, either one regression line could be fitted, both significant only at $p<0.1$.

TABLE 8. Regression parameter and R^2 of the concentration of Cd, Cu, Zn, Pb and Ni in different plant species and the total amount in soil (*Tot*) or extractable fraction by 2.5 mM $CaCl_2$ (*CaCl₂*). * significant at p<0.1. ** significant at p<0.05. Standard error is given in parenthesis

plant species	element	parameter	a	b	R^2
A. stolonifera	Cd	*Tot*	0.41 (0.20)	-1.29 (0.18) **	0.30 *
L. perenne	Cd	*CaCl₂*	0.50 (0.27) *	-0.67 (0.18) **	0.28 *
P. trivialis	Cd	*CaCl₂*	0.60 (0.20) **	-0.50 (0.08) **	0.68 **
	Zn	*CaCl₂*	0.37 (0.17) *	1.07 (0.25) **	0.54 *
	Ni	*CaCl₂*	0.61 (0.25) *	-0.15 (0.13)	0.59 *
T. repens	Cd	*CaCl₂*	0.67 (0.18) **	-0.85 (0.10) **	0.73 **
	Pb	*Tot*	0.57 (0.19) **	-1.15 (0.42) **	0.64 **
	Ni	*CaCl₂*	0.38 (0.11) **	-0.25 (0.06) **	0.72 **
R. repens	Cd	*CaCl₂*	0.63 (0.22) **	-0.17 (0.11)	0.48 **
	Zn	*CaCl₂*	0.20 (0.09) *	1.65 (0.11) **	0.34 *
	Pb	*Tot*	0.68 (0.30) **	-1.50 (0.70) *	0.36 **
	Ni	*CaCl₂*	0.50 (0.19) **	-0.21 (0.09) **	0.44 **
R. obtusifolius	Pb	*Tot*	0.54 (0.26) *	-1.28 (0.63) *	0.35 *
S. alba	Cd	*CaCl₂*	0.21 (0.11) *	0.54 (0.06) **	0.22 *
	Cd	*Tot*	0.17 (0.09) *	0.37 (0.09) **	0.23 *
	Pb	*Tot*	0.31 (0.16) *	-0.55 (0.39)	0.21 *

TABLE 9. Regression parameter and R^2 of the concentration of Cd, Cu, Zn, Pb and Ni in different plant groups and the total amount in soil (*Tot*) or extractable fraction by 2.5 mM $CaCl_2$ (*CaCl₂*). * significant at p<0.1. ** significant at p<0.05. Standard error is given in parenthesis

element	plant group	parameter	a	b	R^2
Cd	*monocotyls*	*CaCl₂*	0.46 (0.12)**	-0.78 (0.06)**	0.26**
	leguminosae	*CaCl₂*	0.44 (0.17)**	-0.93 (0.10)**	0.42**
	dicotyls	*CaCl₂*	0.35 (0.13)**	-0.21 (0.06)**	0.16**
	Salix	*CaCl₂*	0.20 (0.10)*	0.54 (0.05)**	0.22*
Cu	*monocotyls*	*CaCl₂*	0.32 (0.18)*	0.32 (0.26)	0.07*
Zn	*dicotyls*	*CaCl₂*	0.09 (0.05)*	1.71 (0.06)**	0.08*
Pb	*monocotyls*	*CaCl₂*	0.35 (0.16)**	0.21 (0.13)*	0.11**
	leguminosae	*Tot*	0.66 (0.22)**	-1.43 (0.46)**	0.49**
	dicotyls	*Tot*	0.48 (0.18)**	-1.12 (0.42)**	0.15**
	Salix	*Tot*	0.31 (0.16)	-0.58 (0.39)*	0.21*
Ni	*leguminosae*	*CaCl₂*	0.38 (0.14)**	-0.28 (0.07)**	0.45**

6.4 Conclusions

Plants that were sampled in river floodplain areas were, in spite of thoroughly rinsing, contaminated by traces of adhering soil particles. Soaking in 1 mM $CaCl_2$ can reduce the contamination, but still plant samples may be contaminated by up to 25 mg kg^{-1} of soil particles. When the plant uptake is low, as is the case for Pb, the soil contamination may be a relevant part of the metal concentration measured in a plant sample. This makes it more difficult to relate plant uptake with soil parameters. For Cd, Cu and Zn, the traces of contamination by soil were less relevant and did not add much to the calculated average concentrations. We could derive significant soil-plant relations for a number of plant species and metals. In case of Pb, and to a lesser extent Ni, the relations do not only reflect metal uptake by plant, but also include the effect of adhering soil particles that could not be removed from the samples. For the risk assessment of herbivore this may not be relevant, since under field conditions the samples would contain even more soil particles. For the ingestion of soil by grazing cattle or sheep, values are reported between 1.5% to 5.6% and 8% to 11% of dry matter, respectively (Abrahams and Thornton, 1994; Abrahams and Steigmajer, 2003). When the uptake of Pb by herbivores should be assessed, soil ingestion is a significant exposure pathway.

We found a significant seasonal effect on the concentrations in the plants, but from our data we cannot discern whether this is related to the season or reflects the variability between different years. However, the difference is less than a factor of 2, and recalculations of the regression functions including a seasonal correction did not improve the standard error or the significance of the regression parameters (data not shown). Thus including a seasonal effect does not improve the model predictions for our data set.

Because of the relatively small differences in uptake, regression calculations lead only to a small number of significant relations with comparably high standard errors. This is also partly an effect of the small number of samples of each plants species (n=6-15). When we divide the plant species into four groups, this resulted in surprisingly small standard deviations of the average metal concentrations (Figure 5). Even when several plant species have significant different average concentrations than the group mean, this grouping still can deliver a smaller confidence interval due to the larger number of samples. The grouping of plant species thus can be useful, since the more extensively used floodplains consist of a large diversity of plant species. In these floodplains, a risk assessment based on the uptake properties of all abundant plant species will be very costly.

Overall, our investigation shows that differences in plant uptake are rather small despite a variety of plant species, differences in contamination degree of the soils, seasonal differences and also differences due to other local factors not assessed in this study (e.g. grazing intensity, ground water level). The results of this study gives a good assessment of the contamination of plants in floodplain soils and the results can be used to estimate the efforts necessary when a risk assessment with improved accuracy should be performed.

Chapter 7

General conclusions

7.1 Introduction

In the previous chapters, many data were presented on the heavy metal contamination of river floodplain soils in the Netherlands. In this chapter, these data are integrated to formulate a guideline on the risk assessment of contaminated floodplain soils.

In the first section the collected data are discussed and several features are highlighted. A second aspect of this study was of technical nature: how to measure availability and how to generate the necessary input for the model. Extraction of pore water *in situ* by Rhizon soil moisture samplers and soil extractions by 2.5 mM CaCl$_2$ were strong tools for experimental soil research and limitations will be discussed in the second section. The modelling of the solid-solution partitioning of heavy metals in soil systems was a great challenge of this study. The geochemical model needed an extensive input that is discussed in the third section. Furthermore, in this section the outcomes of the model are discussed. A number of gaps in knowledge are pointed out and what would be necessary to improve geochemical modelling. In the fourth section, we assess the variability of several parameters and the relevance of it for the risk assessment. In the last section, we give a resume how both modelling and extractions can be used as tools in risk assessment.

7.2 Heavy metals and As in river floodplain soils

Surprisingly little was known about the availability of heavy metals in these floodplain areas. Therefore it was essential to collect experimental data for this study. The field data of this study covered floodplain areas that are geographically well spread over the Netherlands and resulted in a quite detailed chemical description of the solid and solution composition of floodplain soils.

7.2.1 Patterns of heavy metals in soil

In Chapter 4 we found a strong correlation between the organic matter content and the concentrations of heavy metals in soil. Moreover, the metals were strongly correlated which each other. The R^2 values between the total amounts of Cd, Cu, Zn and Pb were higher than between one of the metals and organic matter (Table 1).

TABLE 1. R^2 matrix for the total amounts of Cd, Cu, Zn, Pb, Ni and OC in both rivers

	log Cd	*log* Cu	*log* Zn	*log* Pb	*log* Ni
log OC	0.80	0.72	0.75	0.71	0.38
log Cd	-	0.83	0.91	0.87	0.43
log Cu	-	-	0.90	0.87	0.65
log Zn	-	-	-	0.96	0.52
log Pb	-	-	-	-	0.53

The deposition of contaminated sediments thus leads to a typical "fingerprint" pattern. The largest R^2 value we found was between the total amount of Zn and Pb, with only minor differences between the two rivers. From our data, we could derive a strong relation with a 95%-confidence interval of prediction of less than ± 0.18 log-units (Figure 1):

$$log \text{ Zn (mg kg}^{-1}) = 1.027 \, log \text{ Pb (mg kg}^{-1}) + 0.457 \qquad \text{(Equation 1)}$$
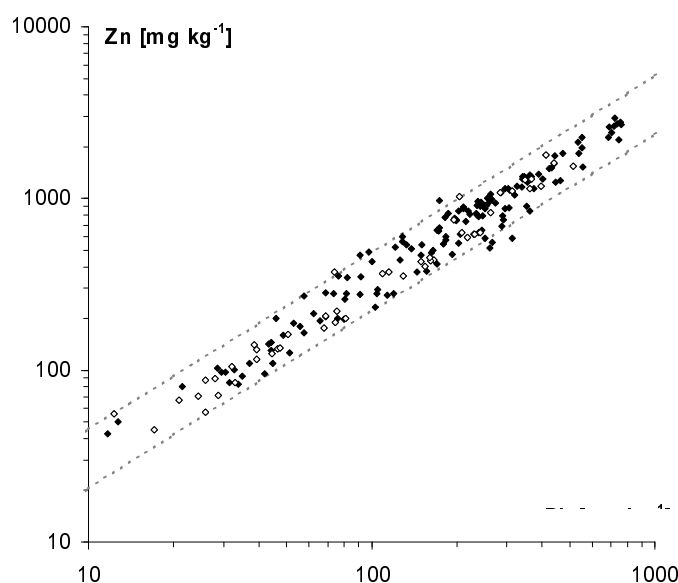
FIGURE 1. Total amount of Zn as function of the total amount of Pb. Open diamonds: Meuse river. Closed diamonds: Rhine branches. The dashed grey lines indicate the 95%-confidence interval of prediction

Soil samples that do not fall in this confidence interval are not necessary artefacts. Our sampling was restricted to the upper 65 cm of the floodplain soils, and samples from layers below this depth might show different patterns. Because the sedimentation rate in the floodplains can vary strongly, and locally even erosion can occur, it is possible that samples taken from the same depth represent sediments deposited in different periods. Furthermore, floodplains are intensively used areas that serve many purposes. Hence, soils not originating from river sediments or soils that are contaminated by other sources are likely to be present.

The statistical model that we introduced in Chapter 4, can predict the solid-solution partitioning very accurately, but one of the disadvantages of this model is that its use is limited to floodplain soils. It is very likely, that this model will fail to give useful predictions for soil samples with a different contamination patterns than those of Chapter 4. The presence of strong correlations as given in Table 1 can be used to define criteria to identify soil

samples from the floodplain areas that have different patterns than the soils our model is based on. We used the simple equation

$$y = ax + b$$ (Equation 2)

to fit statistical regression functions for the most strongly correlated pairs of parameters of Table 1. Since we found in Chapter 4 significant differences between de rivers for As and Cr, we calculated the regression functions for these elements for both rivers independently. Table 2 summarises the regression functions for organic matter and all heavy metals used in this study. All coefficients were highly significant ($p < 0.001$). Soil samples that do not fit into the confidence intervals of these functions should therefore be assessed carefully.

Overall, we conclude that the concentrations of heavy metals, As and organic matter in floodplain soils shows a very specific pattern. This pattern can serve to identify deviant soil samples. Furthermore, the correlation of heavy metals with organic matter is strong enough, that an assessment of the organic matter content of a floodplain soil only may be sufficient to serve as a first estimation of the contamination degree (Van der Scheer and Gerritsen, 1998).

TABLE 2. Regression coefficients and standard error (*se*) for the total amounts of organic matter (OC), Cd, Cr, Cu, Ni, Pb and Zn in floodplain soils of the river Meuse (open diamonds, n=55) and the Rhine branches (closed diamonds, n=139). The standard error of the coefficients is given in parenthesis

parameter	x	river	a	b	se
log OC [%]	*log* Cd [mg kg^{-1}]	both	0.528 (0.019)	0.328 (0.013)	0.15
log As [mg kg^{-1}]	*log* Cu [mg kg^{-1}]	Meuse	0.683 (0.047)	0.273 (0.072)	0.12
log As [mg kg^{-1}]	*log* Cu [mg kg^{-1}]	Rhine	0.830 (0.032)	0.107 (0.061)	0.14
log Cd [mg kg^{-1}]	*log* Zn [mg kg^{-1}]	both	1.197 (0.027)	-2.796 (0.072)	0.16
log Cr [mg kg^{-1}]	*log* Cu [mg kg^{-1}]	Meuse	0.683 (0.051)	0.585 (0.078)	0.13
log Cr [mg kg^{-1}]	*log* Cu [mg kg^{-1}]	Rhine	0.855 (0.017)	0.450 (0.033)	0.07
log Cu [mg kg^{-1}]	*log* Zn [mg kg^{-1}]	both	0.866 (0.021)	-0.565 (0.058)	0.13
log Ni [mg kg^{-1}]	*log* Cu [mg kg^{-1}]	both	0.402 (0.021)	0.891 (0.038)	0.12
log Zn [mg kg^{-1}]	*log* Pb [mg kg^{-1}]	both	1.027 (0.015)	0.457 (0.033)	0.09

7.2.2 Solid-solution partitioning

We used two methods to assess the solid-solution partitioning of As, Cd, Cu, Ni, Pb and Zn. For Cr, more than 98% of samples were below the limit of determination for both methods (<6 µg L^{-1}). Considering the problems on measuring Cr on a low-resolution ICP-MS, we found it not useful to differentiate any of the Cr data further.

