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Effects of Changed Soil Conditions on the Mobility of Trace Metals in Moderately Contaminated Urban Soils

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Abstract Changes in the soil chemical environment can be expected to increase the leaching of trace metals bound in soils. In this study the mobility of trace metals was monitored in a column experiment for two contaminated urban soils. Four different treatments were used (i.e. rain, acid rain, salt and bark). Leachates were analysed for pH, dissolved organic carbon (DOC) and for seven trace metals (cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn)). The salt treatment produced the lowest pH values (between 5 and 6) in the effluent whereas the DOC concentration was largest in the bark treatment (40–140 mg L^{-1}) and smallest in the salt and acid treatments (7–40 mg L^{-1}). Cadmium, Ni and Zn were mainly mobilised in the salt treatment, whereas the bark treatments produced the highest concentrations of Cu and Pb. The concentrations of Cu, Cr, and Hg were strongly correlated with DOC (r^2=0.90, 0.91 and 0.96, respectively). A multi-surface geochemical model (SHM-DLM) produced values for metal dissolution that were usually of the correct magnitude. For Pb, however, the model was not successful indicating that the retention of this metal was stronger than assumed in the model. For all metals, the SHM-DLM model predicted that soil organic matter was the most important sorbent, although for Pb and Cr(III) ferrihydrite was also important and accounted for between 15 and 50% of the binding. The results confirm the central role of DOC for the mobilization of Cu, Cr, Hg and Pb in contaminated soils.

Keywords chemical modelling · contaminated soil · dissolved organic carbon · Fe oxides · leaching · sequential extractions · Stockholm humic model · trace metals · urban soil

1 Introduction

Investigations of soils in city areas all over the world have reported enhanced concentrations of trace metals in general (e.g. Kelly et al., 1996; Paterson et al., 1996; Chen et al., 1997; Pichtel et al., 1997; Peltola & Åström, 2003) and of copper (Cu), lead (Pb) and zinc (Zn) in particular (de Miguel et al., 1997; Hursthouse et al., 2004; Madrid et al., 2004). A survey of soils in the city of Stockholm showed the same results concerning Cu, Pb and Zn but also that the most enhanced metal in the city centre soils compared to rural (arable) soils in the region and park soils outside

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the city centre was mercury (Hg) (Linde et al., 2001). The quantity (calculated as g m^{-2}) of Hg in the upper 30 cm soil layer in the city centre was six times that in park soils outside the city centre, whereas the quantity of Pb was three times and Cu and Zn 1.5–2 times the park soil value.

Deep groundwater in Stockholm is also known to contain higher concentrations of metals than groundwater in pristine forest areas (Aastrup & Thunholm, 2001), in particular of Hg and Cu. In an earlier paper, we showed that these elevated metal concentrations may be due to the occurrence of contaminated soils in the urban area (Öborn & Linde, 2001). Metal leaching was observed even when soils were only exposed to mild leaching with artificial rainwater of ambient pH and ionic strength. Thus, if there are changes in soil conditions that affect metal solubility, a direct influence on the quality of the deep groundwater, such as that observed in Stockholm, can be expected.

Compared to soils in other ecosystems, urban soils are more exposed to human activities. For obvious reasons, building and reconstruction activities almost always make great changes to soil structure and groundwater level (Burghardt, 2002), factors that greatly influence redox conditions and thereby pH and solubility of metals. Oxidation of sulphidic soil material followed by an increased leaching of metals from the soil is one example of this (Sohlenius & Öborn, 2004). Another less dramatic human activity is the application of high amounts of organic material (e.g. bark, compost or peat) to topsoil for soil improvement or as cover to reduce weeds in plantations of bushes and flowers in public gardens and along roads. The organic soil amendments can release soluble organic acids, which can increase the mobility of Pb, Cu and Hg (Berggren, 1990; Ross, 1994; Wu et al., 2002). A third example is application of de-icing salt to roads during winter, which gives rise to high concentrations of Na^+ and Cl^- in soils and groundwater. In an investigation of the groundwater quality in Stockholm, enhanced Cl^- concentrations (>100 mg L^{-1}; 3 mM) were frequently measured, and the largest value was 729 mg L^{-1} (20 mM) (Miljöförvaltningen, 1997). Increased concentrations of soluble salts may displace weakly sorbed metals such as cadmium (Cd) and Zn from soil sorption sites, which may increase the dissolution of these metals. Increased susceptibility to leaching of trace metals on exposure to high NaCl concentrations has been reported by several authors (e.g. Norrström & Jacks, 1998; Bäckström et al., 2004).

Because of stricter legislation on soil contamination, there has been an increasing demand for methods for risk assessment of contaminated soils. Some authors (Anderson et al., 2000; Pueyo et al., 2003) have suggested sequential extractions to obtain data on the potential mobility of trace metals in soils. However in Sweden, as well as in the rest of Europe, leaching tests are increasingly used in risk assessments (Dijkstra et al., 2005; Elert et al., 2006). The tests that are being used were originally set up for waste characterization. The reasons for using them for soils are twofold; (1) if the material is analysed as a waste product, the information could be used if a decision is made to dump the soil material; and (2) there is no standardized leaching test procedure for soil materials. The leaching solution in the commonly used tests is either distilled water or, in the case of the pH-dependence tests (e. g. CEN/TS 14429), distilled water with HNO_3 or NaOH added (Swedish Standards Institute, 2005). Thus, pH is the only chemical parameter that is altered in the tests.

This paper presents the results from a study on the effect of different soil conditions on trace metal mobility. The aim of the study was to describe and quantify how a realistic but not extreme change in soil chemical parameters or leaching solution altered the leaching behaviour of trace metals in typical contaminated urban soils. In the experiment, two moderately contaminated urban soils were leached with four different solutions, i.e. artificial rainwater, bark leachate, salt (NaCl) solution and acid rainwater (dilute H_2SO_4). In addition to dissolved metals, dissolved organic carbon (DOC), electric conductivity (EC) and pH were monitored in the outcoming solutions (leachates). Furthermore, we investigated whether a multi-surface geochemical model could be used to predict dissolved metals in the leachates. The Stockholm Humic Model (SHM) was used (Gustafsson, 2001; Gustafsson & Berggren Kleja, 2005) in combination with the Diffuse Layer Model (DLM) (Dzombak & Morel, 1990) to simulate the binding of metals to organic matter and ferrihydrite (“hydrous ferric oxide”), respectively. The model was applied without optimization for the studied soils. Finally, the results are discussed in relation to sequential extractions, requirements for leaching tests and how they should be used for site-specific risk assessment of contaminated land.

2 Materials and Methods

2.1 Soils

The characteristics of the two studied soils, soil C and soil W, are shown in Table 1, together with mean values for the Stockholm region and for allowable metal concentrations in soils according to Swedish guideline values (Naturvårdsverket, 1997). The soils have previously been described by Öborn and Linde (2001). They had elevated concentrations of trace metals compared to park soils outside the city centre and the rural (arable) soils in the region (Linde et al., 2001).

Soil C was a moderately contaminated sandy loam from a well-drained small green area with thin grass and horse chestnut trees (*Aesculus hippocastanum* L.) located close to a busy road in the city centre of Stockholm. The metal concentrations represented the average for city centre soils which compared to the rural soils were 16 and 8 times higher in Hg and Pb, threefold higher in Cu and Zn and twice as high in Cd (Table 1). The metal contamination was presumed to originate from diffuse emissions from urban activities, i.e. traffic, heating, etc.

Soil W was a contaminated acid clay, sampled at a grass-covered, poorly drained area of the Baltic shoreline that is now used for storage of small boats during winter. Previously there were small-scale industries at the site, which are the most probable contamination source. The acid characteristics of the soil are due to oxidation of sulphides in the soil. The Hg concentration was about 70 times higher than in arable soils (Table 1). The Pb and Cu levels were elevated 20-and 10-fold higher, respectively, whereas Zn was threefold higher.

For the leaching experiment, about 10 L of soil was sampled from 5–20 cm depth at the two sites. The soil was homogenised, sieved fresh at 4 mm and stored for about a week in a cold room (2°C) before the start of the experiment.

2.2 Experimental Design

Four different treatments were included in the study. In all treatments, artificial rainwater was added to the

Table 1 Characterisation of the two soils (Soil C and Soil W) used in this study

	Clay (%)	pH_{H2O}	EC (µS cm^{-1})	Tot – C (%)	Tot – N (%)	Tot – S (%)	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Hg (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})	Fe_o[a] (g kg^{-1})	Al_o (g kg^{-1})	Si_o (g kg^{-1})
Soil C	17	6.1	214	3.4	0.2	0.03	0.58	24.8	56	0.62	10.6	134	260	3.7	1.2	0.4
Soil W	n.d.	4.8	429	17	1.4	0.4	0.25	85.3	200	2.73	19.5	361	229	13.2	3.4	0.3
Stockholm[b]																
All soils	29	6.9	228	2.8	–	–	0.27	33	55	0.41	15.8	79	142	–	–	–
City centre	26	6.7	226	3.3	–	–	0.33	27	67	1.00	10.6	135	193	–	–	–
Wasteland	42	7.1	328	3.0	–	–	0.33	36	142	0.16	18.1	155	134	–	–	–
Rural soils[c]	28	6.3	–	2.6	–	–	0.24	29	19	0.04	15	17	72	–	–	–
Guideline values[d]	–	–	–	–	–	–	0.4	120	100	1	35	80	350	–	–	–

For comparison, data for urban (Stockholm) and rural soils and guideline values for sensitive land use are given. Soil C is one of the soils included in the group City centre and W is one of the soils in group Wasteland listed under Stockholm. Both City centre (n=14) and Wasteland (n=5) are subgroups of Stockholm 'All soils' (n=40). The metal (Cd, Cr, Hg, Ni and Zn) concentrations (mg kg^{-1} dry matter) refer to metals extracted by boiling (120°C) 7 M HNO_3 (Swedish Standards Institute, 1997a)

[a] o=extracted with 0.2 M oxalate buffer (pH 3.0) for 4 h

[b] From Linde et al., (2001), 30 cm depth

[c] Means for arable soils (0–20 cm) in the Stockholm region (n=226; Stockholm, Uppsala and Södermanland Counties; soils with >40% clay excluded) (Eriksson, A. Andersson, & R. Andersson, 1997)

[d] From Naturvårdsverket (1997)

columns. The chemical composition of the artificial rainwater was similar to the average rainwater chemistry measured in central Stockholm ($SO_4 - S$ 0.77 mg L^{-1}, Cl 0.43 mg L^{-1}, $NO_3 - N$ 0.37 mg L^{-1}, $NH_4 - N$ 0.30 mg L^{-1}, Na 0.22 mg L^{-1}, K 0.03 mg L^{-1}, Mg 0.0,04 mg L^{-1}, pH 4.45; Miljöförvaltningen, 1994). The rain treatment was subject to leaching with artificial rainwater only and can be regarded as a reference. In the acid treatment, the inflow water consisted of artificial rainwater that had been acidified with H_2SO_4 to pH 3.1. In the bark treatment, bark was applied on top of the columns, and subjected to leaching with artificial rainwater. The bark used was a slightly composted bark of coniferous trees (mainly pine and spruce), which is commonly used as a soil cover in various types of park plantations. A commercial product bought at a local garden centre was used (*Täckbark Hasselfors Garden*). In the salt treatment, 50 mM NaCl was added to the rainwater used to irrigate the columns. The NaCl concentration was similar in magnitude to that in runoff water from roads during winter (Bäckström, Nilsson, Håkansson, Allard, & Karlsson, 2003) and in Stockholm groundwater (Miljöförvaltningen, 1997).

Glass columns (2 cm ∅ and 20 cm length) were used in the experiment. A 1 cm layer of glass wool was applied in the bottom of the columns, 30 g field moist soil were added and on top another acid-washed glass wool layer was applied. The soil pore volume in the columns was calculated to vary between 38 and 58 ml. In the bark treatments, 20 g moist bark was applied on top of the soil. The water content (e.g. weight reduction when dried at 105°C) was 28% for soil C, 53% for soil W and 63% for bark.

An overview of the 25 columns included in the experiment is given in Table 2. All treatments except the acid treatment were conducted in triplicate for both soil W and soil C. The acid treatment was applied only to soil W (since there was only room for 25 columns in the leaching equipment). Three additional columns were filled with bark, but with no soil, and these were leached with rainwater to investigate the possible contribution of metals from the bark. Furthermore, one control column containing only glass wool was leached with rainwater.

Before the start of the leaching experiment, deionised water was added to the columns up to free drainage of the soil material. During a 3-week period, five portions of 20 ml inflow solution were applied to the top of the columns. The solution was added slowly as droplets during 2 h and a constantly working pump was connected to the outlet of the columns to prevent water saturation and reduce the risk for reducing conditions. In total the volume of solution applied corresponded to 320 mm rainfall, about two thirds of the average total annual precipitation and 1.5–2 times the average annual recharge in the region (Alexandersson et al., 1991). This was equivalent to a liquid to solid ratio of approximately 5 (100 ml solution and 21.6 g dry matter) for soil C and 7 (100 ml solution and 14.1 g dry matter) for soil W.