As discussed in the previous section, the contamination of floodplain soils shows a typical pattern, where increasing amounts of heavy metals are combined with increasing amounts of organic matter. Furthermore, the metal and organic matter content is also correlated to the amounts of clay, Al, Fe and Mn, that all contribute to the sorption capacity of a soil. These correlations are weaker than the correlations with organic matter, but still highly significant ($p < 0.001$). Increasing amounts of heavy metals are thus correlated with increasing amount of sorbents. This should lead to an increase of the metal concentrations in pore water in a smaller ratio than the total amount would increase. However, as found in Chapter 4, the DOC concentration is significantly correlated with the SOC content of the soil. This correlation is also found for DOC in pore water (Figure 2), and though it is less pronounced it is still significant for samples with a $pH > 6.8$. Thus, the presence of higher amounts of DOC in pore water and $CaCl_2$ extractions at higher contamination levels will counteract the flattening by the strong relation between the organic matter concentration and the heavy metal concentration for Cu, and to a lesser extent for Cd and Zn.
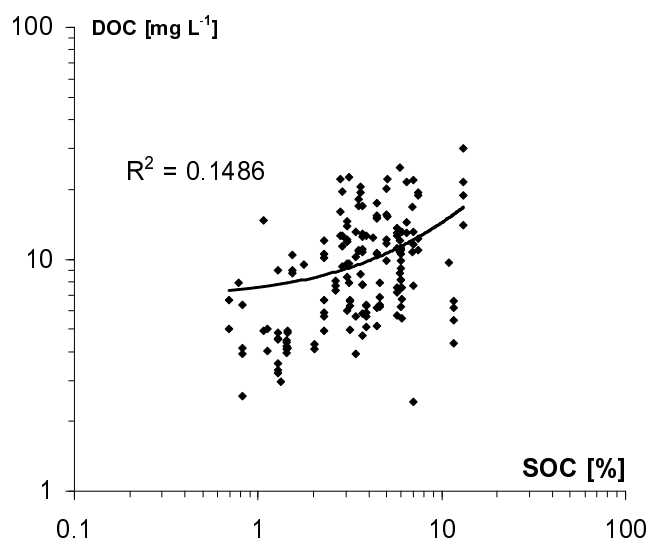
FIGURE 2. DOC concentration in pore water with a pH>6.8 as a function of the soil organic carbon content

Figure 3 shows the pore water concentrations of the heavy metals and As as a function of the total amount in soil. Without considering the differences in pH, DOC concentrations, or other factors, the figure shows already a considerable relationship between the concentrations in soil and the concentrations in pore water. Except for Ni and Pb, where the pore water concentrations were almost constant within the contamination range, all regression fitted for the aerobic samples (Fe<1 mg L^{-1}) by Equation 2 were significant. The slopes of these lines are smaller than 1, except for Cd.

Table 3 shows the standard deviations of the heavy metal concentration in pore water, ranging from 0.28 for Ni to 0.75 for Cd. The standard deviations for the total amounts in soil are in all cases smaller.
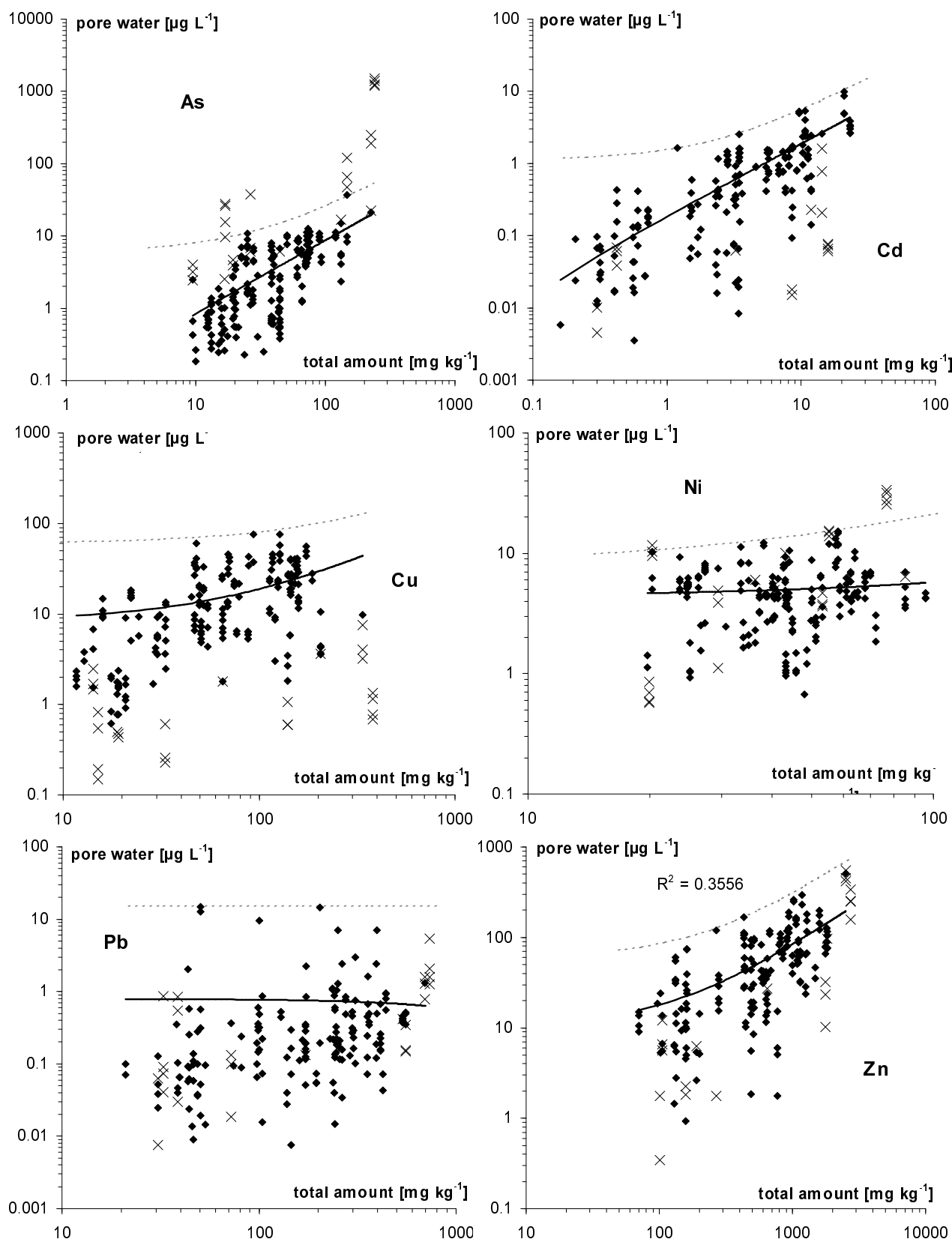
FIGURE 3. Pore water concentrations of As, Cd, Cu, Ni, Pb and Zn as a function of the total amount of these elements. Samples with more than 1mg L^{-1} Fe are marked by crosses. The thick black line is a trend line, the thin line marks the upper boundary of the aerobic samples

TABLE 3. Average and standard deviations (*sd*) of the *log*-transformed concentrations of As, Cd, Cu, Ni, Pb and Zn in pore water and in soil

		log As	*log* Cd	*log* Cu	*log* Ni	*log* Pb	*log* Zn
pore water (all samples)	average [µg L^{-1}]	0.49	-0.50	0.88	0.64	-0.65	1.55
	sd [µg L^{-1}]	0.68	0.75	0.59	0.32	0.62	0.57
pore water (Fe<1 mg L^{-1})	average [µg L^{-1}]	0.35	-0.43	1.01	0.62	-0.66	1.57
	sd [µg L^{-1}]	0.50	0.73	0.49	0.28	0.60	0.51
total amount	average [mg kg^{-1}]	1.58	0.42	1.77	1.63	2.17	2.70
	sd [mg kg^{-1}]	0.35	0.58	0.39	0.17	0.41	0.43

Thus, the range of concentrations of heavy metals present in pore water but also in soil is limited. If we exclude the samples with a total amount smaller than the Dutch reference value, which is an assumed "natural" background concentration in soil (WBB, 1986), the variability is even smaller (Table 4).

TABLE 4. Average and standard deviations (*sd*) of the *log*-transformed concentrations of As, Cd, Cu, Ni, Pb and Zn in pore water of soil samples exceeding the Dutch reference value

		log As	*log* Cd	*log* Cu	*log* Ni	*log* Pb	*log* Zn
pore water (Fe<1 mg L^{-1})	average [µg L^{-1}]	0.56	-0.24	1.19	0.66	-0.56	1.60
	sd [µg L^{-1}]	0.46	0.61	0.37	0.25	0.54	0.50
total amount	average [mg kg^{-1}]	1.83	0.60	1.97	1.70	2.40	2.81
	sd [mg kg^{-1}]	0.23	0.44	0.27	0.11	0.25	0.35

Contrary to the rather small trends present in aerobic samples, the redox conditions of the soil have a considerable effect on the pore water concentrations. In Chapter 5, we found that Cd, Cu, Zn and Pb were immobilised to a great extent in the lower part of a redox profile. The same holds for Ni (Figure 4). The concentrations of Cd were below 0.01 µg L^{-1}, the concentration of Pb below 0.1 µg L^{-1}, and the concentrations of Cu and Ni below 1 µg L^{-1}. The concentrations of Zn can be larger than 1 µg L^{-1}, but were still over two orders of magnitude smaller than under aerobic conditions.

However, at slightly reduced conditions the concentrations of the metals in pore water may be larger than at aerobic conditions. This is clearly the case for As, as shown in Chapter 5 and Figure 3. But also the concentrations of Cd, Ni and Zn can increase under slightly reduced conditions.
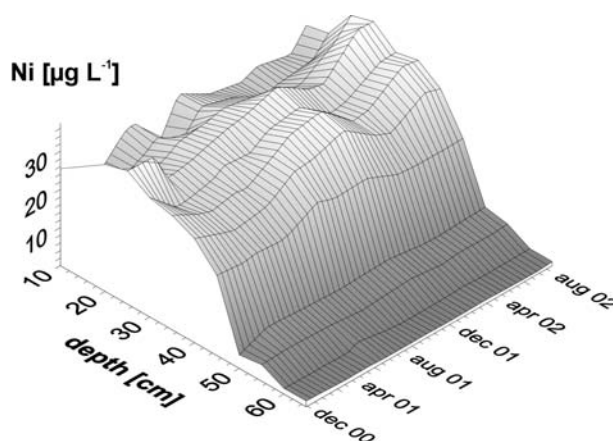
FIGURE 4. Concentrations of Ni in pore water extracted at the Lage Hof site as a function of sampling date and depth

Thus, when after prolonged flooding the redoxpotential decreases, this may lead to an immobilisation of heavy metals on the long term. But before sulphidic conditions are reached, an increase of the pore water concentration is possible. This transient increase should be taken into account when ecotoxicological effects on organisms have to be studied.

7.3 Pore water sampling and extractions by 2.5 mM CaCl$_2$

In Chapter 2, we presented a first study of *in situ* pore water sampling by Rhizons. The results were encouraging, and the low variability of some parameters during the two years sampling described in Chapter 4 may serve as an estimator of the reproducibility of the method. Besides the limited life-time of this rather fragile sampler, there are three mayor limitations for the use of this method: first, the Rhizon samplers have a pore diameter of less than 0.2 µm. Usually, filtering by 0.45 µm is used to define the "dissolved" fraction. The difference in pore size influences the concentrations of DOC and therefore also the concentrations of metals sorbed to DOC. When results are compared, a correction should be applied as outlined in Chapter 3.

The second limitation is a practical one: at low water saturation of a soil, the extraction of pore water is not possible. The sandy soil used in Chapter 2 had a low water retention capacity, and was therefore vulnerable for desiccation This resulted in a loss of 12% of all samples in this experiment. In Chapter 3, about one third of the locations could not be sampled due to desiccation. The implications of the small fractions of pore water, that cannot be extracted by Rhizons, for the risk assessment is difficult to estimate.

The third limitation is related to the time necessary for intruding water to reach equilibrium with the solid phase. In Chapter 2, we could fit a significant relation between Ca concentration and the precipitation pattern. The relevance of this finding for the equilibrium chemistry of metals is unclear, since in Chapter 5 no relation was found between low Ca and Cl concentrations and the deviation between the two methods we compared. However,

it is obvious that even if sampling shortly after rainfall limits the applicability for equilibrium modelling, the possibility to sample pore water in its natural state is most welcome.

The extraction by 2.5 mM $CaCl_2$ is easy, fast, cost-efficient and reproducible. In Chapter 3, we showed that the results were remarkable comparable with the pore water extraction and we quantified how the results of both methods were related to each other. We also discussed the loss of information on the temporal variability and the redox condition of pore water. The fact that the extraction does not reflect any temporal variability can be seen as an advantage or disadvantage, depending on the question that should be answered. None of the three drawbacks sketched for Rhizon extractions in the previous section applies for the $CaCl_2$ extraction. Therefore, the only indisputable drawback of the $CaCl_2$ method is that it hides the redox condition present in the sampled soil.

In Chapter 4, we found that replacement of the pH by the total amount of Ca in soil improved the model prediction for several metals. The measurement of the pH in suspension, as defined by the standard procedures, might not be the best choice, when the results should be used for geochemical modelling. The registration of the pH after centrifugation may therefore deliver better results.

In conclusion, the Rhizon extractions were useful in studying the relation between the extractions and pore water. Considering the results of Chapter 3, the $CaCl_2$ extraction is a good measure to estimate the solid-solution partitioning of heavy metals in pore water. As long as the link with metal uptake by plants or biota is made by deriving empirical relations from the dataset, the small systematic deviations between both methods are not essential. The Rhizons can be used to study the temporal variability without interference by spatial heterogeneity and when an unbiased measure of the pore water composition is needed.

7.4 Modelling of the solid-solution partitioning

One of our main questions was, whether it is possible to predict the solid-solution partitioning of heavy metals by geochemical modelling. However, the design of such a model is far from trivial and several choices have to been made to find a good compromise between the processes and components that should be integrated in such a model, and the imperfection of every model element due to limited understanding, the need to simplify complex processes, the lack of thermodynamic data, or due to the impossiblity to measure or estimate parameter values. For the model presented in this study, many of such choices were made based on the collected field data and the consequences and limitations are discussed in the next sections.

7.4.1 Input parameters

The first step of this study was to identify the relevant processes and parameters necessary to describe the solid-solution partitioning. The statistical model presented in Chapter 4 is rather straightforward in this sense, since it only uses the total amounts of the metal, the amount of soil organic matter and the amount of clay. The amounts of Fe and Mn in soil and the concentration of DOC did not contribute much to the modelling result, and the pH could be substituted without much loss of precision by the total amount of Ca. For the Rhine branches, a generic pH is sufficient, because the pH in $CaCl_2$ is found to be rather constant (7.47 ±0.16). These simplifications of the model meet the limited number of parameters present in governmental databases and enable the prediction of the extractable fractions from the standard set of parameters used for risk assessment in the Netherlands.

The geochemical model is, on the other hand, very demanding. Besides the total amount of all metals we considered, several other anions and cations are necessary that are involved in complexation reactions or that compete for sorption sites.

For Ca, the major background cation, we faced the first limitation of the equilibrium approach: the use of the total amount of Ca together with the presence of $CaCO_3$ would lead to a large pH-dependency of the soluble fraction, which is not supported by our data. Ca is an important parameter in the modelling of metal speciation because it is the major (and only) cation used to define the background electrolyte and can compete with heavy metals for sorption sites. Therefore, we choose for the most obvious option and used the measured pore water concentration of Ca or the concentration of the $CaCl_2$ extractant as model input.

When we use the pore water concentration as input parameter, the total amount of Ca calculated in the system can be larger of smaller than the total amount actually present in the soil sample. The model underestimates the amount of Ca that is present as $CaCO_3$ in soil samples. This has no adverse effect on the modelling results except if one considers to extend the model e.g. by calculating metal sorption on $CaCO_3$. In case of an overestimation of the total amount of Ca in soil, this could influence the system by overestimating the amount of PO_4 in the system bound as hydroxyapatite. However, for none of the samples presented in Chapter 3, we calculated an amount of hydroxyapatite that was larger than the total amount of Ca measured in soil.