2.3 Leachate Analysis

Column leachate was analysed for pH, EC, DOC and for seven trace metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn). Metals and DOC were determined on filtered samples (0.2 μm washed membrane filter), whereas EC and pH were measured on unfiltered samples. DOC was determined by a TC-IC method (Shimadzu TOC-5000), Zn by AAS air-acetylene flame with background correction (IL 551) and the analyses of Cd, Cr, Cu, Ni and Pb were carried out with AAS-graphite furnace technique after addition of matrix modifier ($NH_4H_2PO_4$) (Perkin Elmer Zeeman 4100ZL) (Swedish Standards Institute, 1997b). The concentration of

Table 2 An overview of the experimental design

Material	Treatment			
	Rain (artificial rainwater)	Acid (artificial rainwater + acid)	Salt (artificial rainwater + salt)	Bark (artificial rainwater over bark)
Soil C	3 columns		3 columns	3 columns
Soil W	3 columns	3 columns	3 columns	3 columns
Bark	3 columns			
None	1 column			

total Hg (only for leachate 4 from soil W) was determined at the Swedish Environmental Research Institute with cold vapour atomic fluorescence spectroscopy (CVAFS) after BrCl Oxidation (Bloom & Fitzgerald, 1988; Fitzgerald & Gill, 1979).

2.4 Modelling Work

Equilibrium modelling of the metal concentrations in the leachates was carried out with a combination of the SHM for organic matter and the DLM for oxide components. The SHM is a discrete-site/electrostatic model for proton and metal binding to humic substances. The theory of the model is described in detail in Gustafsson (2001), Gustafsson and van Schaik (2003) and Gustafsson and Berggren Kleja (2005). The SHM is an integrated part of the chemical equilibrium program Visual MINTEQ (Gustafsson, 2006), which was used in this study. A definition of parameters and variables used in the SHM is given in Table 3. Parameterisation of the model was based on a number of assumptions

1. For soil C, which had a relatively low organic C content (3.4%), 30% of the total organic C was assumed to consist of 'active' humic acid whereas an additional 25% was assumed to be 'active' fulvic acid. These figures were based on a simple average of eight Swedish mineral soil samples with organic C contents lower than 7%, for which percentages were fitted from NaOH extractions and from observed acid-base characteristics (Gustafsson et al., 2003).
2. For soil W, which contained 17% organic C, 18.8% of the total organic C was assumed to be 'active' humic acid whereas 6.2% was 'active' fulvic acid, in accordance with results for Swedish mor layers (Gustafsson & Berggren Kleja, 2005).
3. To account for dissolved Al^{3+} and Fe^{3+} that may compete for complexation sites on organic matter, the soils were assumed to be in equilibrium with an $Al(OH)_3$ phase having a log $^*K_s$ (defined as $\{Al^{3+}\}/\{H^+\}^3$) of 8.6 at 20°C, and with a $Fe(OH)_3$ phase with a log $^*K_s$ of 3.0.
4. Dissolved organic matter (DOM) in both soils was assumed to consist of 87% fulvic acid, whereas the rest was inert with respect to metal binding. This was based on DOM fractionation studies for a Swedish mor layer (van Schaik et al., personal communication).

The geochemically active concentrations of trace metals, which are needed as input to the model, were obtained from sequential extractions including the EDTA step (extractions F1–F4). Because dissolved base cations were not measured in the leachates, apparent charge balances were corrected by adding an appropriate amount of Ca^{2+} to the Visual MINTEQ simulations. Other anions and cations were fixed at the total dissolved concentrations of the treatment solutions, and the concentration of bicarbonate ions was predicted using the assumption that the waters were in equilibrium with atmospheric CO_2 (3.8×10^{-4} atm). Proton and metal binding was described by generic proton-binding parameters for humic and fulvic acids (Gustafsson & van Schaik, 2003; see Table 4), in combination with metal complexation constants recently optimized for mor layer material (Gustafsson et al., 2007; see Table 5). The model was applied in a one-cell "batch"

Table 3 Summary of parameters and variables used in the Stockholm Humic Model

n_A	Amount of proton-dissociating type A (carboxylic) sites (mmol g^{-1})
n_B	Amount of proton-dissociating type B (phenolic) sites (mmol g^{-1})
K_A	'Central' log K value defining the proton dissociation constants for type A sites
K_B	'Central' log K value defining the proton dissociation constants for type B sites
ΔpK_A	Distribution term that modifies log K_A
ΔpK_B	Distribution term that modifies log K_B
$K_{M\mathrm{m}}$	Intrinsic equilibrium constant for monodentate complexation of metal M
$K_{M\mathrm{b}}$	Intrinsic equilibrium constant for bidentate complexation of metal M
$K_{M\mathrm{bOH}}$	Intrinsic equilibrium constant for bidentate complexation of hydrolyzed metal MOH
ΔLK_2	Distribution term that modifies the strengths of complexation sites
g_f	Gel fraction parameter

mode, assuming a liquid to solid ratio of 5 (the exact value of the ratio was of minor importance for the result).

In the SHM sorption to oxides (e.g. Fe oxides) and to clay minerals is not considered. Because the soils contained appreciable amounts of oxalate-extractable Fe (Table 1), we included surface complexation to ferrihydrite (“hydrous ferric oxide”) in the model, assuming that the bulk of all oxalate-extractable Fe was ferrihydrite with a specific surface area of 600 m^2 g^{-1} and a site density of 2.31 sites nm^{-2}. The 2-p*K* DLM was used, with surface parameters and complexation constants suggested by Dzombak and Morel (1990). Complexation to Al-oxide-type components such as allophane was not considered, as extraction results suggested that these minerals were insignificant for adsorption. As Table 1 shows, oxalate-extractable Al was much lower than extractable Fe; in addition for soil W the concentration of oxalate-extractable Si was very low in comparison to Al, suggesting that most extractable Al was organically bound (Gustafsson et al., 1995). Although both soils contained appreciable amounts of clay, we did not include clay mineral sorption in the model. This is partly due to the absence of any information on the cation exchange capacity (CEC) for the clay mineral fraction. In addition, preliminary model tests with clay mineral sorption enabled (through ion exchange with the Gaines–Thomas equation, with different CEC:s in the range 0–0.2 mol_c kg^{-1} clay) indicated that ion exchange to clays was of minor importance for the trace metals considered.

Table 4 Generic parameter values for proton binding in the Stockholm Humic Model[a]

Parameter	Solid-phase humic acid	Solid-phase fulvic acid	Dissolved fulvic acid
n_A (mol kg^{-1})	3.55	5.4	5.4
n_B (mol kg^{-1})	1.78	1.62	1.62
log K_A	−4.13	−3.51	−3.51
log K_B	−8.99	−8.81	−8.81
ΔpK_A	3.03	3.48	3.48
ΔpK_B	3.03	2.49	2.49
g_f	1	1	0.72

[a] From Gustafsson and van Schaik (2003)

Table 5 Parameter values for cation complexation to soil organic matter in the Stockholm Humic Model[a]

Cation	Humic acid and fulvic acid				
	Log K_{Mm}	Log K_{Mb}	log K_{MbOH}	log K_{MtOH}	ΔLK_2
Al^{3+}	–	−4.0	−9.0	–	1.0
Ca^{2+}	−2.2	–	–	–	0.3
Cd^{2+}	−1.6	−9.5	–	–	1.3
Cr^{3+}	–	−3.75	−7.75	–	1.0
Cu^{2+}	−0.55	−6.0	−13.6	–	1.4
Fe^{3+}	–	–	–	5.15	1.8
Mg^{2+}	−2.5	–	–	–	0.3
Pb^{2+}	0.15	−6.15	–	–	1.3
Ni^{2+}	−1.15	–	–	–	1.3
Zn^{2+}	−1.65	−8.5	–	–	1.0

[a] Constants for Al^{3+}, Ca^{2+}, Cd^{2+}, Fe^{3+}, Mg^{2+} and Ni^{2+} are from Gustafsson et al. (2007), those for Cu^{2+}, Pb^{2+} and Zn^{2+} were optimized from data of Gustafsson and van Schaik (2003), and those for Cr^{3+} from the solution complexation data of Fukushima, Nakayasu, Tanaka, and Nakamura (1995)

3 Results and Discussion

3.1 pH, DOC and EC in Leachates

For both soils, the pH values in the bark and rain treatments remained approximately constant through the whole experiment (5.7–6.0 for soil W and 5.9–6.3 for soil C) (Fig. 1). The salt treatment (and not the acid treatment) produced the lowest pH values, 5.0 for soil W and 5.7 for soil C. This could be explained by a release of exchange acidity from the soils due to the high Na^+ concentration, or by salt-dependent proton binding by soil organic matter (Gustafsson & Berggren Kleja, 2005). The lowest pH measured in the acid treatment for soil W was 5.4 (leachate 5) but extrapolation of the curve in Fig. 1 suggests that the value would have decreased more if the experiment had been continued.

The DOC concentration was largest in the first leachate and decreased thereafter during the experiment due to removal of the most soluble DOM fractions (Fig. 1), it did not reflect the initial content of soil organic matter, rather it was a result of the different treatments. The DOC concentration was largest in the bark treatment (40–140 mg L^{-1} depending on leachate), due to the larger amount of dissolved organic matter supplied to the columns, and smallest in the salt and acid treatments (7–40 mg L^{-1}),

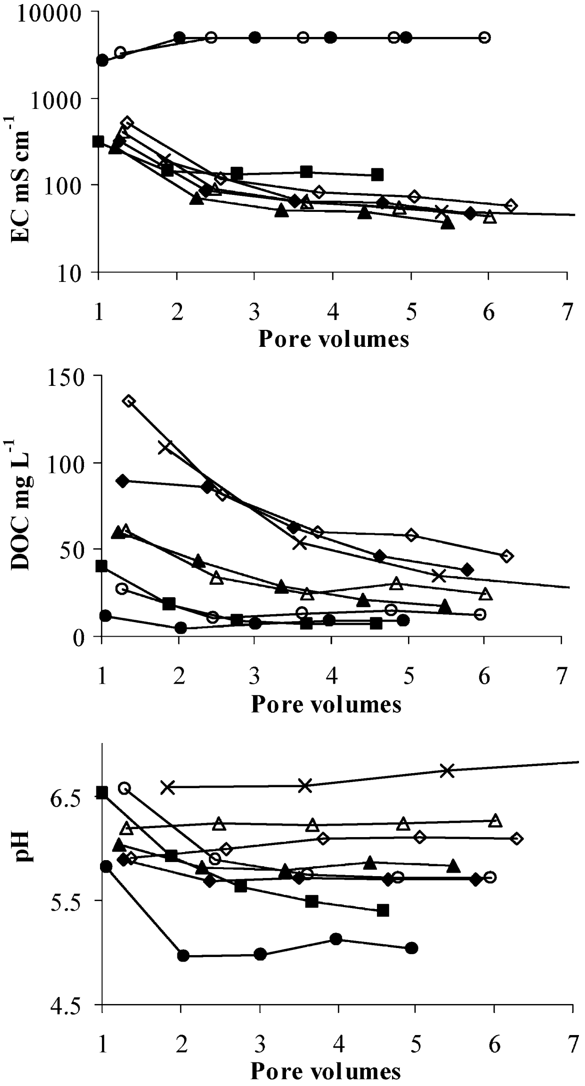

Fig. 1 Electrical conductivity (EC), pH and DOC concentration in leaching solution (♦ = Soil W bark; ◇ = Soil C bark; ● = Soil W salt; ○ = Soil C salt; ▲ = Soil W rain; △ = Soil C rain; ■ = Soil C acid; × = only bark)

probably because of the decreased pH as a result of these treatments.

The electrical conductivity (EC) was low in the bark, rain (25–44 µS cm^{-1}) and acid (115 µS cm^{-1}) treatments, whereas in the salt treatment leachate it was 4,900 µS cm^{-1} (Fig. 1). The NaCl was added with the solution at each leaching event and the EC value in the salt treatment reached a constant level at approximately two pore volumes.

The pH in the leachate from the three columns with only bark was just below neutral and rose slightly during the experiment, from pH 6.6 to 6.9. This was surprising since the pH in the artificial rainwater was 4.3 and in the bark 4.8 (pH_{CaCl2}) (Table 1). One possible explanation for the increase in pH is a reduction of e.g. Fe in the bark columns, despite the fact that technical efforts were made to prevent this. The DOC concentration in the leachate from these columns was similar in magnitude to that of the bark treatment columns (which also contained soil), confirming that the concentration of DOC was controlled by the dissolution of organic substances from the bark. By contrast, the EC values in the bark treatment columns were larger than those in the columns with only bark, but similar to those recorded for the other soil-containing columns (with the exception of the salt treatment columns).

3.2 Metal Leaching

Leaching of the metals from the different soils and treatments is presented both as concentration in the outflow (Fig. 2) and as total amount of leached metals per mass unit dry soil (Table 6).