An alternative would be to calculate an "apparent" solubility constant for calcite, which fits to the data of Chapter 3. Figure 5 shows that the calculated *log* K values spread over a wide range. But also when we introduce a pH-dependency of the *log* K value by fitting a line through the values in Figure 5, the solubility constant would vary by more than a half unit. However, even if we could derive a solubility constant for $CaCO_3$ that fits our data perfect, we still need to measure the inorganic carbon concentrations (IOC) to be able to calculate the Ca^{2+} activity. Our approach to use measured Ca concentrations is therefore more feasible, since the concentration of Ca is easy to measure or can be estimated *in situ* by measuring the conductivity.

As the major background anion we used Cl. In the $CaCl_2$ extractions, sufficient Cl is present to counteract the charge of Ca by definition, but in Chapter 3 we showed that in pore water the molar concentration of Cl was only half of the concentration of Ca. The

concentration of NO_3 in pore water is not critical, since it barely complexes with other ions and no specific binding is defined in the used sorption models. Therefore it can be used to neutralise the charge balance.
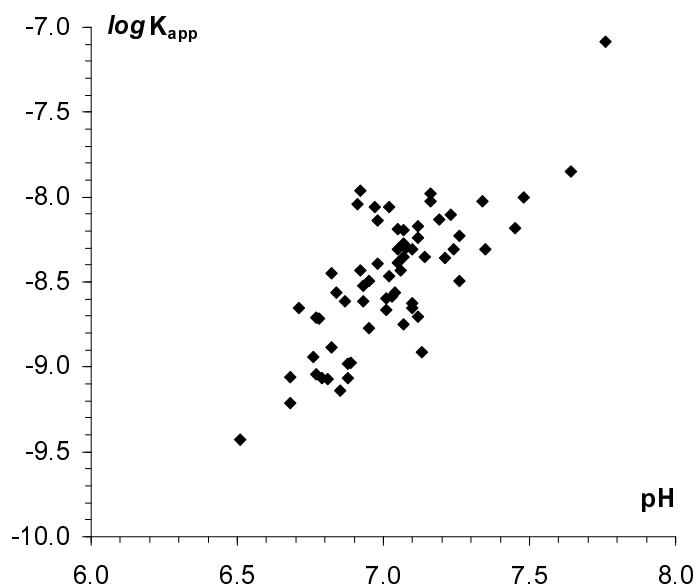
FIGURE 5. "Apparent" *log* K value for $CaCO_3$ calculated by the concentrations of IOC and Ca in pore water

The total amounts of As, Cd, Cu, Pb, Zn, Fe, Mn, P and Al measured in *aqua regia* can be used directly as input for the model. The same applies for the pH.

The concentrations of IOC measured under aerobic conditions on the locations of Chapter 4 are found to barely influence the partitioning of heavy metals (data not shown). However, under reduced conditions, the IOC concentration can be considerably higher and should be measured since it can influence the metal speciation. In Chapter 5, we measured an average concentration of 125 mg L^{-1} IOC and calculated that metal carbonates can account for up to 15% of the pore water metal.

A element that is difficult to model is S. No solid phase can be attributed to S or SO_4 under aerobic conditions and sorption to the solid phase is limited, too. Under aerobic and slightly reduced conditions, complexation by SO_4 is not adding much to the pore water concentrations of the metals. Under these conditions, a generic value based on the measured concentrations of SO_4 is therefore sufficient. But under sulphidic conditions, the total amounts of S in soil are necessary to calculate the amounts of metals that can be precipitated as insoluble metal sulphides. However, neither of both approaches, i.e. to fix the activity of SO_4 (or in case of ORCHESTRA the total amount in the water phase) or to fix the total amount in soil, can be used over the entire redox range. Therefore we used a double strategy in Chapter 5, namely to fix the concentration of SO_4 in pore water to a concentration measured in pore water, as long as the calculated total amount in soil is smaller than the amount measured. Thus, we need both the total amount of S in *aqua regia*

and the concentration in solution to be able to model the metal partitioning under sulphidic conditions.

No simple analytical methods are available at the moment to measure the surface areas of manganese oxides and iron oxides in soil samples. The same holds for the fulvic and humic fractions of DOC and SOC, as discussed in Chapter 4. Therefore we had to make assumptions for the values of these parameters. The importance of a good estimation depends on the sorbed fraction of metals. In Chapter 2, we showed that for Zn the sorption to oxides is negligible, and in Chapter 5, only As binding to oxides was found to be significant. Thus, except for As, the assumptions on the surface areas of the oxides were not critical. In contrast, due to the strong binding of Cd, Cu and Zn by organic matter, assumptions regarding the fractions of fulvic and humic acids were important. Since these fractions are likely to be highly variable, this is not a problem that can easily be solved by calibration. We will discuss the importance of the HA and FA fractions on the modelling in the next section.

Table 5 on the next page summarises all necessary input parameter for the geochemical modelling

7.4.2   Prediction of the solid-solution partitioning by geochemical modelling
In Chapter 3 we compared geochemical modelling with a statistical model. The statistical model reveals very precise results within the limits discussed before. However, we were also interested if geochemical modelling, upgraded with state-of-the-art adsorption modelling, can be used as a tool to get quantitative insight in metal behaviour. One of our starting points was, that considering the number of parameters of the model and the rather simple pattern we had to explain, calibration of model parameter will certainly leads to good results but may not deliver meaningful insights into speciation processes. Therefore we aimed to develope a model that is fully parameterised by literature data. Still, a number of choices could be done for the model set-up, as discussed in section 7.3.1, and for a limited number of parameters that are difficult to measure, values need to be derived. In the following sections, we evaluate geochemical modelling as a quantitative tool and suggest how the model can be improved.

The heavy metal that was predicted best by geochemical modelling was Cu. The chemistry of Cu is, according to the model, very simple under aerobic conditions: almost all Cu is bound to either SOC or DOC. Thus, the solid-solution partitioning of organic matter controls the partitioning of Cu. In the previous chapters, we mentioned that the fractions of FA and HA that we used in the model were based on assumptions and not well supported by literature due to the lack of data. Furthermore we claimed that the fractions are probably not constant but can be highly variable for the different samples. Assuming that

$$\frac{Cu_{porewater}}{Cu_{soil}} = a \times \frac{DOC}{SOC} \qquad\qquad \text{(Equation 3)}$$

with a equal to

$$a = \frac{f_{FA}}{f_{HA}}$$ (Equation 4)

and f_{FA} and f_{HA} the fractions of respectively fulvic acid in DOC and humic acid in SOC, we can estimate the variability of a from our data. The standard deviation of the *log*-transformed values of a was 0.222, comparable to the RMSE for Cu found in Chapter 4, when the RMSE is calculated relative to the trend line. The average value of a was 0.564, therefore we adjust f_{FA} and f_{HA} in Chapter 5 to 0.5 and 0.3, respectively.

TABLE 5. Input parameter for the geochemical model. *anaerobic*: Fe>1 mg L^{-1}. *tot*: total amount in soil

component/ parameter	type input	phase	generic value	parameter replacement
H	pH	pore water	Rhine: 7.5	0.787 *log* Ca$_{tot}$ + 7.588
e	PO_2 / pe	pore water	aerobic: PO_2 = 0.2 atm anaerobic: pe	-
Ca	Ca	pore water	2.5 mM	-
Cl	Cl	CaCl$_2$ pore water	CaCl$_2$: 5 mM pore water: 1.25 mM	-
NO$_3$	NO$_3$	CaCl$_2$ pore water	CaCl$_2$: - pore water: 3.75 mM	-
CO$_3$	IOC	pore water	aerobic: 60 mg L^{-1} CO$_3$ anaerobic: -	-
SO$_4$	S / SO$_4$	soil / pore water	- / 60 mg L^{-1} SO$_4$	-
As	As	soil	-	13.03 SOC$^{0.801}$
Cd	Cd	soil	-	0.3926 SOC$^{1.505}$
Cu	Cu	soil	-	15.42 SOC$^{1.047}$
Pb	Pb	soil	-	37.67 SOC$^{1.083}$
Zn	Zn	soil	-	111.4 SOC$^{1.165}$
Fe	Fe	soil	30,000 mg kg^{-1}	-
Mn	Mn	soil	900 mg kg^{-1}	-
Al	Al	soil	20,000 mg kg^{-1}	-
P	P	soil	1000 mg kg^{-1}	-
DOC	DOC	pore water / CaCl$_2$	10 mg L^{-1} / 25 mg L^{-1}	- / 1.049*10^{-4} SOC$^{0.455}$
SOC	SOC	soil	-	-
FA	fraction	DOC	0.5	-
HA	fraction	SOC	0.3	-
goethite	surface area	goethite	50 m^2 g^{-1}	-
MnO$_2$	surface area	MnO$_2$	50 m^2 g^{-1}	-

However, comparing the variability of *a* and the RMSE of the geochemical model with the RMSE of 0.113 of the statistical model, this implies that some of the factors in the statistical model can explain part of the variability we found in the geochemical model.

More insight on the fractions of FA and HA in organic matter will also improve the modelling of Cd. However, in Chapter 4 was found that it is not possible to find optimum values for the FA and HA fractions that fits for both Cd and Cu. Thus, obviously part of the Cd in soil is present in a form that is not included in the model. One possible sink we suggested was manganese oxide. Manganese oxides can adsorb considerable amounts of heavy metals. The zero point of charge can be low (1.4-2.4 for δ-MnO_2) and the specific surface areas can be high (Murray 1974; McKenzie 1981). Seen the high manganese concentrations in soil, the oxides are therefore potentially important sinks for Cd but also other heavy metals in floodplain soils. The model of Tonkin et al. (2004) could describe successfully the sorption of a number of metal on manganese oxide, but unfortunately it failed to describe all literature data on Cd. As discussed in Chapter 5, the lack of competition for a number of sites also results in a conceptual problem. However, this model could not answer the question if manganese oxide is of relevance for the binding of Cd. More insights on the sorption behaviour of manganese oxides will be helpful for a more detailed geochemical modelling of Cd but also other heavy metals.

The partitioning of Zn was overestimated in Chapter 4. As we discussed, several solutions are possible. Here, lack of thermodynamic data is obviously one of the problems, but the geochemical model delivers enough hypotheses, that an experimental strategy can be formulated from the data. The most obvious choice is to compare measured and calculated Zn^{2+} activities as done by Weng et al. (2001). However, we calculated Zn^{2+} activities between 2 nM and 1 µM, and techniques that are able to measure such low activities in soil samples were not available at the moment our study was done. Alternatively, the presence of a claimed mineral Zn phase can be tested by spectroscopic techniques (Manceau et al., 2000; Scheinost et al., 2002). And, finally, in case that thermodynamic data is not available (hemimorphite) or the quality of it is doubtful, solubility constants or other parameter can be derived experimentally. However, we can also estimate by geochemical modelling, if the results of such an experimental approach will influence the model outcome. In case of the three mineral phases proposed in Chapter 3, spectroscopy can elucidate which mineral actually is present is floodplain soils, but for the calculated behaviour of Zn it barely makes any difference. Hence, seen the good agreement in Chapter 2 and Chapter 5 and also in Chapter 4 after the proposed improvements, it is not clear if the identification of the mineral phase will improve the results of the geochemical model.
Still, as discussed in Chapter 4, the partitioning of Zn is overestimated at low pH by an order of magnitude. The influence of the pH is thus not described well by the model for pH values below 6.8.

The chemistry of Pb was a continuous source of questions during this study. As we stated in Chapter 3, the geochemical model largely overestimated the amount in pore water. If we compare the solid-solution partitioning of organic matter with the solid-solution partition-

ing of Pb, it is obvious that only a minor part of Pb in pore water can be explained by binding to DOC. Generally, three conclusions can be made from the previous chapters:

1. From the data in Chapter 4 we can conclude, that Pb is not preferentially bound to organic matter. Independent of the sorption model or the parameterisation used, this can be derived from the solid-solution partitioning of organic matter, if we assuming that the sorption behaviour of Pb on DOC and SOC is comparable.

2. Based on the sorption parameters for Pb as published by Milne et al. (2003), the calculated Pb^{2+} activity is too low to allow the formation of any of the Pb containing mineral phases present in the cited databases or articles. In Chapter 5, we calculated that the Pb^{2+} activity must be $\leq 10^{-13}$ mol L^{-1} to explain the low concentrations found in pore water.

3. When significant amounts of the Fe measured in pore water under anaerobic conditions are present as oxides, the Pb concentrations presented in Chapter 5 cannot be explained by binding to iron oxide.

The proposed "PbX" component from Chapter 5 does not necessarily refer to a mineral phase. We only demonstrated that any component that is able to limit the activity of Pb^{2+} to 10^{-13} M can explain the behaviour of Pb sufficiently.

The partitioning of As could be explained well by geochemical modelling. However, as for Zn, for samples with low pH values the model overestimated the pore water concentrations. And, as for Zn, these samples had comparable concentrations than the samples with a higher pH (Chapter 4, Figure 2).

Under sulphidic conditions, no sink for As is defined in the model, and it is obvious that it is easy to define a hypothetical compound that will meet the data, but since neither our data nor the modelling suggest any particular compound, we did not define such a compound. Our simple assumption that the sorption behaviour of magnetite under anaerobic conditions is similar to goethite, describes the redox behaviour of As surprisingly well. Since the redox behaviour of As is addressed by many research projects, in future more detailed data on this will be available that makes it possible to judge this assumption.

7.4.3 *Variability and modelling*

One of the major problems in risk assessment is the spatial and temporal variability of parameters. The use of the Rhizon sampler reduces the spatial variability, as it eliminates the need to take different soil samples at the same location. But it is still difficult to extract trends and to distinguish between the temporal variability and the variability of the analytical method used. This was one of the reasons to test the extraction by 2.5 mM $CaCl_2$ as an alternative. However, sometimes it can be necessary to account for the temporal variability of the pore water composition, e.g. to study the kinetic uptake of metals in organisms. Then, the sampling of pore water is required.

In Chapter 3, all Rhizons in soil were inserted in duplicate, with a horizontal distance of approximately 20 cm between duplicates. The differences between these duplicates can be used to estimate the sum of the small scale heterogeneity of the soil and the variations within the used method. Table 6 shows the average standard deviations between all

samples collected in duplicate, and indicates that only a minor part of the variability is explained by both factors.

TABLE 6. Averaged standard deviations (*sd*) of the *log*-transformed concentrations in the duplicate Rhizon pore water sample

	log DOC	pH	*log* As	*log* Cd	*log* Cu	*log* Ni	*log* Pb	*log* Zn
sd	0.01	0.01	0.06	0.10	0.04	0.01	0.11	0.07

To be able to extract seasonal trends from the data, a large numbers of data are required. Physical, chemical and biological processes can influence the variability of parameters like the pH and can lead to a complex pattern (Chapter 2, Chapter 5). In floodplain soils, e.g. the high water period in spring can be earlier or later, longer or shorter, continuous or consisting of several peaks (e.g. Chapter 5, Figure 2). This is obviously a practical limitation, because in risk assessment the available time is usually too short to repeat sampling for a number of years. It is therefore highly speculative to derive seasonal trends from the data in this study. However, we can use the data to estimate the variability of several parameters.

Thus, when we are not able to assess a trend, the temporal variability might be limiting for the precision of the outcome of the assessment.

In Figure 6, we plotted the standard deviations of the repeated pore water sampling of Chapter 3 and Chapter 5. These values can be used to estimate the temporal variability under field conditions. For the pH, DOC, Ca and Ni, the variability is below 0.2 for most values. Thus pore water sampling with 3 or 4 replicates will lead to a good estimation of the average value. But for Pb, about 9 samples are necessary to estimate the average within a factor of two.

When the variability is compared with the values as given in Table 4 and 5, a generic value or a value calculated by the statistical model might give an estimation as good as a sampling campaign with a too small number of observations.
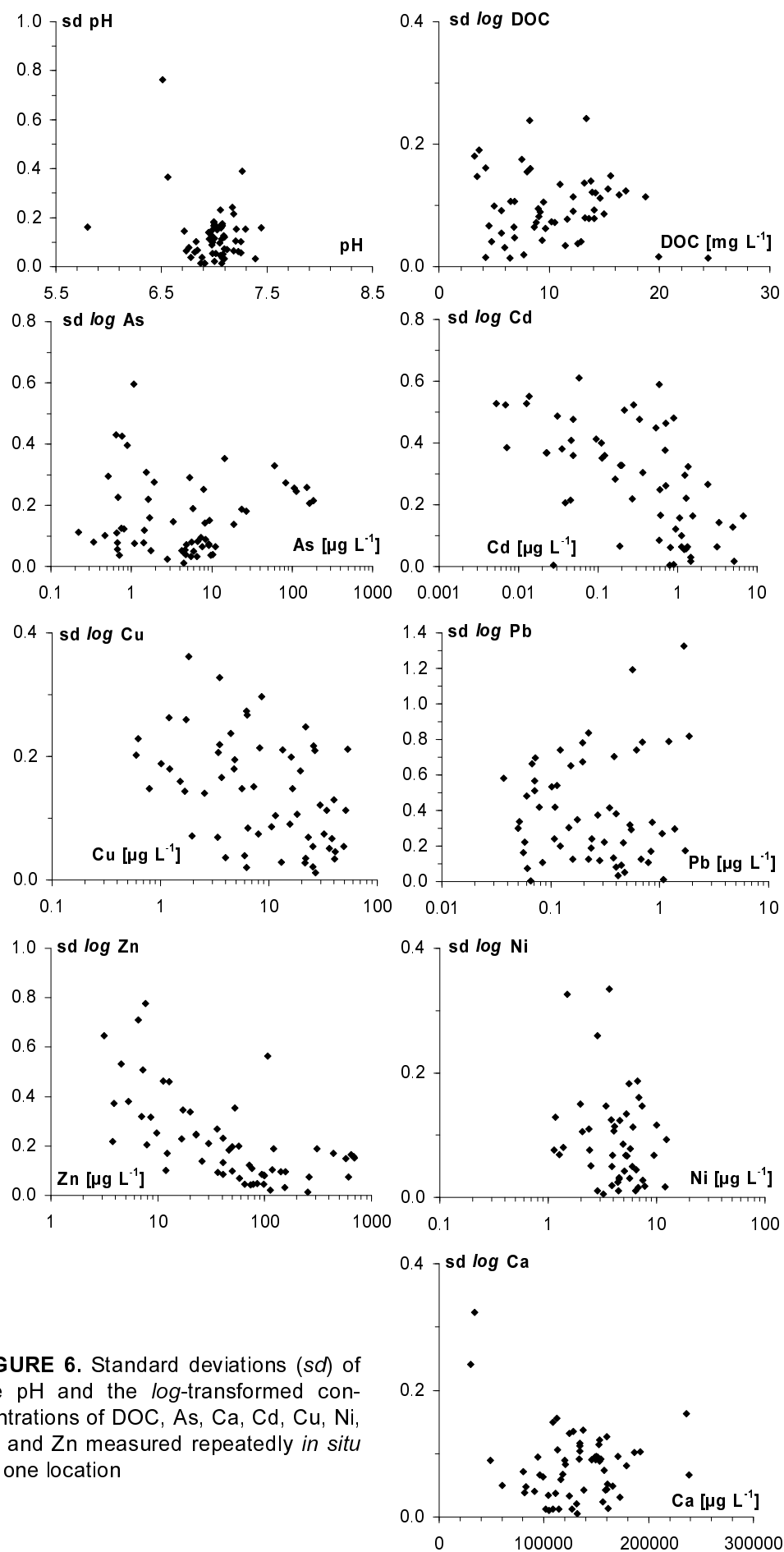
FIGURE 6. Standard deviations (*sd*) of the pH and the *log*-transformed concentrations of DOC, As, Ca, Cd, Cu, Ni, Pb and Zn measured repeatedly *in situ* on one location

7.5 Tools for the risk assessment of soil systems

Oreskers et al. (1994) stated that the primary value of a model is a heuristic one. This is definitely true for the geochemical model presented in this study. It can be used for sensitivity analysis, exploring gaps in understanding and testing hypothetical solutions like the PbX mineral, and it can serve as a guide for designing further experimental studies or sampling campaigns. Moreover, geochemical modelling also can delivers quantitative insights that, placed in the right context, will be useful in judging risks. However, the predicting force of the statistical model is much better as long as we limit the application of this model to aerobic situations. Therefore, both tools have their benefit in risk assessment.

Equally contrasting as geochemical and statistical modelling, were the two analytical tools presented in this study: on one hand the $CaCl_2$ extraction, an efficient and easy to apply method providing much of the information necessary for risk assessment, and on the other hand the Rhizon extraction of pore water, a very suitable method to sample repeatedly without interference by spatial heterogeneity, but carrying the whole burden of temporal heterogeneity.

In Chapter 6, we assess the risk of metal uptake by plants. Here, we choose a strategy to estimate first the variability present under field conditions by a initial sampling campaign and thereafter adapt the main focus of our sampling scheme to the results. Once we noticed that the differences between locations and plant species were rather small, and a generic model with four plant groups worked already well without considering any soil-plant relation, the logical step was to confirm the small variations between species, location and seasons by extending the number of sites and plant species. Obviously, considering the small variations that could be explained, a statistical approach combined with $CaCl_2$ extractions was sufficient to get a detailed picture of the risk due to metal uptake by plants. The standard deviations found in pore water (Table 3) were larger than the standard deviations found in Chapter 6. Thus, if we had applied a high resolution pore water monitoring, it is questionable if we had been able to explain more of the variations we found, since still a large number of unknown factors will be present that could influence the soil-plant relationship but that are not measured. E.g. the root zone may vary for every location and species or the water saturation might differ between locations due to spatial heterogeneous precipitation pattern and differences in groundwater level. Also the application of a geochemical model to compare several fraction in pore water (i.e. free ion activity, dissolved fractions, DOC bound fractions) with the uptake pattern in plant, did not improve the quality of the prediction by the model (data not shown).

Thus the choice for one of the tools above depends on the question to be answered, the number of samples that can be taken, and the variability of the parameters that are assessed.

Chapter 8

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Appendix
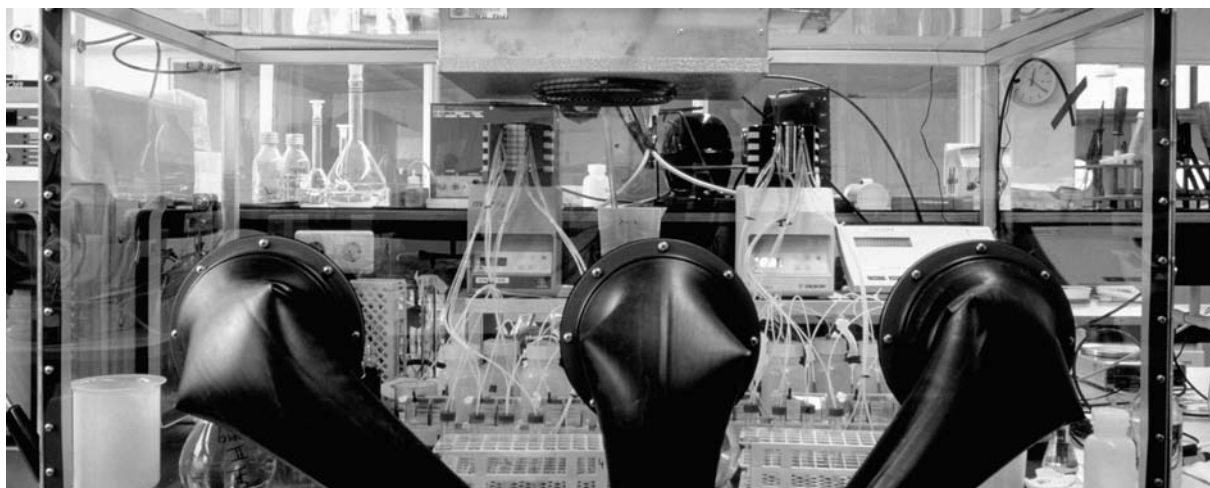
TABLE 1. Charge and site density of the surface sites used for the modelling of cation and anion adsorption to goethite by the CD-MUSIC model. C=0.9 F m^{-2} (Basic Stern approach)

surface site	charge	N_s [nm^{-2}]
FeOH	-0.5	3.0
Fe$_3$O	-0.5	3.0
FeOH$_h$	-0.5	0.1

TABLE 2. Surface species, affinity (*log* K), species and surface sites composition and charge distribution to 0- and 1-plane used for the modelling of cation and anion adsorption to goethite by the CD-MUSIC model (continuation on the next page)

surface species	*log* K	composition		surface sites			charge distribution	
				FeOH	Fe$_3$O	FeOH$_h$	0- plane	1-plane
FeOH2	9.2	1 H		1			1	
FeOH2-Cl	8.7	1 Cl	1 H	1			1	-1
Fe3OH	9.2	1 H			1		1	
Fe3OH-Cl	8.7	1 Cl	1 H		1		1	-1
FehOH2	9.2	1 H				1	1	
FehOH2-Cl	8.7	1 Cl	1 H			1	1	-1
Fe2OPO2	29.4	1 PO$_4$	2 H	2			0.39	-1.39
(Fe)2OPO2OH	35.7	1 PO$_4$	3 H	2			0.9	-0.9
(Feh)2OPO2	29.4	1 PO$_4$	2 H			2	0.39	-1.39
(Feh)2OPO2OH	35.7	1 PO$_4$	3 H			2	0.9	-0.9
Fe2O2-CO	22.3	1 CO$_3$	2 H	2			0.67	-0.67
FeOHh-CO	22.3	1 CO$_3$	2 H			2	0.67	-0.67
(Fe2OH)2Fe	12.7	1 Fe^{2+}		2			1.9	0.1
(FehOH)2Fe	12.7	1 Fe^{2+}				2	1.9	0.1
FeOHCa	3.6	1 Ca		1			0.2	1.8
FehOHCa	3.6	1 Ca				1	0.2	1.8
Fex-Pb	10.1	1 Pb		1	1		1.14	0.86
(Fe2OH)2Pb	12.3	1 Pb				2	1.14	0.86
Fex-CuOH	2.9	1 Cu	-1 H	1	1		0.77	0.23
FehOH2CuOH	6.1	1 Cu	-1 H			2	0.77	0.23

TABLE 2 (continued). Surface species, affinity (*log* K), species and surface sites composition and charge distribution to 0- and 1-plane used for the modelling of cation and anion adsorption to goethite by the CD-MUSIC model

surface species	log K	composition		surface sites			charge distribution	
				FeOH	Fe$_3$O	FeOH$_h$	0- plane	1-plane
Fe2O2H2Cd	7.0	1 Cd		2			0.71	1.29
Fe2OH2CdOH	-2.9	1 Cd	-1 H	2			0.71	0.29
FehOH2Cd	9.6	1 Cd				2	1.31	0.69
FehOH2CdOH	-0.3	1 Cd	-1 H			2	1.31	-0.31
Fe2OH2-Zn	8.0	1 Zn		2			1	1
Fe2OH2ZnOH	0.1	1 Zn	-1 H	2			1	
FehOH2-Zn	8.0	1 Zn				2	1	1
FehOH2ZnO	0.1	1 Zn	-1 H			2	1	
Fe2OAsO2	28.4	1 AsO$_4$	2 H	2			0.39	-1.39
Fe2OAsOOH	34.8	1 AsO$_4$	3 H	2			0.9	-0.9
Feh2OAsO2	28.1	1 AsO$_4$	2 H			2	0.39	-1.39
Feh2OAsOOH	34.8	1 AsO$_4$	3 H			2	0.9	-0.9
FeOH2AsO3	6.9	1 AsO$_3$		2			0.2	-0.2
FeOHh2AsO3	6.9	1 AsO$_3$				2	0.2	-0.2
Fex-PbPO4 *	28.0	1 Pb	1 PO$_4$	1	1		1.14	-2.14

* see explanation in Chapter 4

TABLE 3. Soil organic carbon content (*SOC*), clay fraction (*<2 µm*) and total amount of heavy metals and Ca in soil samples collected in October 2001

location	SOC [%]	<2 µm [%]	Cd [mg kg^{-1}]	Cu [mg kg^{-1}]	Zn [mg kg^{-1}]	Pb [mg kg^{-1}]	Ni [mg kg^{-1}]	Ca [mg kg^{-1}]	Fe [mg kg^{-1}]
IJ01A	1.3	8.5	0.5	18.1	103	28.4	20.2	33833	13765
IJ04C	6.0	30.2	3.2	65.0	646	172	43.1	35776	32735
IJ05A	3.5	14.6	2.4	39.9	468	90.9	36.6	28367	20130
IJ05B	3.7	32.6	2.3	54.7	512	138	44.9	26098	34697
IJ09A	3.4	20.2	1.4	25.3	279	73.4	22.3	12380	21544
IJ11A	4.1	10.6	4.2	63.0	968	173	27.9	33338	22012
M09A	4.2	33.4	3.6	45.4	617	229	30.8	7342	28161
M09B	2.9	12.2	2.2	25.6	401	154	24.0	3525	23604
M11C	1.2	5.9	0.5	13.6	71.5	29	12.6	1146	15906
M11E	8.4	25.0	17.8	140	1630	420	44.2	31321	42115
M11F	8.8	29.4	20.3	159	1878	587	46.9	28254	44523
M15A	2.7	30.6	2.3	32.9	372	115	42.5	4422	39850
M17A	1.3	12.5	0.6	16.0	133	46.6	23.7	2129	22939
M24A	1.3	8.3	1.0	14.9	207	68.8	18.9	10689	13445
M24C	8.1	21.1	13.7	101	1298	366	38.6	5819	33575
R02A	6.0	22.9	5.7	116	690	289	50.2	38081	24473
R03B	5.3	29.2	4.1	106	585	315	60.2	13178	30430
R06A	3.0	31.6	0.6	30.3	160	48.7	33.5	5528	30937
R08C	3.4	31.5	0.9	38.3	199	80.0	51.8	16309	33496
R09B	2.8	32.8	2.4	69.4	584	251	50.0	42140	31742
R13A	5.6	29.9	8.6	120	796	246	95.8	30049	32737
W01A	3.5	34.3	3.6	89.8	747	199	51.0	33177	36425
W01C	5.2	42.5	6.7	117	888	211	69.0	24182	44146
W02C	4.6	28.3	2.5	76.5	655	170	49.6	27516	31347
W03B	3.6	24.5	3.0	70.1	536	133	44.8	35489	31870
W09C	4.6	38.8	3.9	92.3	845	220	56.0	15192	36357
W11B	4.5	21.5	4.1	95.2	822	234	41.4	40205	28843
W12C	4.2	9.5	3.2	46.3	410	91.3	24.3	13067	16601