The Cd concentration was highest in the solution from the salt treatment columns, between 10 and 12 µg L^{-1} in the first leachate (sampled after approx. 1 pore volume). The Cd concentration decreased to about 3 µg L^{-1} in the fifth leachate (Fig. 2). In the other treatments the Cd concentration was low, between 0.1 and 0.3 µg L^{-1} in the rain and bark treatments and 0.5 µg L^{-1} in the acid treatment. Nickel and Zn were mainly mobilised in the salt treatment for soil W, whereas small effects were observed for the other treatments (Table 6). Although the treatment-specific effects were seen most clearly for soil W, the effects could be seen also for soil C. The acid treatment caused a small but steadily increased concentration of all three metals mentioned (Cd, Ni and Zn), probably as a result of the decreasing pH. As a result, approximately 5 times more Cd, 1.5 times more Ni and 2 times more Zn were released in the acid treatment compared to the rain treatment (Table 6).

The leaching of Cu, Cr, and Pb was consistently larger from soil W than from soil C (Fig. 2), reflecting the higher concentrations of the metals in soil W (Table 1). However, the three metals exhibited different treatment-specific effects. The rain and bark treatments produced the highest leachate concentra-

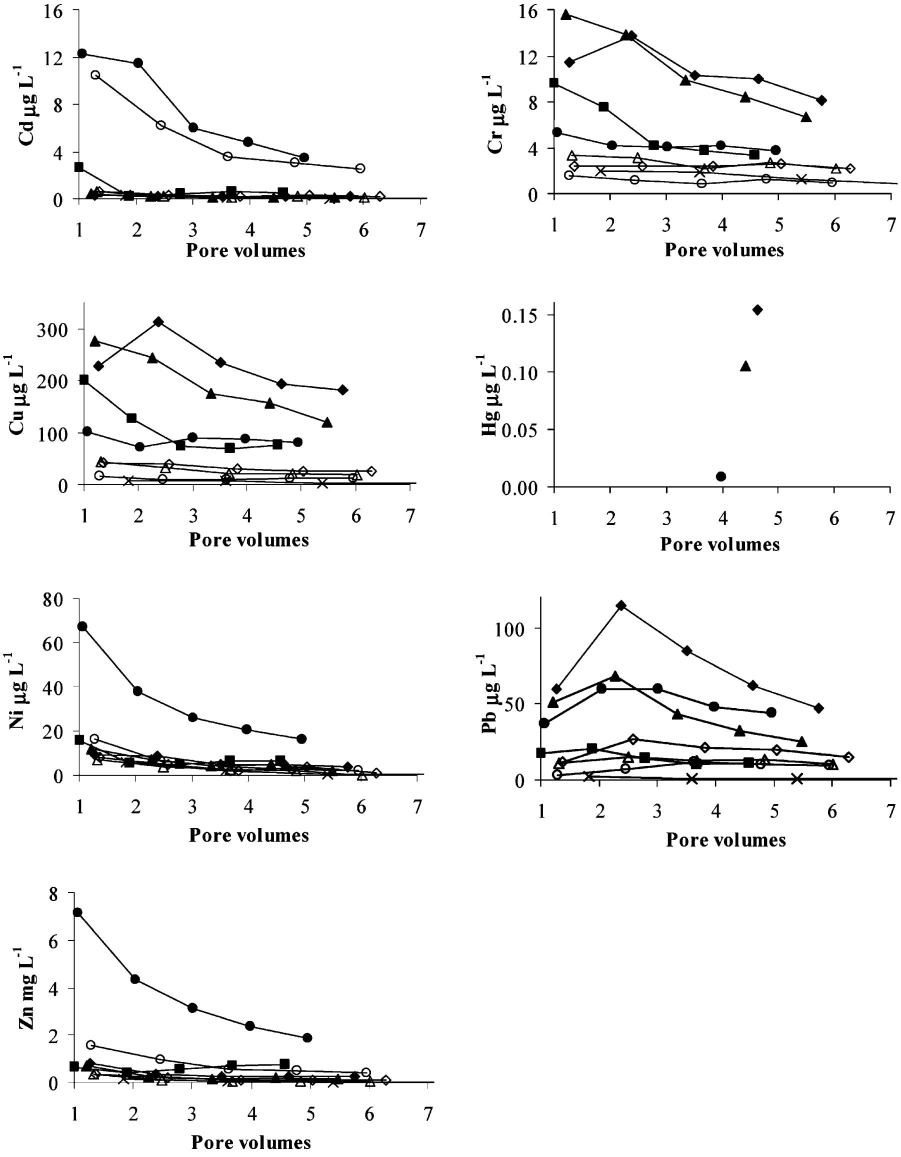

Fig. 2 Metal concentrations (g L^{-1}) in the leaching solution (♦ = Soil W bark; ◇ = Soil C bark; ● = Soil W salt; ○ = Soil C salt; ▲ = Soil W rain; △ = Soil C rain; ■ = Soil C acid; × = only bark)

tions of Cu and Cr (Fig. 2). For the same metals, the lowest concentrations were seen in the salt treatments (Table 2). For Pb, the highest concentrations were observed in the bark treatments. The total amount of Pb leached was 1.5 times higher in the bark treatment compared to the rain and salt treatments. From the second leachate and onwards, the concentration was approximately 2 times higher. The lowest Pb concentrations were seen in the acid treatments. Reduced solubility of organic substances due to the lower pH might provide an explanation for these results. The relationship between leaching solution chemistry and metal concentrations is discussed further below.

Even though the Hg concentration was measured only for one soil and in the fourth leachate, effects of the different treatments could be observed. In comparison with the rain treatment, the concentration in the bark leachate was 1.5 times higher, whereas the concentration in the salt leachate was much smaller than that in the rain treatment, 0.02 and 0.11 µg L^{-1}, respectively.

3.3 Metal Concentrations and Leachate Chemistry

To get a better understanding of the leaching behaviour of each single metal, we analysed the

Table 6 The total amounts of Cd, Cr, Cu, Ni, Pb and Zn leached during five leaching events, with different extraction solutions (Treatments) in relation to soil mass (dry weight) in the columns

Treatment		Cd		Cr		Cu		Ni		Pb		Zn	
		µg kg^{-1}	% HNO$_3$	µg kg^{-1}	% HNO$_3$	mg kg^{-1}	% HNO$_3$	µg kg^{-1}	% HNO$_3$	mg kg^{-1}	% HNO$_3$	mg kg^{-1}	% HNO$_3$
Soil C													
Rain[a]	Mean	2.7 a	0.5	31 a	0.1	0.31 ab	0.6	35 a	0.3	0.14 a	0.1	1.5a	0.6
	Min	2.4		29		0.31		31		0.12		1.4	
	Max	2.9		32		0.32		40		0.16		1.5	
Bark	Mean	3.8 a	0.7	28 a	0.1	0.38 a	0.7	50 a	0.5	0.22 a	0.2	2.0 a	0.8
	Min	3.7		26		0.36		41		0.20		1.9	
	Max	3.9		31		0.39		56		0.25		2.1	
Salt	Mean	59 b	10	13 a	<0.1	0.14 b	0.2	70 ab	0.7	0.09 a	<0.1	9.1 bdf	3.5
	Min	55		12		0.13		65		0.09		8.9	
	Max	61		13		0.15		77		0.09		9.3	
Soil W													
Rain[a]	Mean	3.7a	1.5	213 b	0.2	3.8 c	1.9	117 bc	0.6	0.84c	0.2	5.9bc	2.6
	Min	3.3		208		3.7		109		0.81		5.8	
	Max	4.2		219		4.0		126		0.88		6.2	
Bark	Mean	4.6 a	1.8	214 b	0.2	4.6 d	2.3	130 c	0.7	1.45 d	0.4	8.0 cd	3.5
	Min	4.4		204		4.5		126		1.44		7.7	
	Max	4.8		226		4.7		134		1.46		8.2	
Salt	Mean	149 c	60	84 c	0.1	1.7 e	0.8	664 d	3.4	0.96 c	0.3	74.7 e	33
	Min	143		72		1.6		616		0.84		70.6	
	Max	156		99		1.8		689		1.06		76.8	
Acid	Mean	18 d	7.1	112 d	0.1	2.2 f	1.1	155 c	0.8	0.28 b	<0.1	12.0 f	5.2
	Min	14		102		2.1		145		0.26		11.0	
	Max	23		123		2.3		169		0.32		12.9	

The means, minimum and maximum values of three replicates are given. The mean values are also calculated as % of total HNO$_3$-extractable fraction (% HNO$_3$). For each metal, mean values marked with the same letter are not significantly different ($p<0.05$)

[a] From Öborn and Linde (2001)

relationships between the measured metal concentrations and pH, EC and DOC for all leachate samples.

For both soils there was a strong positive correlation between the DOC concentration and the Cu, Cr, and Hg concentrations (Fig. 3). This was not surprising given that all these metals are known to form strong complexes with organic substances (Tipping, 2002). The same is also true for Pb and a strong relationship between dissolved Pb and DOC in the solutions was suspected. To some extent this was observed, but the correlation was much weaker ($R^2=0.36$) than for Cu and Cr; this seems to be due to some outliers in the salt treatment. For most metals there was a nonlinear relationship between DOC and the metal concentrations. In the case of strongly complex-forming metals such as Cu and Cr(III) this is somewhat surprising as their concentrations would be determined by partitioning between solid and dissolved organic matter, and thus a linear relationship would have been more logical. A possible explanation is that the DOM of the bark leachates (which contained the highest DOC concentrations) bound metals less strongly; this would in turn be explained by different metal-binding properties of the DOM released from the bark.

Overall, there was no obvious relationship between metal concentrations and the other chemical parameters (pH and EC) measured in the leachate. The only linear relationship with R^2 values above 0.2 was found for Cu, Cr and Hg concentration versus pH. For the same metals the concentration was negatively correlated to EC.

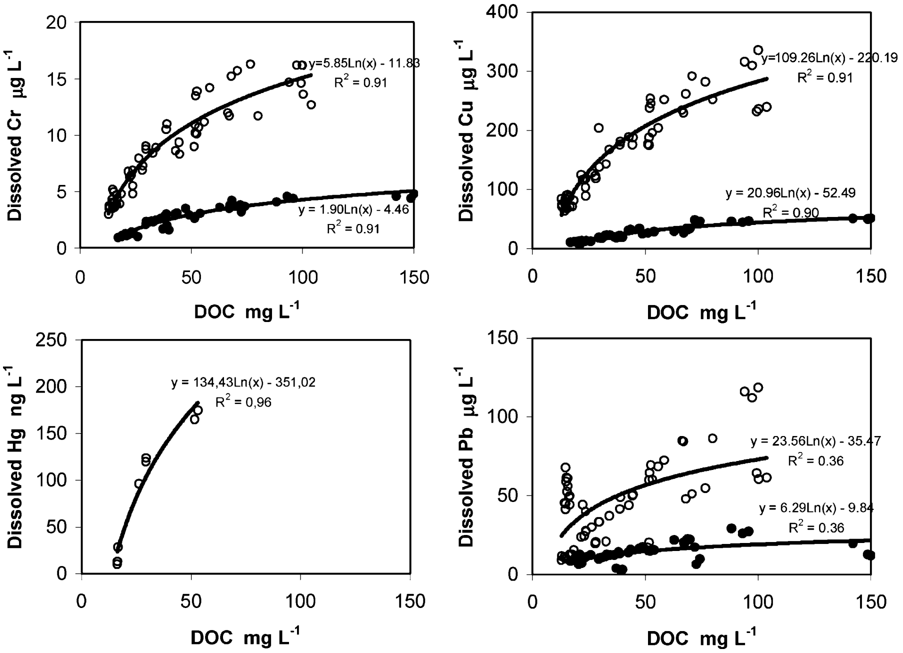

Fig. 3 Correlation between metal concentration and DOC in leachates. Both soils (C and W), all treatments (rain, salt, bark and acid), leaching events (1–5) and replicates (n=3) are included (○ = Soil W; ● = Soil C)

3.4 Simulated Metal Concentrations

Results from the model simulations of dissolved metal concentrations are presented in Fig. 4 (soil C) and Fig. 5 (soil W). Mercury was not included due to the small number of data points available. One simulation was made for the bark and rain treatment and one for the salt treatment due to the differences in ionic strength and pH. To simplify the comparison, averaged pH values were used in the simulations for (1) the bark and rain treatment and for (2) the salt treatment (thus model fits appear as single lines in Fig. 4 and 5). The acid treatment of soil W is not included in the plot due to the large pH differences between individual data points, which rendered a direct comparison difficult (the range of pHs was from 5.4 to 6.7).

According to the multi-surface model used, organic complexation dominated metal binding for all metals, although for Pb and Cr(III) surface complexation to ferrihydrite was also significant. The percentages bound to ferrihydrite ranged from 35 to 50% (Pb) and from 15 to 30% (Cr(III)); for all other metals <5% was bound to ferrihydrite. For all treatments, the simulated values for Zn were somewhat lower than the measured data, although usually within a factor of 2 from the observed concentrations. For Cd, Cr(III), Cu and Ni there were larger deviations for some of the data sets but the magnitude of the concentrations was predicted reasonably well and the influence of DOC was also mimicked. The results suggest that the dissolution of these metals at low (i.e. normal) salt concentrations was to a large extent governed by binding to humic substances in the solid and dissolved phases, a result which is consistent with earlier short-term column experiments in which a related multi-surface model (NICA-Donnan-DDL-CD-MUSIC) was used for model simulations (Weng et al., 2001, 2002).