TABLE 4. Dissolved organic carbon (DOC), pH and concentrations of heavy metals extractable by 2.5 mM $CaCl_2$ in soil samples collected in October 2001

| location	DOC [mg L^{-1}]	pH [-]	Cd [µg L^{-1}]	Cu [µg L^{-1}]	Zn [µg L^{-1}]	Pb [µg L^{-1}]	Ni [µg L^{-1}]
IJ01A	11.7	7.54	0.06	10.8	1.28	0.06	1.46
IJ04C	51.4	7.61	0.35	39.4	9.79	0.22	5.25
IJ05A	26.2	7.44	0.31	27.6	4.12	0.09	2.39
IJ05B	31.7	7.46	0.17	22.5	3.13	0.04	3.22
IJ09A	41.5	7.46	0.25	26.0	5.29	0.22	3.70
IJ11A	26.6	7.52	0.72	34.4	10.4	0.37	3.04
M09A	27.2	7.15	0.50	18.2	12.7	0.43	2.16
M09B	18.7	6.74	0.74	10.5	36.6	0.70	3.35
M11C	7.80	5.86	1.65	5.80	109	0.30	4.10
M11E	24.2	7.70	1.91	45.2	24.4	0.30	2.79
M11F	34.9	7.75	2.17	50.5	32.0	0.70	3.27
M15A	33.3	6.33	1.27	10.5	37.6	0.16	4.86
M17A	15.7	6.58	1.30	8.98	51.1	0.17	13.8
M24A	12.4	6.61	0.23	10.3	10.7	0.37	1.64
M24C	26.1	7.00	1.95	31.0	16.2	0.42	2.66
R02A	30.7	7.43	0.49	47.9	12.9	0.53	3.71
R03B	22.8	7.23	0.49	42.4	19.3	0.73	4.78
R06A	26.9	7.23	0.12	17.5	3.18	0.08	3.97
R08C	7.90	7.49	0.12	17.2	2.60	0.11	3.87
R09B	27.8	7.36	0.20	37.1	7.88	0.28	2.48
R13A	18.3	7.42	0.59	40.6	17.8	0.14	3.76
W01A	44.9	7.65	0.24	35.3	5.28	0.12	2.24
W01C	36.4	7.33	0.46	16.0	7.96	0.22	4.06
W02C	41.5	7.60	0.26	39.9	11.3	0.34	4.28
W03B	25.2	7.50	0.22	26.4	4.43	0.08	2.06
W09C	45.9	7.35	0.64	44.9	21.6	0.30	7.39
W11B	34.8	7.69	0.42	45.3	7.92	0.33	3.16
W12C	27.7	7.50	0.67	30.1	17.1	0.48	5.16
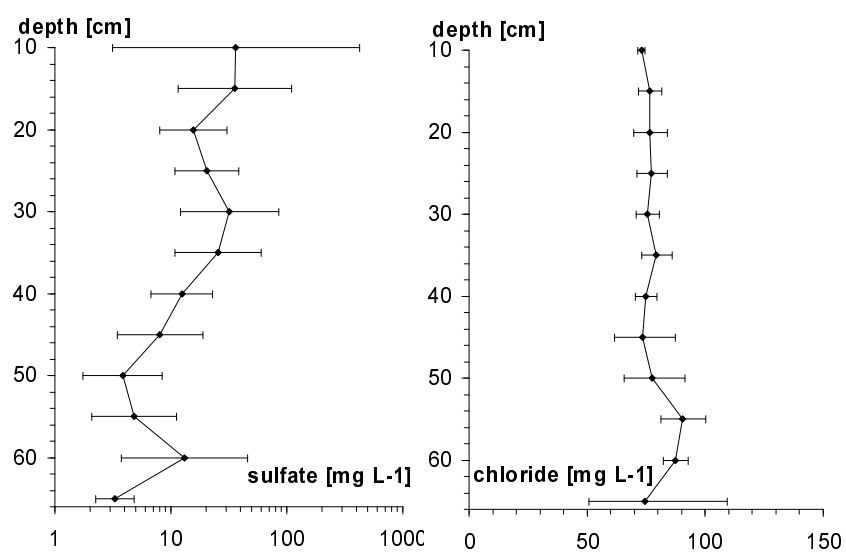
FIGURE 1. Geometric average concentration of 12 sample times and standard deviations of sulphate and chloride in pore water extracted at the Lage Hof site
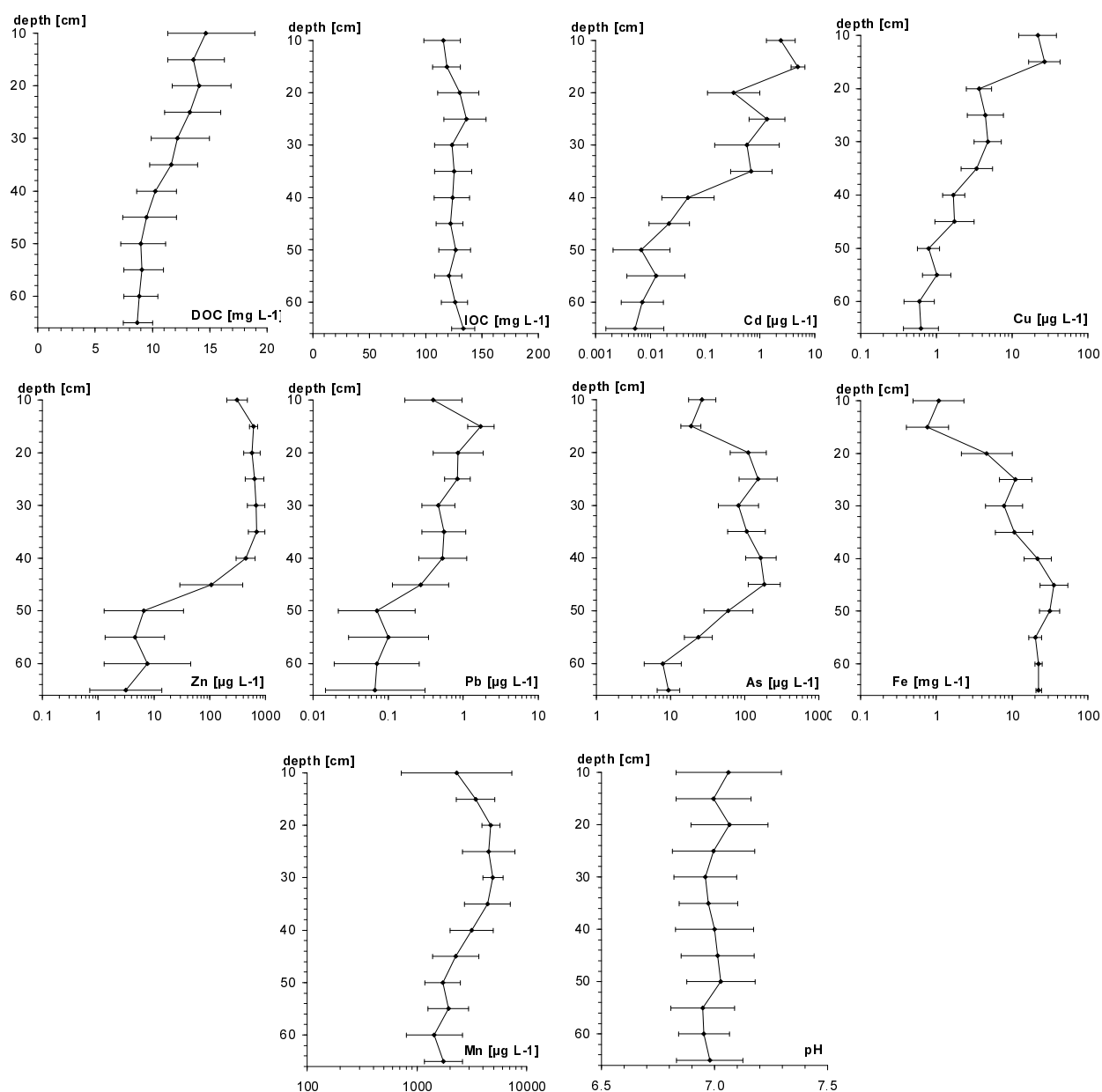
FIGURE 2. Geometric average concentration of 12 sample times and standard deviations of DOC, IOC, Cd, Cu, Zn, Pb, As, Fe, Mn and the pH in pore water extracted at the Lage Hof site

Summary

The rivers Rhine and Meuse are large European river systems with a catchment area of approximately 200,000 km^2 that covers eight European countries. Both rivers have their delta in the Netherlands, and for the protection of the surrounding areas against flooding during the peak discharges between January and April, the rivers are usually embanked by dikes. To be able to handle the large amount of water during these periods, the rivers are surrounded by large floodplain areas. The floodplains of the rivers Rhine and Meuse in the Netherlands cover an area of approximately 500 km^2 and are used during the larger part of the year for grazing cattle or other purposes (e.g. arable land, mining of clay and gravel, recreation, natural habitats).

Both rivers pass heavily industrialised countries with substantial industrial activities along the rivers, e.g. coal mining, steelworks and chemical industry. During the last century, enormous amounts of organic contaminants and heavy metals were emitted to the rivers. Together with the river water large amounts of contaminated sediments have entered the Netherlands, and parts of these sediments were deposited in riverbeds, harbours, lakes and the floodplains. Since the beginning of the last century, an increase of the heavy metal concentrations can be found in the sedimented layers of the floodplain soils. The highest concentrations of Cu, Zn and Pb were dated to the 1930s, and after a decrease during the Second World War a second peak is found in the 1960s. However, in the last three decades, many efforts were done to minimise the emissions. Between 1972 and 1993 the amounts of heavy metals that enters the Netherlands via the Rhine were reduced by more than 80%.

For the management of the river areas it can be necessary to alter the river topology by moving or removing sediments in the floodplains. Projects for river restoration or flood protection have therefore to consider the presence of contaminated sediments. The question whether there is a potential or actual risk connected to contaminated floodplain sediments is a complex one. The most simple measure to quantify the contamination is the total amount of heavy metals in soil. Environmental regulations of many countries are based on these total amounts. But in risk assessment there is a general agreement that the "intensity" or "availability" of a metal is a better measure for the risks that are connected to metal contamination than the total amount present in soils. Since the removal of contaminated sediments can have a great impact on the costs of the projects, there is an urgent need to understand more about environmental risks that are linked to the presence of heavy metals in floodplain soils.

A simple and successful tool to measure the "available" fraction of metals in soil is the use of "weak" extractants, e.g. 0.01 M CaCl$_2$. Although many strong correlations are found between extractable metal fractions and the uptake by plants, the fraction of metals extractable by CaCl$_2$ can not be related directly to the speciation and the chemical composition of the soil or the pore water itself. Therefore the suitability to extrapolate these results to other soil systems is limited. Moreover, extractions do not provide any information about either the temporal variability under natural conditions nor the redox conditions of the sampled soil. Thus extractions may be well correlated with metal uptake, the link with the solid phase and pore water chemistry is unclear.

The most convenient way to describe the complex interactions of sorption, speciation and mineral formation is by geochemical modelling. Geochemical modelling can be linked 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.

Nevertheless, this approach is difficult to apply to soil systems. In the past, the geochemical modelling of metals in soil systems led to unsatisfying results because of the lack of elaborate models that were able to describe adsorption processes to the soil matrix. Recent improvements in sorption modelling makes it possible to study the complexation of metals with dissolved or soil organic matter and iron oxides on molecular scale, taking into account the effects of pH, competition, ionic strength and background electrolyte on the metal binding. Integration of these sorption models into a multisurface model has successfully explained the speciation of a number of metals in soils under laboratory conditions. However, a geochemical model that combines state-of-the-art sorption modelling, mineral formation and redoxchemistry to calculate the partitioning of several metals simultaneously under natural conditions is, to our knowledge, never published before.

In this study, the chemical behaviour of Cd, Cr, Cu, Ni, Pb, Zn and As in floodplain soils of the Dutch part of the river Meuse and the three branches of the river Rhine is assessed by combining extensive field sampling with advanced geochemical modelling. The aim of this study was threefold:
- to develop tools to study the solid-solution partitioning of heavy metals and As in river floodplain soils for the risk assessment
- to characterise the solid-solution partitioning of heavy metals and As including the temporal and spatial variability and the effect of the redox condition on the partitioning
- to investigate the feasibility to analyse and predict the solid-solution partitioning of heavy metals and As by geochemical modelling

To do this, the following steps are done during this study:
1. Acquisition of field data: the solid-solution partitioning of heavy metals in soil is quantified and the parameters influencing the partitioning are elaborated
2. Monitoring of temporal variability: the variability of the metal partitioning under natural conditions and the parameters influencing the metal partitioning are assessed
3. Development of a geochemical model: the parameters and processes relevant for the modelling of the solid-solution partitioning of heavy metals are identified
4. Comparing modelling results with field data: the usability of geochemical modelling as a tool to predict the partitioning is tested. The heavy metals that can be described by geochemical modelling are evaluated and gaps in understanding or thermodynamic data are identified

In a first case study a method was assessed to sample pore water repeatedly *in situ* with minor disturbance to the soil system. The main focus of this case study was to find out if pore water is a good starting point for the risk assessment and whether geochemical modelling can be used to predict the concentrations of heavy metals in pore water in a soil system under natural conditions. In a semi-field lysimeter, filled with a sandy soil (pH 6) that was treated with increasing Zn concentrations, pore water was collected by Rhizon[®] soil moisture samplers. These samplers consist of a membrane with a length of 10cm and have a pore diameter of <0.2μm. The Rhizons were permanently installed in the lysimeter

at three plant treatments and two Zn concentrations. Pore water was collected periodically *in situ* during the growing season to acquire data on the spatial and temporal variability of Zn and other parameters influencing the Zn speciation. The results showed that pore water pH and Zn concentrations were affected by plant species and precipitation pattern. A geochemical model, fully parameterised by literature data and including speciation, mineral formation and advanced sorption modelling, was able to predict the concentrations of Zn in pore water in the lysimeter soil within ±0.5 log-unit. The calculations showed that the Zn^{2+} activity was mainly influenced by pH, whereas the total amount of Zn in soil had only a minor effect. DOC and Ca concentrations in pore water are necessary input parameters for the model, but the use of generic values is sufficient because the influence of the variability of both parameters was limited.