For Pb the model simulations overestimated the dissolved Pb concentrations, particularly for soil C, for which simulated Pb levels were often a factor 5 larger than the observations.

The discrepancies between the model results and observations may be due to several different reasons, two of them are (1) The EDTA extraction may not always be specific for the geochemically active concentration of the metal; (2) The estimated site concentrations may not be correct. The overestimated concentrations of dissolved Pb may possibly also be explained by stronger binding by Pb to either organic matter or ferrihydrite. This may be caused for example by the presence of phosphate adsorbed to ferrihydrite, which might have increased Pb sorption through surface charge adjustment or surface precipitation (Weesner & Bleam, 1998); this was not considered in

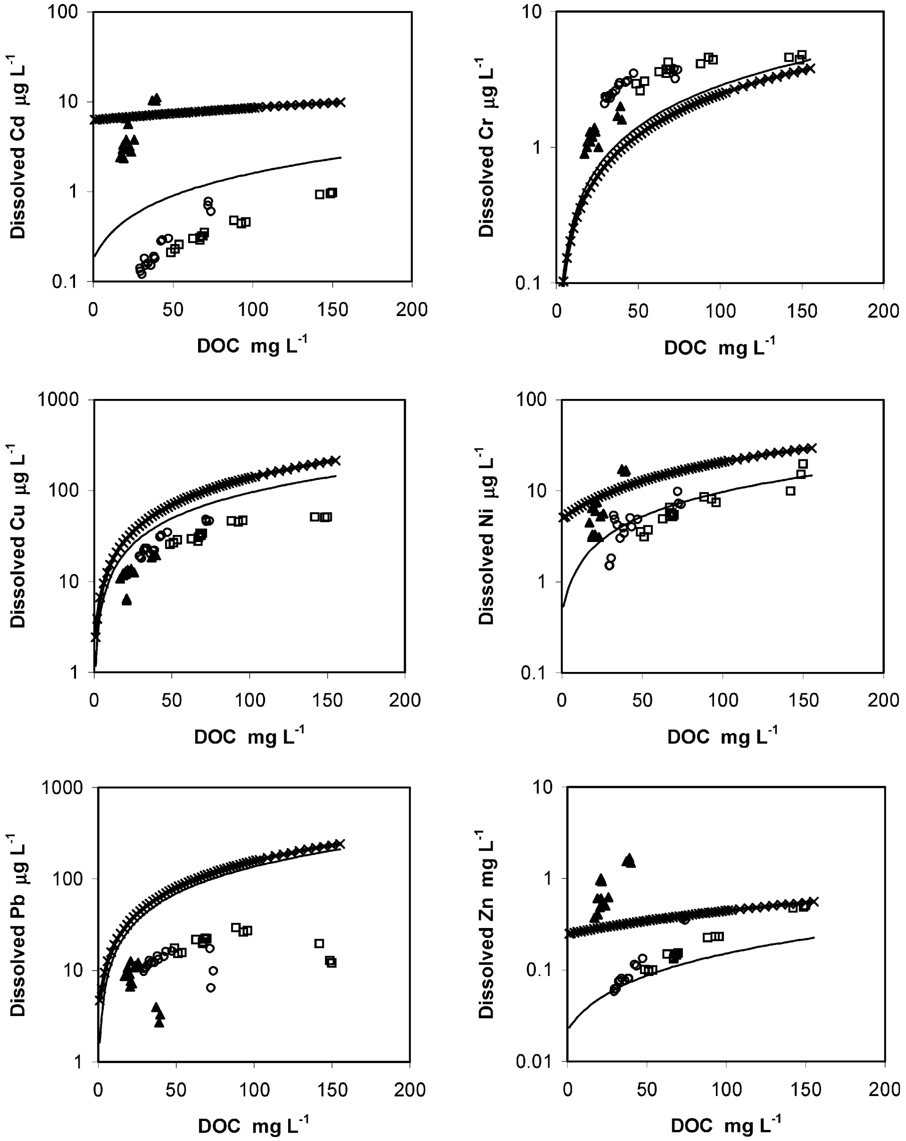

Fig. 4 Measured and simulated metal concentrations in relation to DOC concentration in leachates from soil C. (— = rain and bark simulated; ~~xxx~~ = salt simulated; □ = bark measured; ○ = rain measured; ▲ = salt measured). See text for details

the model. Our observations are in general agreement with other results from soils with low or moderately high Pb contents, and for which multi-surface models were used to interpret the results (Weng et al., 2001; Dijkstra et al., 2004).

The results from the multi-surface model simulations are thus not unambiguous but despite a partly rough supposition being used in parameterisation of the model and no optimization of the model settings being made, they illustrate how equilibrium modelling could be used for a better mechanistic interpretation of the experimental results. The simulations suggest that a multi-surface model with SHM and DLM may be able to correctly simulate the concentrations of most dissolved metals within a factor of 5, when no soil-specific optimization is being made, for slightly acid soils similar to the ones used in this work.

3.5 Sequential Extraction and Leaching Tests for Assessment of Metal Mobility

In a paper on the mobility of potentially toxic elements in contaminated land, Anderson et al. (2000) suggested the use of sequential extractions as