In a field experiment, we compared two methods to assess the solid-solution partitioning in floodplains: the sampling of pore water *in situ* by using Rhizon samplers and the extraction of soils by 2.5 mM $CaCl_2$, an efficient measure for the "available" metal fraction in soil. To characterise the seasonal variability of the pore water composition and the solid-solution partitioning of heavy metals in contaminated river floodplain soils, we collected pore water *in situ* at 15 and 45 cm depth in spring, summer and autumn at 46 locations within the Dutch part of the Rhine and Meuse river systems. The concentrations of Cd, Cu, Ni and Zn in pore water varied less than one log-unit between the seasons. Ca and Cl were more variable, but the overall influence on the metal concentration is found to be small. Metal concentrations measured in pore water and $CaCl_2$ extractions showed a surprisingly good agreement, and systematic differences between both could be explained by differences in pH and DOC concentration. Both methods are found to have their advantages and a choice for one of the methods depends on question that should be assessed.

A large sampling campaign, comprising 194 soil samples from 133 floodplains sites and covering the entire Dutch part of the river Meuse and the three branches of the river Rhine, was done to characterise the solid-solution partitioning of As, Cd, Cu, Pb and Zn in floodplain soils. We tested if the extractable metal fractions can be predicted by a fully parameterised geochemical model. To generate the necessary input for this model, several characteristic properties of floodplain soils were elaborated. We found a strong correlation between heavy metal contamination and organic matter content, which was almost identical for both river systems. Comparison of model predictions with the fractions extractable by 2.5 mM $CaCl_2$ showed the strengths and weaknesses of the mechanistic geochemical modelling approach. Cu and Cd concentrations were predicted within one log-unit, whereas the modelling of Zn and Pb needs adjustment of some model parameters. The mechanistic geochemical modelling was compared with a statistical approach. The statistical model produced more precise results, with an RMSE of the *log*-transformed data that varied between 0.11 and 0.32 for the different metals. Nevertheless, the careful modelling of speciation and adsorption processes is found to be a useful tool for the investigation and the understanding of metal availability in river floodplain soils. The statistical approach produced better results but is limited with regard to the understanding it provides.

To study the influence of the redoxchemistry on heavy metal partitioning, pore water was monitored *in situ* in a heavily contaminated river floodplain soil. Pore water samples were

collected 12 times during two years with a high spatial resolution in a profile ranging from aerobic to sulphidic redox conditions. The variability of pH, IOC, DOC and Ca was found to be rather small during the year and within the profile. The temporal variability of the metal concentrations was small, too, whereas changes with depth were distinct. As, Cd, Cu, Ni, Pb and Zn were immobilised in the sulphidic layers. The general pattern of the pore water concentrations of Cd, Cu, Zn and As in the profile was predicted well by mechanistic geochemical modelling. Metals strongly bound to organic matter were predicted better than metals mainly present as 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 results also pointed out that the chemical behaviour of Pb is still not understood sufficiently. The results lead to the hypothesis that an yet unidentified mineral or compound, that fix the Pb^{2+} activity to 10^{-13} mol L^{-1}, must be present in the soil to explain our data.

To assess the uptake of heavy metals by plant vegetation typical for a floodplain, we compared the total amounts of Cd, Cu, Ni, Pb and Zn in soil and the fractions extractable by 2.5 mM $CaCl_2$ with the concentrations in 119 plant samples. The plant samples cover 28 different plant species and were collected in 1999, 2000 and 2001 on 36 locations. For a number of plant species, a seasonal effect on the metal uptake was found. Differences in metal uptake were small between the locations. The uptake by plants was significantly correlated to the total amount or the extractable metal fractions for several combinations of plants and metals. Four different groups of plants were defined according to their physiological properties and their uptake behaviour: monocotyls, leguminosae, willows and other dicotyls. Distinguishing this four plant groups provided small enough intra-group variation to enable risk assessment of the metal uptake by a floodplain vegetation.

Overall, we conclude that the concentrations of heavy metals, As and organic matter in floodplain soils shows a very specific pattern. The amounts of heavy metals in soil are strongly correlated with the amount of organic matter and also with other heavy metals. This pattern can serve to identify deviant soil samples, for which the statistical model should be applied with care. Furthermore, the correlation of heavy metals with organic matter is strong enough, that an assessment of the organic matter content of a floodplain soil may be sufficient to serve as a first estimation of the contamination degree.
The Rhizon sampler were useful in studying the relation between 2.5 mM $CaCl_2$ extractions and pore water. The extraction by $CaCl_2$ is a good measure to estimate the concentration of heavy metals in pore water, avoiding the problems of temporal variability. When a link with the metal uptake by plants or biota is made by fitting empirical relations to a dataset, the systematic deviations between both methods are not essential. The Rhizons can be used to study the temporal variety without interference by spatial heterogeneity and when an unbiased measure of the pore water composition is needed.
The statistical model presented in this study is a strong tool to predict the metal fraction extractable by 2.5 mM $CaCl_2$, based on a small number of input parameters usually measured for risk assessment. The geochemical model is less precise and needs the calibration of a few parameters to predict the behaviour of Pb and Zn within one log-unit. However, the geochemical model has a large heuristic value. It can be used for sensitivity

analysis, exploring gaps in understanding and testing hypothetical solutions for it, and it can serve as a guide for designing further experimental studies or sampling campaigns. Still, geochemical modelling delivers quantitative insights that, placed in the right context, can be useful in judging risks. Therefore, both tools have their benefits in risk assessment. Thus the choice for one of the tools presented in this study, i.e. *in situ* pore water extraction, 2.5 mM $CaCl_2$ extractions, geochemical modelling or statistical modelling, depends on the question that has to be answered, the number of samples that can be taken, and the variability of the parameters that are assessed.

Samenvatting

De Rijn en Maas zijn grote Europese rivieren met een stroomgebied van rond de 200.000 km^2. De rivieren stromen door acht Europese landen en de delta's van beide rivieren liggen in Nederland. Om het land dat de rivieren omgeeft tegen overstromingen te beschermen, zijn deze in Nederland omgeven van dijken. Voor een betere afvoer van de grote hoeveelheid water die tussen januari en april het land binnenstroomt, liggen tussen de dijken en de rivieren uiterwaarden. De uiterwaarden van de Maas en de Rijntakken bestrijken een gebied van ongeveer 500 km^2 en kunnen tijdens het grootste gedeelte van het jaar gebruikt worden; vooral als grasland, maar ook als bouwland, voor de winning van klei en grind of als recreatie- en natuurgebied.

Beide rivieren stromen door zeer geïndustrialiseerde landen, en veel van deze industriële activiteiten vinden plaats langs de rivieren, zoals mijnbouw, staalverwerking of chemische industrie. In de laatste eeuw werden enorme hoeveelheden organische verbindingen en zware metalen geloosd op deze rivieren. Met het rivierwater werden grote hoeveelheden met zware metalen verontreinigde sedimenten naar Nederland getransporteerd. Een deel van deze sedimenten is neergeslagen in de uiterwaarden. De sedimentlagen bevatten sinds het begin van het laatste eeuw toenemende concentraties aan zware metalen. De grootste hoeveelheden zijn vermoedelijk in de jaren dertig neergeslagen, en, na een afname tijdens de Tweede Wereldoorlog, is er een tweede piek aan zware metalen in de jaren zestig gemeten. In de laatste dertig jaar zijn er veel maatregelen genomen om de verontreinigingen te verminderen; als gevolg daarvan zijn de hoeveelheden zware metalen, die Nederland binnenstromen via de Rijn, tussen 1972 en 1993 dan ook met meer dan 80% afgenomen.

Voor het beheer van het rivierengebied kan het noodzakelijk zijn om de topologie van de uiterwaarden aan te passen door sedimentenlagen te verplaatsen of te verwijderen. Projecten voor de herinrichting van de uiterwaarden of voor de hoogwaterbescherming hebben dan ook regelmatig te maken met de aanwezigheid van verontreinigde sedimenten. De vraag of de aanwezigheid van verontreinigde sedimenten daadwerkelijk met een concreet dan wel potentieel risico voor de gezondheid of het milieu verbonden is, is moeilijk te beantwoorden. De meest eenvoudige maat om een bodemverontreiniging te kwantificeren, is de totale hoeveelheid aan zware metalen die aanwezig is in een bodem. De wettelijke regelingen in Nederland, maar ook in veel andere landen, zijn hierop gebaseerd. Tegenwoordig wordt echter ervan uitgegaan dat de "beschikbaarheid" van zware metalen een veel betere maat is voor het risico dan het totaalgehalte in de bodem. Aangezien de verwijdering van grote hoeveelheden diffuus verontreinigde sedimenten een grote kostenpost kan zijn, is een beter inzicht in de risico's, die verbonden zijn met de zware metalen verontreiniging van de uiterwaarden, wenselijk.

Een eenvoudige methode om de "beschikbare" fractie van metalen in de grond te meten is de extractie met zogenaamde "zachte" extractiemiddelen, bijvoorbeeld 0,01 M CaCl$_2$. Ondanks de vaak aanwezige sterke verbanden tussen extraheerbare metalen en de opname door planten, is er geen rechtstreeks verband tussen de extraheerbare fractie metalen enerzijds en de speciatie en de samenstelling van het poriewater in de bodem anderzijds. Daarom kunnen verbanden, die de opname met de extraheerbare gehaltes beschrijven, maar beperkt worden toegepast op andere bodemsystemen. Daarnaast levert een extractie geen informatie op over de temporele variabiliteit, die zich onder natuurlijke omstandigheden in

de bodem voordoet. Ook gaat de informatie over de redoxtoestand van de bemonsterde bodemlaag verloren. Extracties kunnen dus goed gecorreleerd zijn met de metaalopname door planten, maar het verband met de samenstelling van het poriewater in natuurlijke bodemsystemen is onduidelijk.

De beschikbaarheid van zware metalen in de bodem kan worden beïnvloed door sorptie aan oppervlaktes, complexatie met andere ionen of de vorming van mineralen. De meest mechanistische manier om de complexe wisselwerkingen van deze processen kwantitatief te beschrijven, is het gebruik van geochemische modellering. Een groot voordeel van de geochemische modellering is dat de resultaten gekoppeld kunnen worden met het "free ion activity model" (FIAM) of het "biotic ligand model" (BLM), twee belangrijke modellen in de risicobeoordeling, die een verband leggen tussen de metaalspeciatie en de opname door of toxische effecten op biota.

Tot nu was deze aanpak moeilijk toe te passen op bodemsystemen. Eén reden hiervoor was het gebrek aan goed onderbouwde modellen om de sorptie processen in de bodemmatrix te beschrijven. Recente ontwikkelingen in de sorptiemodellering maken het echter mogelijk om de complexering van metalen met organische stof of ijzeroxide op moleculaire schaal te modelleren waarbij rekening wordt gehouden met pH-effecten, competitie met andere ionen en het achtergrondelektrolyt. Integratie van deze modellen tot een "multisurface" model heeft in een aantal gevallen het gedrag van metalen in de bodem onder lab-omstandigheden goed kunnen beschrijven. Echter, een geochemisch model dat state-of-the-art sorptiemodellering combineert met de precipitatie van metaalbevattende mineralen en de effecten van de redoxchemie om zo de speciatie van meerdere metalen tegelijk in een natuurlijk bodemsysteem te berekenen, is, voor zover ons bekend, nog nooit eerder gepubliceerd.

In dit proefschrift wordt het chemische gedrag van Cd, Cr, Cu, Ni, Pb, Zn en As in de uiterwaarden van het Nederlands gedeelte van de Maas en de drie Rijntakken bestudeerd door een intensieve veldbemonstering te combineren met geavanceerde geochemische modellering. Dit onderzoek had drie doelen:

- het ontwikkelen van methoden om de partitieverdeling van zware metalen en As tussen de opgeloste en de vaste fase in de bodem te bestuderen ten behoeve van de risicobeoordeling
- het karakteriseren van de partitieverdeling van zware metalen en As in de bodem, de temporele en ruimtelijke variabiliteit hiervan, en de invloed van de redoxtoestand in de bodem op de partitieverdeling
- het onderzoeken van de mogelijkheid, om de partitieverdeling van zware metalen en As te analyseren en te voorspellen met behulp van geochemische modellering

Om dit te bereiken, werden de volgende stappen uitgevoerd:
1. Verzamelen van veldgegevens: de partitieverdeling van zware metalen in de bodem is gemeten en de parameters die invloed hebben op de verdeling zijn geïdentificeerd
2. Monitoren van de temporele variabiliteit: de variabiliteit van de zware metalen in het poriewater onder veldomstandigheden, en de parameters die de metaalconcentraties beïnvloeden, zijn gemeten

3. Ontwikkeling van een geochemisch model: de parameters en processen die relevant zijn voor de berekening van de partitieverdeling van zware metalen zijn geïdentificeerd

4. Vergelijking van veldgegevens met de resultaten van de modelberekeningen: er is geëvalueerd, welke metalen door geochemische modellering beschreven kunnen worden, en de bruikbaarheid van de geochemische modellering als werktuig voor de risicobeoordeling is getest. Hiaten in kennis en ontbrekende thermodynamische data zijn geïdentificeerd

In een eerste verkennend onderzoek werd een methode getest om poriewater *in situ* herhaaldelijk te bemonsteren, zonder het bodemsysteem te verstoren. Het hoofddoel van dit onderzoek was om erachter te komen of poriewater een geschikte maat is voor de risico-beoordeling van zware metalen verontreinigingen in de bodem en of geochemische modellering in staat is om de verdeling van zware metalen over de vaste en opgeloste fase in een bodemsysteem onder natuurlijke omstandigheden te voorspellen. Daarvoor werd in een lysimeter, gevuld met een zandgrond (pH 6) met oplopende Zn-concentraties, poriewater bemonsterd met behulp van Rhizons®. Rhizons met een membraanlengte van 10 cm en een porie diameter van <0,2 µm werden permanent in de lysimeter geïnstalleerd. De Rhizons waren geïnstalleerd bij drie verschillende plantensoorten en twee verschillende concentraties. Poriewater werd tijdens het groeiseizoen regelmatig verzameld om de ruimtelijke en temporele variatie van Zn en andere parameters te kwantificeren, die invloed zouden kunnen hebben op de metaalspeciatie. De resultaten lieten zien, dat de aanwezige plantensoorten en het neerslagpatroon van invloed waren op de Zn concentratie in poriewater. Een geochemisch model, dat volledig geparameteriseerd was met behulp van literatuurgegevens, en dat naast speciatieprocessen ook geavanceerde sorptiemodellen en de mogelijkheid voor de precipitatie van Zn-mineralen bevatte, kon de Zn-concentratie in poriewater binnen een halve log-schaal voorspellen. De berekeningen lieten zien dat de activiteit van het vrije Zn^{2+} species vooral beïnvloed werd door de pH, terwijl het totaalgehalte van Zn in de bodem maar een beperkte invloed had. De concentraties aan opgelost organisch koolstof (DOC) en Ca zijn noodzakelijke invoervariabelen voor het model, maar een generieke waarde voor DOC and Ca was afdoende, omdat de variabiliteit van beide parameters geen relevante invloed op de resultaten had.