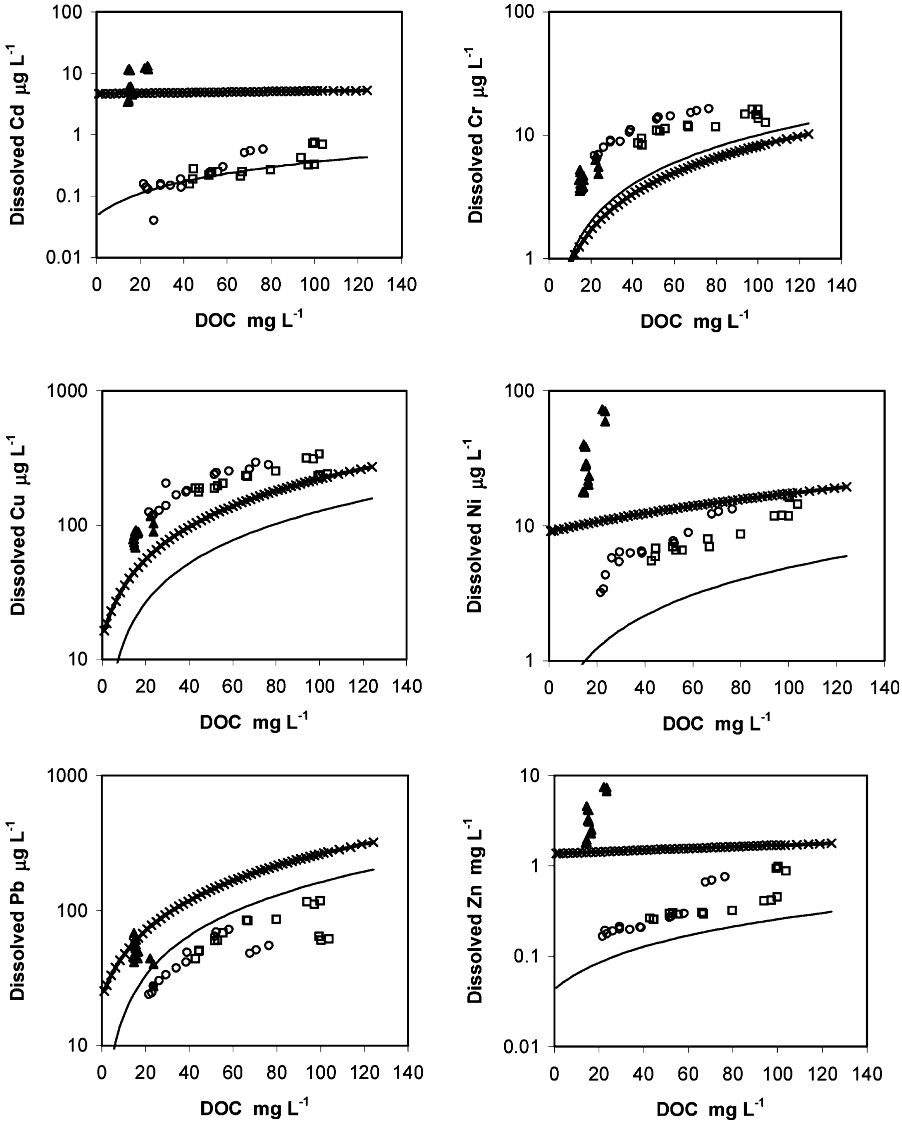

Fig. 5 Measured and simulated metal concentrations in relation to DOC concentration in leachates from soil W. (— = rain and bark simulated; ~~xxx~~ = salt simulated; □ = bark measured; ○ = rain measured; ▲ = salt measured). See text for details

a method for assessment of potential mobility of heavy metals in soils. In an effort to test the validity of this assumption we used the sequential extraction data for the two soils, originally presented by Öborn and Linde (2001), and compared them to the amounts of metals leached from the different treatments. Because NH_4NO_3 is intended to extract the most soluble metal fraction, we expressed the amount of Cu and Cd leached from the columns (Table 6) as a percentage of the amount of NH_4NO_3-extractable metal (as reported in Table 7). For the rain treatment the percentage of leached Cd was low (6.8% for soil C and 4.1% for soil W) whereas for leached Cu it was much higher (34.1% for soil C and 149% for soil W). Similar percentages were obtained for the bark treatment, but for the salt treatment the percentage of leached Cd was high (148 and 166% for soils C and W, respectively) whereas for Cu it was lower (15.4 and 66.4%). For Pb and Zn the trends were similar to those of Cu and Cd, respectively.

These results show that the NH_4NO_3 extraction failed to give a consistent estimate of the concentration of soluble metal, not only for a given treatment but also when comparing across treatments. The consistency of the results was not improved when the leached amounts were compared to the results

Table 7 Concentration (mg kg^{-1} dry matter) of four different fractions of trace metals (Cd, Cu, Pb, and Zn) extracted by different solutions in a sequential extraction procedure (Öborn & Linde, 2001)

Extraction	Cd		Cu		Pb		Zn	
	μg kg^{-1}	$\%_{HNO3}$	mg kg^{-1}	$\%_{HNO3}$	mg kg^{-1}	$\%_{HNO3}$	mg kg^{-1}	$\%_{HNO3}$
Soil C								
F1	40	6	0.91	2	0.17	0	12.8	5
F1–F2	50	8	2.32	4	0.35	0	22.5	9
F1–F3	390	67	7.18	13	22.0	16	26.7	11
F1–F4	530	91	30.1	54	76.8	57	47.9	19
Soil W								
F1	90	37	2.55	1	6.89	2	66.6	29
F1–F2	140	56	4.07	2	8.59	3	144	63
F1–F3	190	75	14.7	7	65.4	19	146	64
F1–F4	240	94	93.9	47	208	59	161	70

The amount of each metal is also expressed as % of the HNO_3-extractable fraction ($\%_{HNO3}$) (F1="exchangeable," extractable with 1 M NH_4NO_3; F2="Cl-complex-forming," extractable with 0.1 M NaCl; F3="bound to pH-dependent sites," extractable with 1 M NH_4Ac pH 4.8; F4="strongly bound to organic matter and oxides," extractable with 0.5 M NH_4Ac + 0.02 M EDTA pH 4.65)

from the other extractions. There are probably several reasons for these inconsistencies, one example is the high ionic strength used in the extractions of the sequential extraction procedure of Öborn and Linde (2001), which may alter the pH and promote flocculation of dissolved organic matter and of metal-bearing inorganic colloids. Possibly more consistent results may have been obtained using another extraction procedure with a low-ionic-strength solution as a first step. In any case the sequential extraction procedure used, with 1 M NH_4NO_3 as a first step, was not able to describe the mobility of different metals in a consistent manner.

As mentioned in the introduction, pH is the only factor altered in the standardised leaching tests used for site-specific risk assessment of contaminated land (e. g. CEN/TS 14429, see Dijkstra et al., 2005). According to the results from this study it could be questioned if this is sufficient for assessment of trace metals mobility, i.e. leaching to ground and surface water. Many contaminated sites are found in urban areas and the risk for changing soil conditions, not only pH, is obvious. A step forward would be to measure the DOC concentration in leaching test solutions. Knowledge of the DOC concentration in the leaching tests solutions would give much more useful date for calculation and predictions of mobility of the metals in the contaminated soil.

4 Conclusions

This study has demonstrated that even relatively mild changes in soil chemistry could be important for the mobility of trace metals. Enhanced salt concentrations caused considerably increased dissolution of Cd, Ni and Zn. The dissolution of more strongly bound metals (Cu, Cr, Hg and Pb) was not affected considerably by the salt concentration; for these metals the concentration of dissolved organic matter was the most important governing factor for dissolution. The SHM-DLM simulation results showed that the concentrations of most dissolved metals could be predicted within a factor of 5. In the case of Pb, the model was not successful; this is probably due to stronger binding to either soil organic matter or to the oxide fraction than was predicted by the model used.

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