In een veldexperiment werden twee methoden vergeleken om de verdeling van zware metalen over de vaste en opgeloste fase te bestuderen: de extractie van poriewater *in situ* met behulp van Rhizons en de extractie van grondmonsters met behulp van 2,5 mM $CaCl_2$, een efficiënte methode voor de bepaling van de "beschikbare" fractie in de bodem. Om seizoensvariaties van de poriewatersamenstelling in de uiterwaarden te karakteriseren, werd in het voorjaar, de zomer en het najaar op 15 cm en 45 cm diepte poriewater bemonsterd op in totaal 46 verschillende locaties in de uiterwaarden van de Maas en de Rijntakken. De poriewaterconcentraties van Cd, Cu, Ni en Zn varieerden minder dan een log-eenheid tussen de seizoenen. De concentraties van Ca en Cl waren variabeler, maar de invloed van deze parameters op de metaalconcentraties was gering. De concentraties aan zware metalen gemeten in het poriewater enerzijds en in de grondextracties met behulp van 2.5 mM $CaCl_2$ anderzijds, waren verrassend vergelijkbaar, en systematische verschillen tussen beide methoden konden worden verklaard door de verschillen in pH en de

concentraties aan DOC. Beide methoden kennen hun eigen voordelen, en de keuze voor één van de twee methoden hangt af van de onderzoeksvraag.

Door middel van een grootschalige bemonsteringscampagne in de uiterwaarden langs de Maas en de drie Rijntakken, is het gedrag van As, Cd, Cu, Pb end Zn gekarakteriseerd. In totaal 194 bodemmonsters afkomstig van 133 verschillende locaties werden geëxtraheerd met 2,5 mM CaCl$_2$ en er werd getest of de extraheerbare fracties aan zware metalen met behulp van een volledig geparameteriseerd geochemisch model voorspeld kunnen worden. Een aantal karakteristieken van uiterwaardgronden konden uit de gegevensset afgeleid worden. Sterke verbanden zijn gevonden tussen de graad van verontreiniging met zware metalen en de hoeveelheid organisch stof in de bodem. Deze verbanden waren zeer vergelijkbaar voor beide riviersystemen. Een vergelijking van extraheerbare hoeveelheden zware metalen met de hoeveelheid berekend door het geochemische model laat de sterke en zwakke punten van deze mechanistische aanpak zien. De concentraties van Cu en Cd konden worden voorspeld binnen een log-eenheid, terwijl voor de modellering van Zn en Pb een aanpassing van enkele modelparameters noodzakelijk was. Een statistisch model dat op de gegevensset gefit werd, was nauwkeuriger dan het geochemisch model: de RMSE (root mean square error) van de *log*-getransformeerde gegevens lag tussen de 0,11 en 0,32 voor de verschillende metalen. Het zorgvuldig modelleren van de speciatie- en adsorptieprocessen was een nuttig methode voor de analyse en het voorspellen van de partitieverdeling van zware metalen in de bodem. Het statistische model leverde preciezere resultaten op, maar het kon desondanks weinig toevoegen aan het begrip van de achterliggende processen.

Om de invloed van redoxprocessen op de verdeling van zware metalen over de vaste en opgeloste fase te bestuderen, werd poriewater herhaaldelijk met een hoge ruimtelijke resolutie bemonsterd in een bodemprofiel dat van aërobe tot sulfidische omstandigheden strekte. Twaalf keer binnen twee jaar werd poriewater bemonsterd. De temporele en ruimtelijke variabiliteit van de pH en de concentraties aan bicarbonaten, DOC en Ca was klein binnen het profiel. De temporele variatie van de metaalconcentraties was ook klein, terwijl daarentegen duidelijke verschillen in de diepte gemeten werden. As, Cd, Cu, Ni, Pb en Zn werden in de sulfidische zone geïmmobiliseerd. Het concentratieprofiel van Cd, Cu, Zn en As in het poriewater kon in grote lijnen goed voorspeld worden door het geochemische model. Metalen die sterk gecomplexeerd waren met organische stof worden daarbij beter voorspeld dan de metalen die in minerale vorm aanwezig zijn. Meer gedetailleerde informatie over de colloïdale fractie van Fe en Mn in poriewater zouden de resultaten van de geochemische berekeningen kunnen verbeteren. De resultaten lieten bovendien zien dat de speciatieverdeling van Pb in de bodem niet voldoende is begrepen. Uit de resultaten kan de hypothese afgeleid worden, dat de aanwezigheid van een Pb-mineraal of een andere component vereist is, die de activiteit van Pb^{2+} tot een niveau van 10^{-13} mol L^{-1} beperkt, om de gevonden resultaten te verklaren.

Om de opname van zware metalen door een vegetatie typisch voor de uiterwaarden te onderzoeken, werden de totaalgehaltes van Cd, Cu, Ni, Pb en Zn in de bodem en de fracties extraheerbaar met 2,5 mM CaCl$_2$ vergeleken met de opname van deze metalen door

planten. De 119 bemonsterde planten omvatten 28 verschillende soorten en werden in 1999, 2000 en 2001 op 36 verschillende locaties verzameld. Voor een aantal planten werden seizoensafhankelijke verschillen in opname gevonden. De verschillen in opname tussen de locaties waren echter gering. Voor een aantal plant-metaal combinaties werd een significant verband met het totaalgehalte of de extraheerbare fractie gevonden. De planten werden aan de hand van fysiologische eigenschappen en hun opnamegedrag verdeeld in vier verschillende groepen: monocotylen, leguminosae, wilgen en andere dicotylen. Het verschil in opname binnen deze groepen was voldoende klein, zodat deze groepsindeling gebruikt kan worden voor de risicobeoordeling van de zware metaalopname door uiterwaardvegetaties.

Samenvattend kan worden gesteld dat de concentraties van zware metalen en As in de uiterwaarden een zeer specifiek patroon vertonen. Er bestaat een sterk verband met het gehalte aan organische stof, maar ook tussen de zware metalen onderling. Deze verbanden kunnen gebruikt worden om afwijkende bodemmonsters te identificeren, waarop het statistische model alleen met bedachtzaamheid toe te passen is. Het verband tussen de zware metalen en het organische stofgehalte is zo sterk, dat het bepalen van het organische stofgehalte van een uiterwaardgrond voldoende is om een eerste schatting van de graad van verontreiniging te maken.

De bemonstering van poriewater met behulp van de Rhizons was nuttig om het verband tussen de extractie met 2,5 mM $CaCl_2$ en de samenstelling van het poriewater zelf op te helderen. De $CaCl_2$-extractie is een goede methode om de verdeling van zware metalen over de vaste en de opgeloste fase te schatten. Bovendien vermijdt deze methode problemen als gevolg van de temporele variatie van de poriewater-samenstelling. Wanneer een verband met de metaalopname door planten of biota door middel van het fitten van een overdrachtsfunctie afgeleid wordt, zullen de kleine systematische verschillen tussen beide methoden geen belemmering zijn. De Rhizons zijn bij uitstek geschikt, wanneer de temporele variabiliteit van belang is of een onverstoorde waarneming van de samenstelling van poriewater gewenst is.

Het statistische model dat in dit proefschrift gepresenteerd werd, is een goede methode om de extraheerbare fracties aan zware metalen te voorspellen met behulp van een klein aantal standaard gemeten parameters. Het geochemisch model is minder precies en heeft een calibratie van een klein aantal parameters nodig, om de extraheerbare fracties van Pb en Zn binnen één log-eenheid te kunnen voorspellen. Desondanks heeft het geochemisch model een grote heuristieke waarde: het kan gebruikt worden voor gevoeligheidanalyses, het is in staat om kennishiaten aan te tonen en om mogelijke oplossingen voor deze te testen en het kan gebruikt worden als leidraad voor verder onderzoek of veldbemonsteringen. Daarnaast levert de geochemische modellering ook kwantitatieve resultaten op, die - binnen de beperkingen van de methode - nuttig kunnen zijn voor de risicobeoordeling. Dus, beide modellen hebben hun nut voor de risicobeoordeling.

De keuze voor één van de methoden of modellen die gebruikt zijn in dit proefschrift, namelijk de *in situ* bemonstering van poriewater, de extracties met behulp van 2,5 mM $CaCl_2$, de geochemische modellering of de statistische modellering, hangt af van de vraagstelling, het aantal monsters dat genomen kan worden, en de variabiliteit van de parameters die gemeten worden.

Zusammenfassung

Der Rhein und die Maas sind große europäische Flüsse mit einem Einzugsgebiet von ungefähr 200.000 km². Beide Flüsse haben ihr Deltagebiet in den Niederlanden, wo sie zum Schutze gegen Überschwemmungen der umliegenden Gebiete in weiten Teilen eingedeicht sind. Um die Hochwasserspitzen bewältigen zu können, die zwischen Januar und April auftreten, sind die Flüsse von Auen umgeben. Die Flußauen von Rhein und Maas in den Niederlanden umfassen ein Gebiet von etwa 500 km² und werden den größten Teil des Jahres anderweitig genutzt, zum größten Teil als Weideland, aber auch als Ackerland, zum Abbau von Ton und Kies, als Erholungsgebiet oder als Naturgebiet.

Beide Flüsse passieren dicht besiedelte und hoch industrialisierte Gebiete mit vielen industriellen Aktivitäten, z.B. dem Kohlebergbau, der Stahlverhüttung oder der chemischen Industrie. Während des letzten Jahrhunderts wurden enorme Mengen an organischen Verbindungen und Schwermetallen in die Flüsse eingeleitet. Mit dem Flußwasser gelangten große Mengen an schwermetallbelasteten Schwebstoffen in die Niederlande, und ein Teil dieser Schwebstoffe sedimentierte in den Flußauen. In den Bodenprofilen dieser Flußauen wurden seit Anfang des letzten Jahrhunderts zunehmende Konzentrationen an Schwermetallen gemessen. Die größten Konzentrationen von Cu, Zn und Pb sind vermutlich in den 30er Jahren abgelagert, und nach einer Abnahme der Konzentrationen während des Zweiten Weltkrieges läßt sich ein zweiter Scheitelwert in den Sechzigern beobachten. In den letzten drei Jahrzehnten wurden viele Maßnahmen ergriffen, um die Emissionen an Schwermetallen zu reduzieren. Zwischen 1972 und 1993 haben sich die Mengen an Schwermetallen, die über den Rhein in die Niederlande transportiert werden, um mehr als 80% vermindert.

Aus wasserwirtschaftlichen Gründen ist es oft notwendig, um die Topologie der Flußauen anzupassen. Dieses bedeutet oft eine Entnahme oder Umlagerung von Sedimentschichten. Bei der Renaturierung von Flußauen oder bei Maßnahmen zum Schutz vor Überschwemmungen hat man es regelmäßig mit durch Schwermetalle belasteten Sedimenten zu tun, wodurch die Kosten solcher Projekte erheblich verteuert werden. Die Frage, ob die Schwermetallbelastung auch tatsächlich zu einer konkreten oder potentiellen Gefährdung für Mensch und Umwelt führt, ist sehr komplex. Angesicht der großen Kosten die mit der Deponierung von Sedimenten verbunden sind, gibt es daher einen Bedarf, um die Risiken von schwermetallbelasteten Böden besser zu verstehen.

Das einfachste Maß zur Quantifizierung der Bodenbelastung ist der Gehalt an Schwermetallen im Boden. Die Gesetzgebungen zum Bodenschutz in vielen Ländern basieren auf diesen Gehalten, obwohl man mittlerweile davon ausgeht, daß bei der Risikobeurteilung die "Verfügbarkeit" von Schwermetallen für Pflanzen oder Organismen ein besseres Maß ist als der Gehalt im Boden. Eine einfache Methode um den "verfügbaren" Anteil an Schwermetallen im Boden zu messen, ist die Extraktion von Bodenproben mit einem "weichen" Extraktionsmittel, zum Beispiel 0,01M $CaCl_2$. Obwohl oft ein starker Zusammenhang zwischen den extrahierbaren Metallen und der Aufnahme in Pflanzen besteht, können die extrahierbaren Metalle nicht direkt in einem kausalen Zusammenhang gebracht werden mit der chemischen Zusammensetzung des Bodens. Darum können solche empirische abgeleiteten Zusammenhänge zwischen Aufnahme und extrahierbaren Metallen nur bedingt übertragen werden auf andere Bodensysteme.

Außerdem geben Extraktionen keinerlei Informationen über die zeitliche Variabilität der Zusammensetzung des Bodenwassers, die unter natürlichen Bedingungen im Boden zu erwarten ist, oder den Redoxpotentialen in den beprobten Bodenlagen. Extrahierbare Metallkonzentrationen sind also oft zwar gut korreliert mit der Aufnahme in Pflanzen, der Zusammenhang mit der chemischen Zusammensetzung des Bodens oder des Bodenwassers ist allerdings undeutlich.

Eine Methode, um den Einfluß der komplexen Wechselwirkungen von Speziierung, Adsorptionsprozessen und der Bildung von Mineralen auf die Konzentrationen von Metallen im Bodenwasser zu quantifizieren, ist die geochemische Modellierung. Die Resultate der geochemischen Modellierung können überdies gekoppelt werden mit dem "free ion activity model" (FIAM) oder dem "biotic ligand model" (BLM), zwei Modellen zur Berechnung der Schwermetallaufnahme oder der toxischen Effekte aus der Metallspeziierung in der Lösungsphase.

Die geochemische Modellierung ist in der Vergangenheit nur wenig erfolgreich auf Bodensysteme angewandt worden, da nur sehr einfache Modelle zur Beschreibung von Adsorptionsprozessen an der Bodenmatrix zur Verfügung standen. Neuerliche Fortschritte auf diesem Gebiet ermöglichen die Beschreibung der Komplexbildung von Metallen mit organischen Stoffen oder Eisenoxiden auf molekularem Niveau, inklusive pH-Effekten, der Verdrängung durch andere Ionen und den Elektrolytkonzentrationen in der löslichen Phase. Die Integration dieser Adsorptionsmodelle zu einem "Multisurface Modell" konnte die Speziierung einer Anzahl von Elementen unter Laborbedingungen erfolgreich erklären. Wie dem auch sei, ein geochemisches Model, das state-of-the-art Adsorptionsmodellierung, die Bildung schwermetallhaltiger Minerale und redoxchemische Prozesse verknüpft, um in natürlichen Bodensystemen die Speziierung von mehreren Metallen gleichzeitig zu berechnen, ist soweit uns bekannt ist noch nie zuvor publiziert worden

In dieser Studie wurde das chemische Verhalten von Cd, Cr, Cu, Ni, Pb, Zn und As in den niederländischen Flussauen des Rheins und der Maas untersucht indem extensive Feldprobennahme kombiniert wurde mit avancierter geochemischer Modellierung.

Diese Studie hatte drei Ziele:
- die Entwicklung von Methoden um das Lösungsverhalten von Schwermetallen und As in Flußauen zu studieren zum Zwecke der Risikobeurteilung
- das Lösungsverhalten von Schwermetallen und As im Boden zu charakterisieren in Abhängigkeit der zeitlichen und räumlichen Variabilität und des Einflusses der Redoxbedingungen im Boden
- die Möglichkeit zu untersuchen, um das Lösungsverhalten von Schwermetallen in den Flußauen mit Hilfe von geochemischer Modellierung zu analysieren und vorherzusagen

Dazu wurden die folgenden Schritte ausgeführt:
1. Sammeln von Felddaten: das Lösungsverhalten der Schwermetalle im Boden wurde quantifiziert und die Parameter, die es beeinflussen, wurden erkundet
2. Überwachen der zeitlichen Variabilität: die Variabilität des Lösungsverhalten unter natürlichen Bedingungen wurde ermittelt
3. Entwicklung eines geochemischen Modells: die relevanten Parameter und Prozesse zur Modellierung des Lösungsverhaltens von Schwermetallen wurden identifiziert

4. Vergleichen von Felddaten und Modellberechnungen: der Nutzen des Modells für die Vorhersage des Lösungsverhalten von Schwermetallen wurde geprüft. Es wurde ausgewertet, von welchen Metallen sich das Lösungsverhalten mit Hilfe von geochemischer Modellierung beschreiben läßt und Wissenslücken oder fehlende thermodynamische Parameter wurden identifiziert

In einer ersten Fallstudie wurde eine Methode getestet, um Bodenwasser *in situ* wiederholt und mit geringst möglicher Störung des Bodensystems zu beproben. Das Ziel dieser Fallstudie war es, um herauszufinden, ob extrahiertes Bodenwasser eine geeignete Entität für die Risikoanalyse ist und ob es möglich ist, mit Hilfe von geochemischer Modellierung das Lösungsverhalten von Schwermetallen in einem Bodensystem unter natürlichen Bedingungen vorherzusagen. Dazu wurde in einem Lysimeter, der mit einem mit unterschiedlichen Konzentrationen von Zn behandelten Sandboden (pH 6) gefüllt war, unter feldnahen Bedingungen mit Hilfe von Rhizons® Bodenwasser extrahiert. Rhizons mit 10 cm Membranlänge und einem Porendurchmesser von <0,2 µm wurden permanent im Lysimeter bei drei verschieden Bepflanzungen und zwei Zn-Konzentrationen eingebaut. Bodenwasser wurde regelmäßig während der Wachstumsperiode der Pflanzen extrahiert, um Daten über die zeitliche und räumliche Variabilität der Zn-Konzentrationen und anderer Parameter, die die Speziierung von Zn beeinflussen, zu versammeln. Der pH im Bodenwasser und die Zn-Konzentrationen wurden beeinflußt durch die Pflanzensorte und Niederschlagsmengen. Ein geochemisches Modell, welches neben der Speziierung auch die Existenz von Zn-Mineralen und avancierte Adsorptionsmodelle berechnen konnte, wurde durch Daten aus der Literatur vollständig parameterisiert. Dieses Model konnte die Zn-Konzentrationen im Bodenwasser mit der Genauigkeit einer halben log-Einheit vorhersagen. Die Berechnungen zeigten außerdem auf, daß die Aktivität des Zn^{2+} Kations hauptsächlich durch den pH beeinflußt wurde, während der Gehalt an Zn im Boden wenig Einfluß auf die Aktivität oder das Lösungsverhalten von Zn hatte. Die Konzentrationen an gelösten organischem Kohlenstoff (DOC) und Ca im Bodenwasser sind notwendige Parameter für die Modellberechnungen, aber ein generischer Mittelwert war ausreichend.

In einem Feldversuch wurden zwei Methoden zur Bestimmung des Lösungsverhalten von Schwermetallen in den Auenböden miteinander verglichen: Zum einen die *in situ* Probennahme von Bodenwasser mit Hilfe von Rhizons und zum anderen die Extraktion von Bodenproben mit 2,5 mM $CaCl_2$. Die $CaCl_2$-Extraktion ist eine effiziente Methode, um die "verfügbare" Fraktion von Metallen im Boden zu ermitteln. Um die zeitliche Variabilität der Bodenwasserzusammensetzung und des Lösungsverhalten der Metalle zu untersuchen, wurde auf 46 Probennahmestellen in den Flußauen von Rhein und Maas jeweils im Frühling, Sommer und Herbst Bodenwasser *in situ* in 15 und 45 cm Tiefe extrahiert. Die Konzentrationen von Cd, Cu, Ni und Zn im Bodenwasser variierten dabei um weniger als einen Faktor 10. Die Konzentrationen von Ca und Cl waren variabler, aber ihr Einfluß auf die Metallkonzentrationen im Bodenwasser war gering. Die Metall-konzentrationen im Bodenwasser und in den $CaCl_2$-Extraktionen kamen überraschend gut überein; systematische Unterschiede zwischen beiden konnten zurückgeführt werden auf unterschiedliche pH-Werte und unterschiedliche Konzentrationen an DOC. Beide Methoden zur Ermittlung des Lösungsverhalten haben ihre Vorteile, und die Wahl für eine der beiden Methoden hängt von der genauen Fragestellung ab.

Mit einer großflächigen Feldprobennahme, die das Gebiet der niederländischen Rhein- und Maasauen vollständig umfaßte, wurden das Lösungsverhalten von As, Cd, Cu, Pb und Zn im Boden charakterisiert. 194 Bodenproben wurden von 133 verschieden Probennahme-stellen gesammelt und mit 2,5 mM $CaCl_2$ extrahiert. Die Resultate wurden verglichen mit den Vorhersagen eines vollständig aus Literaturdaten parameterisierten geochemischen Modells. Eine Anzahl von charakteristischen Eigenschaften der Böden in den Flußauen konnten aus dem Datenbestand abgeleitet werden. So wurden starke Korrelationen zwischen der Schwermetallbelastung und dem Gehalt an organischem Substanzen gefunden, die obendrein sehr vergleichbar waren für beide Flüsse. Ein Vergleich der mit 2,5 mM $CaCl_2$ extrahierbaren Metallfraktionen mit den Modellberechnungen ließ die Stärken und Schwächen des mechanistischen Modells sichtbar werden. Die Konzentratio-nen von Cu und Cd konnten innerhalb einer log-Einheit vorhergesagt werden, während für die Modellierung von Zn und Pb jeweils ein Modellparameter angepasst werden mußte. Das geochemische Modell wurde verglichen mit einem statistischen Ansatz. Mit dem statistischen Modell sind präzisere Vorhersagen möglich; es konnte dabei ein RMSE (root mean square error) der *log*-transformierten Daten zwischen 0,11 und 0,32 für die verschiedenen Metalle erreicht werden. Das sorgfältige Modellieren von Speziations- und Adsorptionsprozessen wird als ein nützliches Hilfsmittel für die Untersuchung und dem Verständnis der Metallverfügbarkeit in den Flussauenböden angesehen. Die Statistische Methode gibt zwar eine genauere Vorhersage, konnte aber wenig zum Verständnis der Metallverfügbarkeit beitragen.

Um den Einfluß von Redoxprozessen auf das Lösungsverhalten der Schwermetalle zu untersuchen, wurde in einer sehr stark mit Schwermetallen belasteten Flußaue die Zusammensetzung des Bodenwassers *in situ* überwacht. Dabei wurden innerhalb zweier Jahre 12 Mal in einem Profil, das von aeroben bis zu sulfidischen Bodenlagen reichte, mit einer hohen räumlichen Auflösung Bodenwasserproben genommen. Die Variabilität des pH-Wertes und der Konzentrationen an Bikarbonaten, DOC und Ca war relativ klein, sowohl in der Zeit als auch innerhalb des Bodenprofils. Die zeitliche Variabilität der Schwermetallkonzentrationen war ebenfalls klein, aber die Konzentrationen im Bodenprofil nahmen deutlich ab. In den sulfidischen Bodenlagen waren As, Cd, Cu, Ni, Pb und Zn weitgehend immobilisiert. Das prinzipielle Lösungsverhaltens von Cd, Cu, Zn und As im Profil konnte durch das mechanistische geochemische Modell gut vorhergesagt worden. Metalle, die stark komplexiert waren mit organischem Substanzen, waren dabei besser vorhersagbar als Metalle, die vor allem in mineraler Form im Boden vorkamen. Detailliertere Daten über die Präsenz von kolloidalem Fe und Mn im Bodenwasser könnte die Modellberechnungen verbessern. Die Resultate zeigten auch auf, daß das chemische Verhalten von Pb nicht gut erklärt werden kann mit dem jetzigen Wissensstand. Die Resultate legen die Hypothese nahe, daß ein Bleimineral oder ein anderes Bleikomplex existieren muß, das in der Lage ist, die Aktivität des Pb^{2+} Kations auf 10^{-13} mol L^{-1} zu begrenzen.

Um die Aufnahme von Schwermetallen durch Pflanzenvegetationen in den Flussauen zu bestimmen, wurden die Gehalte von Cd, Cu, Ni, Pb und Zn im Boden und die mit 2,5 mM $CaCl_2$ extrahierbaren Konzentrationen verglichen mit den Konzentrationen in 119 Pflanzenproben. Die beprobten Pflanzen umfaßten 28 verschiedene Spezies und wurden in den Jahren 1999, 2000 und 2001 an 36 verschiedenen Stellen gesammelt. Bei einigen

Pflanzen wurden signifikante jahreszeitliche Unterschiede gefunden. Die Unterschiede in der Schwermetallaufnahme durch die Pflanzen waren relativ klein zwischen den verschiedene Probennahmestellen. Für eine Zahl von Metall-Pflanzen-Kombinationen war die Aufnahme signifikant korreliert mit dem Gehalt im Boden oder den extrahierbaren Fraktionen. Die Pflanzen konnten aufgrund ihrer Physiologie und der Metallaufnahme in vier verschiedene Gruppen eingeteilt werden: Monokotylen, Leguminosae, Weiden und andere Dikotylen. Die Unterschiede in der Metallaufnahme innerhalb dieser Gruppen war klein genug, daß diese Vereinfachung sinnvoll ist bei der Risikobeurteilung der Schwermetallaufnahme in den Flußauen.

Alles in allem zeigt diese Studie auf, daß die Schwermetallbelastung in den Flußauen von Rhein und Maas ein sehr spezifisches Muster aufweist. Die Gehalte der Schwermetalle im Boden sind mit den Gehalten an organischem Substanzen, aber auch untereinander stark korreliert. Mit Hilfe dieses Musters können abweichende Bodenproben identifiziert werden, bei denen das statistische Model nur bedingt herangezogen werden sollte. Der Zusammenhang zwischen organischen Substanzen und der Schwermetallbelastung ist so prägnant, daß die Bestimmung des Gehaltes an organischen Substanzen genügen sollte, um eine erste Abschätzung der Bodenbelastung in den Flussauen machen zu können.

Die Beprobung von Bodenwasser mit Hilfe der Rhizons waren sehr nützlich um die Beziehung zwischen Bodenwasser und den Extraktionen mit 2,5 mM $CaCl_2$ zu untersuchen. Die $CaCl_2$-Extraktionen erwiesen sich dabei als ein gutes Maß für das Lösungsverhalten von Schwermetallen im Boden, unter Umgehung der Probleme der zeitlichen Variabilität. Wenn die Schwermetallaufnahme von Pflanzen oder Organismen mit empirischen Gleichungen an das Lösungsverhalten relatiert wird, spielen die kleinen systematischen Unterschiede gegenüber dem Bodenwasser keine entscheidende Rolle. Rhizons sollten dann benutzt werden, wenn die zeitliche Heterogenität eine Rolle spielt oder unverfälschte Messungen der chemischen Zusammensetzung des Bodenwassers nötig sind.

Das statistische Modell, das in dieser Studie präsentiert wurde, ist sehr gut geeignet, um die mit 2,5 mM $CaCl_2$ extrahierbaren Metalle vorherzusagen. Das Modell basiert dabei auf einer kleinen Anzahl an Parametern, die üblicherweise bei Bodenuntersuchungen bestimmt werden. Das geochemische Modell ist weniger präzise als das statistische, und um das Lösungsverhalten von Pb und Zn innerhalb einer log-Einheit vorherzusagen, ist die Kalibrierung einiger Parameter notwendig. Trotzdem hat das geochemische Modell einen großen heuristischen Wert: es kann eingesetzt werden für Sensitivitätsanalysen, um Lücken im Wissen zu aufzuspüren und mögliche Lösungsansätze zu testen, und es kann hilfreich sein, um zukünftige experimentelle Studien zu entwerfen oder Probennahmen zu planen. Daneben liefert es quantitative Resultate, die, im Rahmen der Methode, nützlich für die Risikobeurteilung der Bodenbelastungen sein können. Deshalb werden beide Modelle als sehr nutzbringend für die Risikobeurteilung erachtet.

Die Wahl für eine in dieser Studie besprochen Methoden, nämlich der *in situ* Beprobung von Bodenwasser, der Extraktionen mit 2,5 mM $CaCl_2$, der geochemischen Modellierung und der statistischen Modellierung ist abhängig von der Fragestellung, der Anzahl der Proben die genommen werden können und der Variabilität der zu untersuchenden Parametern.

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Nawoord

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Thomas

Curriculum vitae

Thomas Joseph Schröder was born on July 21, 1966 in Oldenburg, Lower Saxony, Germany. In 1986 he got his school certificate (Abitur) from the Liebfrauenschule in Oldenburg. From 1986 to 1988 he accomplished the alternative national service at the Städtische Kliniken hospital in Oldenburg. In 1988 he started the study of Energy and Process Engineering at the Technical University in Berlin. From September 1991 on he studied Environmental Sciences at the Wageningen University. He wrote an MSc thesis in Soil Science about the immobilisation of Cd and Zn by manganese oxides and a second one in Microbiology on the reductive dehalogenation of chlorinated ethenes by methanogenic sludge. During his practical period he worked at the ITÖ of the ETH Zurich on the phytoremediation. He obtained his MSc degree "with distinction" in February 1998. In October 1998 he started his PhD study on the availability of heavy metals in floodplain soils at the department of Soil Quality (formerly Soil Science and Plant Nutrition) at the Wageningen University. In 2004 he was employed at the Soil Quality department as researcher and developed a geochemical module for the risk assessment of heavy metals in floodplain soils for the RIZA, Lelystad. He completed his research in October 2005 with the defence of this thesis.

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